Access to 3-Methyl-4-methylene-*N*-tosylpyrrolidine and 3,4-Dimethyl-*N*-tosylpyrroline by Ruthenium-Catalyzed Cascade Cycloisomerization/Isomerization Reactions

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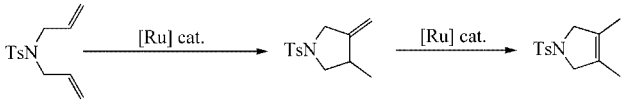
New $RuCl_2$(benzimidazole)(arene) complexes have been prepared. Upon reaction with 1,1-diphenylprop-2-ynol they generate catalyst precursors which perform the cycloisomerization of diallyltosylamide into 3-methyl-4-methylene-*N*-tosylpyrrolidine. The presence of *N*-(2,4,6-trimethylbenzyl)benzimidazole as ligand leads to a subsequent isomerization and gives the 3,4-dimethyl-*N*-tosylpyrroline.

Introduction

Transition metal complexes with nitrogen-containing ligands have recently shown their potential to perform selective catalytic transformations of molecules with atom economy.[1] Especially, a variety of RuX_2(arene)(L) complexes promoting catalytic reactions such as nucleophilic addition to triple bonds to form furans (L = imidazoline, tetrahydropyrimidine,[2] benzimidazole[3]), hydrogen transfer (L = amino acid,[4] amino alcohol,[5] diamine[6]), cyclopropanation (L = diamine[7]), or Diels−Alder cycloaddition and Claisen rearrangement [L = bis(oxazoline)[8,9]]. It is also well established that $RuCl_2$(arene)(L) complexes can easily be transformed by activation of propargylic alcohols into cationic ruthenium(allenylidene) complexes, which have shown catalytic properties in olefin metathesis.[10]

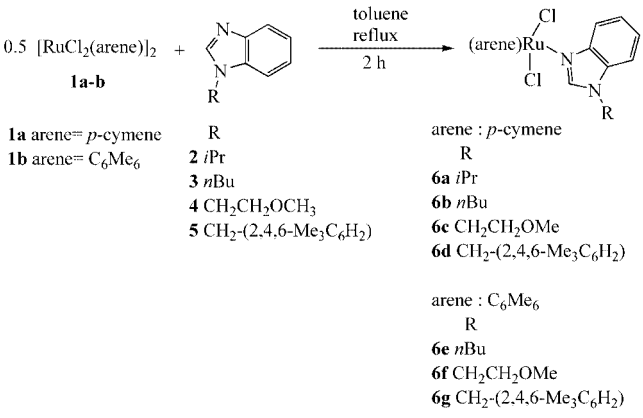
We now report (i) the straightforward preparation of new $RuCl_2$(η^6-arene)(L) complexes with an *N*-coordinated benzimidazole ligand and (ii) their in situ transformation into efficient catalyst precursors for cycloisomerization of diallyltosylamide into 3-methy-4-methylene-*N*-tosylpyrrolidine followed, when a suitable benzimidazole is used (R = mesityl-CH_2), by double bond isomerization to form a pyrroline derivative. This study reveals a very efficient ruthenium catalyst for isomerization of the exocyclic C=CH_2 double bond of 3-methyl-4-methylenepyrrolidine into the tetrasubstituted C=C bond of 3,4-dimethylpyrrolidine derivatives (Scheme 1).



Scheme 1

Results and Discussion

The reaction of *N*-alkylbenzimidazoles **2**−**4** and the *N*-(aralkyl)benzimidazole **5** with the dinuclear [$RuCl_2$(*p*-cymene)]$_2$ (**1a**) and [$RuCl_2$(hexamethylbenzene)]$_2$ (**1b**) com-



Scheme 2

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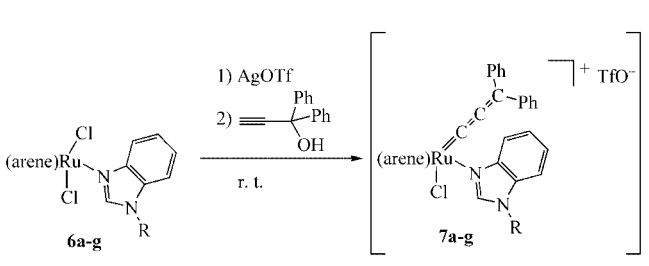
Table 1. Selected analytical data for the new (benzimidazole)ruthenium complexes (**6**)

Complex	Yield of isolated product [%]	M.p. [°C]	$\nu_{(C-N)}$ [cm^{-1}]	^{13}C NMR, C-2 signals δ [ppm] ($^{1}J_{C,H}$ [Hz])	^{1}H NMR, 2-H signals δ [ppm]
6a	85	183.0	1506	142.96 (197.3)	8.44
6b	87	206.5	1612	144.52 (198.8)	8.34
6c	87	197.0	1616	145.54 (199.5)	8.22
6d	90	224.0	1610	144.18 (203.0)	7.92
6e	86	307.5	1612	145.08 (201.4)	8.12
6f	82	276.0	1508	146.18 (202.6)	7.97
6g	86	310.5	1612	144.81 (205.6)	7.70

plexes proceeded smoothly in refluxing toluene to give the $RuCl_2$(benzimidazole)(arene) complexes **6a**−**g** as crystalline solids in 82−90% yields (Scheme 2, Table 1).

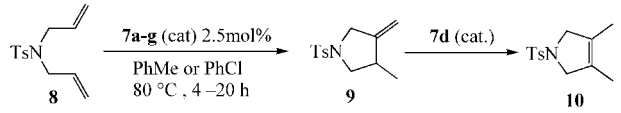
Complexes **6a**−**g**, which are very stable in the solid state have been characterized by analytical and spectroscopic techniques (Table 1). The IR data show the presence of a C=N bond with a ν(C=N) vibration at 1506−1616 cm^{-1}, and the ^{1}H NMR spectra clearly exhibit a singlet at δ = 7.70−8.44 ppm typical of the N=CH−N fragment. In the ^{13}C NMR spectrum, the chemical shift of the corresponding C-2 atom was detected in the region δ = 142.96−146.18 ppm with a $^{1}J_{C,H}$ coupling constant close to 200 Hz. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other $RuCl_2$(arene)(benzimidazole) complexes with R = Me, Et, $(CH_2)_2NEt_2$, $(CH_2)_2CO_2Et$.[3]

In contrast with the related (arene)$RuCl_2$(phosphane),[11] (arene)$RuCl_2$(diaminocarbene) complexes,[12,13a] **6** presented no metathesis catalytic activity for the transformation of *N*,*N*-diallyltosylamide (**8**). The known catalytic activities of [RuCl(=C=C=CPh_2)(arene)(L)][X] (L = PCy_3,[10] diaminocarbene[13]) to perform the ring-closing metathesis of dienes and ring-opening metathesis polymerization of cyclic olefins, provided impetus to prepare the corresponding cationic ruthenium(allenylidene)(benzimidazole) complexes according to the reaction depicted in Scheme 3. Indeed, purple complexes were prepared in dichloromethane but they were not stable enough to be cleanly isolated and characterized. Based on previous results obtained with more stable ruthenium(allenylidene) complexes from analogous precursors,[10,13] we assumed that the new organometallic species **7a**−**g** (Scheme 3) contained the $[RuCl(arene)(benzimidazole)(allenylidene)]^+$ cation. In order to circumvent this instability problem, they were generated in situ from complexes **6a**−**g** just before use, by abstraction of chloride with silver triflate followed by addition of 1,1-diphenylprop-2-ynol at room temperature in the selected solvent (Scheme 3).



Scheme 3

The catalytic performances of these in situ generated precursors were evaluated in the transformation of *N*,*N*-diallyltosylamide (**8**) at 80 °C in various solvents (Scheme 4, Table 2).



Scheme 4

Table 2. Catalytic transformation of *N*,*N*-diallyltosylamide (**8**)

Catalyst	Solvent	Time [h]	Conversion [%]	**9** [%]	**10** [%]
7a	PhCl	18	100	100	
7b	PhMe	13	76	76	
7b	PhCl	10	100	100	
7c	PhMe	12	37	37	
7c	PhCl	10	82	82	
7d	PhMe	4	100	100	
7d	PhMe	10	100		100
7d	PhCl	6	98	60	38
7d	PhCl	10	100		100
7e	PhCl	18	65	65	
7f	PhMe	10	58	58	
7f	PhCl	20	100	100	
7g	PhCl	20	79	40	39

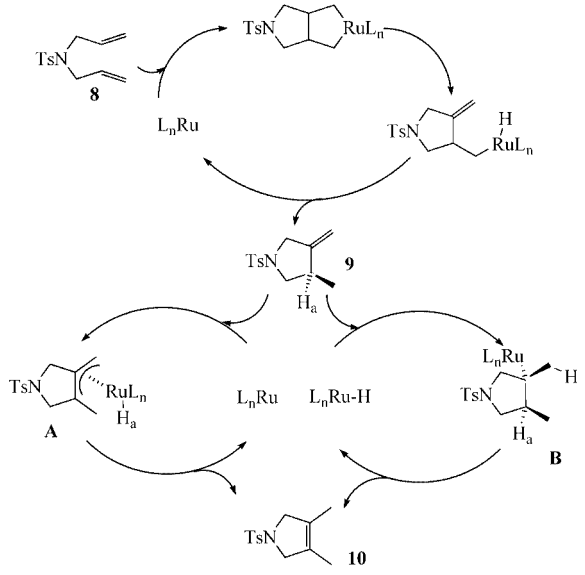
Thus, the catalyst was first generated by successive additions of silver triflate (0.0125 mmol) and HC≡$CCPh_2OH$ (0.0125 mmol) to a solution of **6** (0.0125 mmol, 2.5 mol %) in 2.5 mL of solvent and stirred at room temperature for 20 min. The diene **8** (0.5 mmol) was then added and the solution was heated at 80 °C for 4−20 h. The catalytic precursors thus prepared in situ showed catalytic activity for the transformation of the 1,6-diene **8** into the cycloisomerization compounds **9** or **10**. According to this procedure, the presence of the diene **8** added just after the preparation of **7** might stabilize organometallic intermediates and generate catalyst precursors with long-lasting activity.

In contrast with the catalyst arising from the allenylidene complex [RuCl(=C=C=CPh_2)(PCy_3)(*p*-cymene)][OTf],[10]

no trace of *N*-tosyl-2,5-dihydropyrrole was detected, which indicated that no metathesis reaction took place with precursors **7**.

The catalysts resulting from **6a**−**c** and **6e**−**f**, which bear an aliphatic R group as substituent of the benzimidazole ligand led to the formation of the 3-methyl-4-methylene heterocycle **9**. The reaction was faster in chlorobenzene than in toluene and the total conversion of the starting substrate could be achieved in 10 h with the precatalyst **7b** and within 18−20 h with **7a** and **7f**.

The catalytic species generated from **7d** containing the *N*-(2,4,6-trimethylbenzyl)-substituted benzimidazole ligand **5** was much more efficient and the complete conversion of **8** to **9** was carried out in toluene in less than 4 h. Under the reaction conditions, a subsequent isomerization took place which led to 3,4-dimethyl-*N*-tosylpyrroline (**10**) bearing a tetrasubstituted endocyclic double bond in quantitative yield at 80 °C after 10 h, whatever the solvent. Apparently, in toluene, as the formation of **10** starts only after complete conversion of **8**, the presence of the starting diene inhibits the isomerization of **9** to **10**. The analogous catalytic system **7g** resulting from the C_6Me_6-containing precursor was less active at 80 °C after 20 h, as the conversion reached only 79 % and a 1:1 mixture of **9** and **10** was obtained. This observation is consistent with the hypothesis of the initial displacement of the arene ligand to generate the catalytic species (Scheme 5).[13b,14,15] During the catalytic process, the formation of indenylidene complexes by rearrangement of the allenylidene ligand, cannot be ruled out.[16]



Scheme 5

From a separate experiment, it was possible to show that **10** resulted from the catalytic isomerization of **9** in the presence of **7d** as catalyst. Thus, by using the catalytic system prepared in situ from 2.5 mol % of the ruthenium precursor **6d**, AgOTf (2.5 mol %) and HC≡CCPh$_2$OH (2.5 mol %) in 2.5 mL of toluene, **9** (0.5 mmol) was completely converted into **10** at 80 °C after 4 h. Two possible mechanisms could account for this isomerization: (i) allylic C−H activation and H migration via an (allyl)(hydrido)ruthenium intermediate **A** or (ii) if a Ru−H species is formed, by insertion of the exocyclic double bond into a Ru−H bond followed by β-elimination (Scheme 5). Both processes should be stereoselective as the coordination of the Ru atom should preferentially take place on the less hindered face of **9**. Thus, β-elimination from **B** should be favored with H_a in the *syn* position, as well as the (allyl)ruthenium formation by coordination to **9** on the sterically less hindered face.

Transition-metal-catalyzed cycloisomerization reactions from α,ω-dienes is a topic of current interest.[17] The formation of 3-methyl-4-methylene cyclic derivatives of type **9** has already been observed with several metal catalysts including palladium,[18,19] nickel,[19] rhodium[20] and titanium.[21] Other efficient catalytic systems based on ruthenium precursors such as $[Ru(cod)Cl_2]_n$ or Cp*Ru(cod)Cl in protic solvents,[22] or generated in situ from $[RuCl_2(p\text{-cymene})]_2$, an imidazolinium salt and a base,[15] have been reported.

A few examples of cycloisomerization of 1,6-diene into 1,2-dimethylcyclopentene derivatives involve palladium catalysts in the presence of silane[23] or rhodium catalysts,[20] and most of the substrates which lead to these cycloisomerization products are 2,2-diallylmalonate derivatives. In the present ruthenium-catalyzed isomerization of **8** to **10**, the role of the 2,4,6-trimethylbenzyl ligand in **7d** appears to be crucial. It might result from temporary interaction of the mesityl group with the metal center as its coordination operates with closely related diaminocarbene ligands.[13b,14]

Conclusion

New ruthenium species generated in situ from $RuCl_2$(arene)(benzimidazole) complexes in the presence of 1,1-diphenylprop-2-ynol are active catalysts to perform the cycloisomerization of *N*,*N*-diallyltosylamide to the *N*-tosylpyrrolidine **9** featuring an exocyclic methylene group under neutral and mild conditions. The catalyst containing the benzimidazole **5** (R = 2,4,6-$Me_3C_6H_2CH_2$) exhibits specific catalytic properties. It leads to the fastest cycloisomerization reaction and in addition offers the first example of ruthenium-catalyzed isomerization of 3-methyl-4-methylene-*N*-tosylpyrrolidine (**9**) to 3,4-dimethyl-*N*-tosylpyrroline (**10**).

Experimental Section

General: Manipulations were carried out with standard Schlenk techniques under nitrogen with previously dried solvents. The complexes $[RuCl_2(arene)]_2$ were prepared according to known methods.[24] 1-Substituted benzimidazoles **2**−**5** were prepared by alkylation of the potassium salt of benzimidazole. Infrared spectra were recorded as KBr pellets in the range 400−4000 cm^{-1} with an ATI UNICAM 2000 spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were recorded with a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK analyses centre.

Preparation of the Ruthenium(benzimidazole) Complexes 6a−g: A solution of the *N*-substituted benzimidazole **2**−**5** (1.05 mmol) and $[RuCl_2(p\text{-cymene})]_2$ or $[RuCl_2(hexamethylbenzene)]_2$ (0.5 mmol) in toluene (15 mL) were heated under reflux for 2 h. Upon cooling to room temperature, orange crystals of **6a**−**g** were obtained. The crystals were filtered, washes with diethyl ether (3 × 10 mL) and dried under vacuum.

$RuCl_2$(*p*-cymene)(*N*-isopropylbenzimidazole) (6a): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, N=C*H*), 7.33 (m, 4 H, C_6H_4), 5.42 and 5.32 [2 × d, *J* = 6.00 Hz, 4 H, $(CH_3)_2CHC_6H_4CH_3$], 4.58 [sept, *J* = 6.70 Hz, 1 H, C*H*$(CH_3)_2$], 2.06 [s, 3 H, $(CH_3)_2CHC_6H_4CH_3$], 1.83 [sept, *J* = 7.00 Hz, 1 H, $(CH_3)_2CHC_6H_4CH_3$], 1.49 [d, *J* = 6.70 Hz, 6 H, CH$(CH_3)_2$], 1.18 [d, *J* = 7.00 Hz, 6 H, $(CH_3)_2CHC_6H_4CH_3$] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 142.9 (N=*C*H), 142.2, 133.2, 123.8, 123.5, 120.7, 111.5 (m, C_6H_4), 102.4, 97.9, 82.8, 81.2 $[(CH_3)_2CHC_6H_4CH_3]$, 49.0 [*C*H$(CH_3)_2$], 30.7 $[(CH_3)_2CHC_6H_4CH_3]$, 22.5 [CH$(CH_3)_2$], 22.3 $[(CH_3)_2CHC_6H_4CH_3]$, 18.5 $[(CH_3)_2CHC_6H_4CH_3]$ ppm. Yield 0.39 g (85%). $C_{20}H_{26}Cl_2N_2Ru$ (466.42): calcd. C 51.50, H 5.62, N 6.01; found C 51.40, H 5.71, N 6.10.

$RuCl_2$(*p*-cymene)(*N*-butylbenzimidazole) (6b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H, N=C*H*), 7.95−7.27 (m, 4 H, C_6H_4), 5.47 and 5.32 [2 × d, *J* = 5.96 Hz, 4 H, $(CH_3)_2CHC_6H_4CH_3$], 3.98 (t, *J* = 7.21 Hz, 2 H, CH_2CH$_2$CH$_2$CH$_3$), 2.77 [sept, *J* = 6.89 Hz, 1 H, $(CH_3)_2CHC_6H_4CH_3$], 2.05 [s, 3 H, $(CH_3)_2CHC_6H_4CH_3$], 1.72 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 1.26 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 1.21 [d, *J* = 4.82 Hz, 6 H, $(CH_3)_2CHC_6H_4CH_3$], 0.86 (t, *J* = 7.38 Hz, 3 H, CH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.5 (N=*C*H), 142.5, 133.7, 124.0, 123.4, 120.5, 110.9, (C_6H_4), 102.4, 97.8, 82.9, 81.1$[(CH_3)_2CHC_6H_4CH_3]$, 45.7 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.6 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 30.7 $[(CH_3)_2CHC_6H_4CH_3]$, 22.3 $[(CH_3)_2CHC_6H_4CH_3]$, 19.9 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 20.0 $[(CH_3)_2CHC_6H_4CH_3]$, 13.6 (CH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. Yield 0.42 g (87%). $C_{21}H_{28}Cl_2N_2Ru$ (480.45): calcd. C 52.50, H 5.87, N 5.83; found C 52.43, H 6.01, N 5.96.

$RuCl_2$(*p*-cymene)[*N*-(2-methoxyethyl)benzimidazole] (6c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, N=C*H*), 7.94−7.26 (m, 4 H, C_6H_4), 5.47 and 5.31 [2 × d, *J* = 6.00 Hz, 4 H, $(CH_3)_2CHC_6H_4CH_3$)], 3.92 (t, *J* = 5.00 Hz, 2 H, CH$_2$CH_2OCH$_3$), 3.47 (t, *J* = 5.10 Hz, 2 H, CH_2CH$_2$OCH$_3$), 3.16 (s, 3 H, CH$_2$CH$_2$OCH_3), 2.78 [sept, *J* = 6.90 Hz, 1 H, $(CH_3)_2CHC_6H_4CH_3$], 2.38 [d, *J* = 6.90 Hz, 6 H, $(CH_3)_2CHC_6H_4CH_3$)], 2.03 [s, 3 H, $(CH_3)_2CHC_6H_4CH_3$)] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 145.5 (N=*C*H), 142.2, 133.4, 124.1, 123.2, 120.2, 111.3 (C_6H_4), 102.5, 97.8, 82.9, 81.2 $[(CH_3)_2CHC_6H_4CH_3)]$, 69.9 (CH$_2$*C*H$_2$OCH$_3$), 58.7 (CH$_2$CH$_2$O*C*H$_3$), 45.6 (*C*H$_2$CH$_2$OCH$_3$), 30.6 $[(CH_3)_2CHC_6H_4CH_3]$, 21.9 $[(CH_3)_2CHC_6H_4CH_3)]$, 18.4 $[(CH_3)_2CHC_6H_4CH_3)]$ ppm. Yield 0.42 (87%). $C_{20}H_{26}Cl_2N_2ORu$ (482.42): calcd. C 49.80, H 5.43, N 5.81; found C 49.97, H 5.55, N 6.03.

$RuCl_2$(*p*-cymene)[*N*-(2,4,6-trimethylbenzyl)benzimidazole] (6d): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, 1 H, N=C*H*), 7.99−7.20 (m, 4 H, C_6H_4), 6.85 [s, 2 H, $(CH_3)_3C_6H_2CH_2$], 5.29 and 5.20 [2 × d, *J* = 5.75 Hz, 4 H, $(CH_3)_2CHC_6H_4CH_3$], 5.14 [s, 2 H, $(CH_3)_3C_6H_2CH_2$], 2.54 [sept, *J* = 6.90 Hz, 1 H, $(CH_3)_2CHC_6H_4CH_3$], 2.26 [s, 3 H, $(CH_3)_2CHC_6H_4CH_3$), 2.13, 2.23 [s, 9 H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 1.01 [d, *J* = 6.90 Hz, 6 H, $(CH_3)_2CHC_6H_4CH_3$] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.2 (N=*C*H), 142.5, 133.7, 124.0, 123.4, 120.5, 110.9 (C_6H_4), 139.1, 137.8, 129.9, 126.7 $[(CH_3)_3C_6H_2CH_2]$, 101.9, 98.1, 83.0, 80.9 $[(CH_3)_2CHC_6H_4CH_3]$, 43.9 $[(CH_3)_3C_6H_2CH_2]$, 30.6 $[(CH_3)_2CHC_6H_4CH_3]$, 24.1 $[(CH_3)_2CHC_6H_4CH_3]$, 21.1, 19.8 $[(CH_3)_3C_6H_2CH_2]$, 18.5 $[(CH_3)_2CHC_6H_4CH_3]$ ppm. Yield 0.5 g (90%). $C_{27}H_{32}Cl_2N_2Ru$ (556.54): calcd. C 58.27, H 5.80, N 5.04; found C 58.32, H 5.86, N 5.21.

$RuCl_2$(hexamethylbenzene)(*N*-butylbenzimidazole) (6e): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (s, 1 H, N=C*H*), 7.80−7.21 (m, 4 H, C_6H_4), 3.99 (t, *J* = 7.20 Hz, 2 H, CH_2CH$_2$CH$_2$CH$_3$), 1.96 [s, 18 H, $C_6(CH_3)_6$], 1.67 (m, 2 H, CH$_2$CH_2CH$_2$CH$_3$), 1.25 (m, 2 H, CH$_2$CH$_2$CH_2CH$_3$), 0.87 (t, *J* = 7.38 Hz, 3 H, CH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 145.1 (N=*C*H), 133.7, 128.2, 123.8, 121.2, 110.6 (C_6H_4), 90.9 $[C_6(CH_3)_6]$, 45.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.7 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.1 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 15.8 $[C_6(CH_3)_6]$, 13.6 (CH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. Yield 0.44 g (86%). $C_{23}H_{32}Cl_2N_2Ru$ (508.49): calcd. C 54.33, H 6.34, N 5.51; found C 54.58, H 6.19, N 5.73.

$RuCl_2$(hexamethylbenzene)[*N*-(2-methoxyethyl)benzimidazole] (6f): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (s, 1 H, N=C*H*), 7.20−7.90 (m, 4 H, C_6H_4), 3.85 (t, *J* = 5.00 Hz, 2 H, CH$_2$CH_2OCH$_3$), 3.41 (t, *J* = 5.09 Hz, 2 H, CH_2CH$_2$OCH$_3$), 3.12 (s, 3 H, CH$_2$CH$_2$OCH_3), 1.94 [s, 18 H, $C_6(CH_3)_6$] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 146.2 (N=*C*H), 140.5, 133.2, 123.8, 122.4, 120.7, 111.2 (C_6H_4), 90.9 $[C_6(CH_3)_6]$, 69.8 (CH$_2$*C*H$_2$OCH$_3$), 58.6 (CH$_2$CH$_2$O*C*H$_3$), 45.3 (*C*H$_2$CH$_2$OCH$_3$), 15.7 $[C_6(CH_3)_6]$ ppm. Yield 0.42 g (82%). $C_{22}H_{30}Cl_2N_2ORu$ (510.47): calcd. C 51.76, H 5.92, N 5.49; found C 51.70, H 5.83, N 5.67.

$RuCl_2$(hexamethylbenzene)[*N*-(2,4,6-trimethylbenzyl)benzimidazole] (6g): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 1 H, N=C*H*), 8.05−7.26 (m, 4 H, C_6H_4), 6.95 [s, 2 H, $(CH_3)_3C_6H_2CH_2$], 5.21 [s, 2 H, $(CH_3)_3C_6H_2CH_2$], 2.31, 2.23 [s, 9 H, $(CH_3)_3C_6H_2CH_2$], 1.87 [s, 18 H, $C_6(CH_3)_6$] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.8 (N=*C*H), 141.2, 134.1, 123.9, 123.0, 121.0, 110.3 (C_6H_4), 139.1, 137.3, 129.7, 126.9 $[(CH_3)_3C_6H_2CH_2]$, 90.7 $[C_6(CH_3)_6]$, 43.7 $[(CH_3)_3C_6H_2CH_2]$, 21.1, 19.8 $[(CH_3)_3C_6H_2CH_2]$, 15.6 $[C_6(CH_3)_6]$ ppm. Yield 0.50 g (86%). $C_{29}H_{36}Cl_2N_2Ru$ (584.60): calcd. C 59.58, H 6.21, N 4.79; found C 59.37, H 6.26, N 4.93.

Compounds **9**[15a] and **10**[25] were separated by GCMS chromatography and identified by ^{1}H NMR and compared with data from the literature.

3-Methyl-4-methylene-*N*-tosylpyrrolidine (9): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.1 Hz, 2 H, arom. C*H*), 7.30 (d, *J* = 8.1 Hz, 2 H, arom. C*H*), 4.93 (dm, *J* = 1.6 Hz, 1 H, C=CH*H*), 4.88 (dm, *J* = 1.6 Hz, 1 H, C=C*H*H), 3.93 (dm, *J* = 14.1 Hz, 1 H, CH_2C=), 3.71 (dm, *J* = 14.1 Hz, 1 H, CH_2C=), 3.35−3.65 (m, 1 H, C*H*Me), 2.66 (m, 2 H, NCH_2CH), 2.41 (s, 3 H, CH_3Ar), 1.01 (d, *J* = 6.3 Hz, 3 H, CHMe) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 149.3, 143.7, 137.1, 129.7, 127.8, 106.1, 55.1, 52.2, 37.5, 21.6, 16.1 ppm.

3,4-Dimethyl-*N*-tosylpyrroline (10): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.36 (m, 4 H, arom. C*H*), 4.04 (s, 4 H, 2 × CH_2), 2.48 (s, 3 H, CH_3Ar),1.60 (s, 6 H, 2 × CH_3C=) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 143.7, 134.6, 130.2, 128.2, 127.3, 126.6, 66.3, 21.9, 11.6 ppm.

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