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PAPER

Assessing the ligand properties of 1,3-dimesitylbenzimidazol-2-ylidene in ruthenium-catalyzed olefin metathesis†

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The deprotonation of 1,3-dimesitylbenzimidazolium tetrafluoroborate with a strong base afforded 1,3-dimesitylbenzimidazol-2-ylidene (BMes), which was further reacted *in situ* with rhodium or ruthenium complexes to afford three new organometallic products. The compounds [RhCl(COD)(BMes)] (COD is 1,5-cyclooctadiene) and *cis*-[RhCl(CO)$_2$(BMes)] were used to probe the steric and electronic parameters of BMes. Comparison of the percentage of buried volume (%V_{Bur}) and of the Tolman electronic parameter (TEP) of BMes with those determined previously for 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-dimesitylimidazolin-2-ylidene (SIMes) revealed that the three *N*-heterocyclic carbenes (NHCs) had very similar profiles. Nonetheless, changes in the hydrocarbon backbone subtly affected the stereoelectronic properties of these ligands. Accordingly, the corresponding [RuCl$_2$(PCy$_3$)(NHC)(=CHPh)] complexes displayed different catalytic behaviors in the ring-closing metathesis (RCM) of α,ω-dienes. In the benchmark cyclization of diethyl 2,2-diallylmalonate, the new [RuCl$_2$(PCy$_3$)(BMes)(=CHPh)] compound (**1d**) performed slightly better than the Grubbs second-generation catalyst (**1a**), which was in turn significantly more active than the related [RuCl$_2$(PCy$_3$)(IMes)(=CHPh)] initiator (**1b**). For the formation of a model trisubstituted cycloolefin, complex **1d** ranked in-between catalyst precursors **1a** and **1b**, whereas in the RCM of tetrasubstituted cycloalkenes it lost its catalytic efficiency much more rapidly.

Introduction

Since the first imidazol-2-ylidene derivative was isolated and characterized by Arduengo in 1991,[1] stable *N*-heterocyclic carbenes (NHCs) have become efficient tools in organic synthesis and catalysis.[2] Over the past two decades, these divalent carbon species have emerged as powerful nucleophilic organocatalysts for asymmetric synthesis.[3] They have also afforded an impressive range of transition-metal complexes that have found countless applications in homogeneous catalysis.[4] In particular, NHC ligands have largely contributed to the advent of highly efficient ruthenium catalysts for olefin metathesis and related reactions.[5] Indeed, mixed complexes bearing both a phosphine and an NHC ligand were quickly identified as superior metathesis initiators compared to their bis(phosphine) or bis(NHC) analogues.[6] These observations sparked the development of a broad family of so-called second-generation ruthenium initiators for olefin metathesis, whose most prominent representatives include the 16-electron benzylidene complexes of type **1**[7] and the related indenylidene compounds of type **2** (Fig. 1).[8]

Extensive catalytic screening,[9–13] supported by mechanistic investigations[14] and theoretical studies,[15,16] allowed us to better understand the role of the NHC ligand in complexes of type **1** or **2**. It was soon recognized that the presence of large *N*-aryl substituents on the imidazole ring system, such as the mesityl (2,4,6-trimethylphenyl) or 2,6-diisopropylphenyl groups, usually provided the right balance of steric protection and electronic

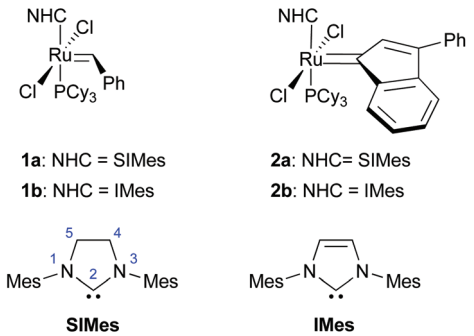

Fig. 1 Second-generation ruthenium–benzylidene (**1**) and indenylidene (**2**) catalysts for olefin metathesis (PCy_3 = tricyclohexylphosphine, Mes = 2,4,6-trimethylphenyl).

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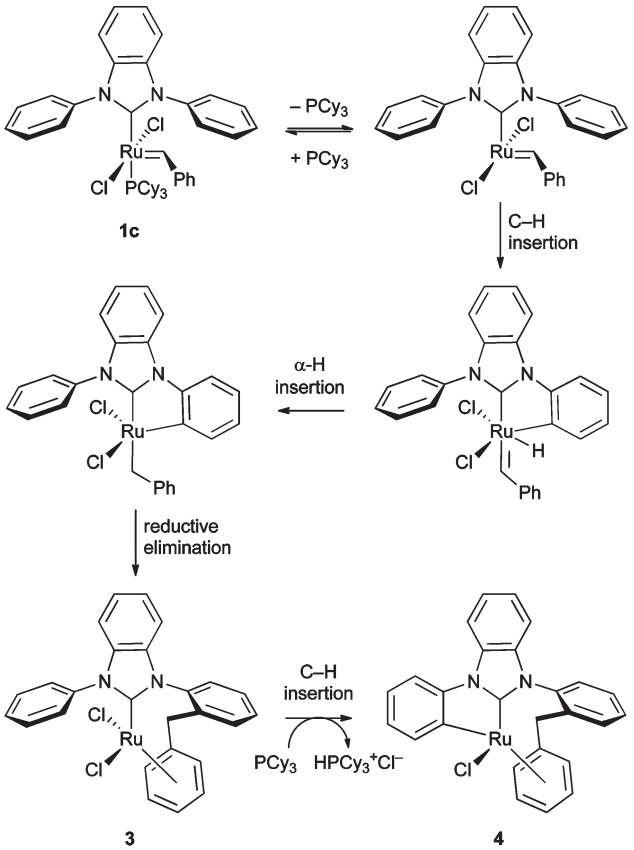
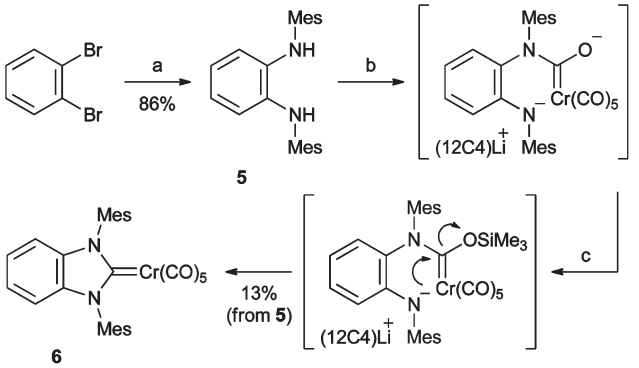


Scheme 1 Possible mechanism for the decomposition of complex **1c**.



Scheme 2 Synthesis of [(BMes)Cr(CO)$_5$] (**6**). *Reaction conditions*: (a) $MesNH_2$, $Pd(OAc)_2$, BINAP, $NaOBu^t$, $PhCH_3$, reflux, 12 h; (b) [$Cr(CO)_6$], BuLi, 12-crown-4, THF, −78 °C, 15 min then 0 °C, 30 min; (c) Me_3SiCl, −78 °C, 15 min, then 0 °C, 30 min, and RT, 3 h.

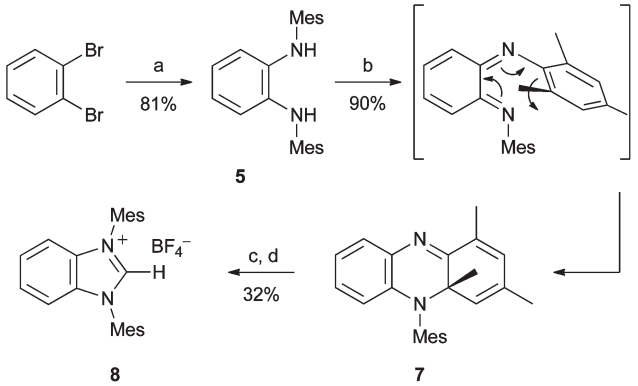
donation to many NHC-based catalytic systems, while avoiding *ortho*-metalation side-reactions.[17,18] Thus, complexes **1a**[19] and **2a**[20] featuring the 1,3-dimesitylimidazolin-2-ylidene ligand (nicknamed SIMes) have become standard catalysts for olefin metathesis and are now commercially available.

Tinkering with their hydrocarbon backbone offers additional options to fine-tune the stereoelectronic properties of NHC ligands. Hence, modifications of the heterocycle core have attracted a great deal of attention from the catalysis community.[21,22] It should be pointed out, however, that introducing variations on the C^4 or C^5 positions of the imidazole ring system is often more challenging from a synthetic point of view than altering the nature of the N^1 or N^3 substituents.[23] In parallel with the development of the "saturated" imidazolin-2-ylidene ligand SIMes, early investigations focused on the use of the corresponding "unsaturated" imidazol-2-ylidene compound nicknamed IMes (Fig. 1). These studies led to complexes **1b**[24] and **2b**[25] that were usually found to be less active than compounds **1a** and **2a**,[9,12,13,26,27] although the exact reasons for this discrepancy are still unclear.[16,28,29]

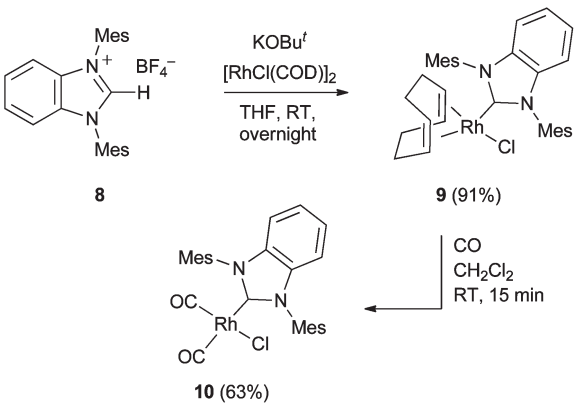
Several fused polycyclic NHCs were successfully designed for asymmetric organocatalysis,[30] but they were seldom used as ligands in ruthenium-promoted olefin metathesis reactions.[18,19,31] To the best of our knowledge, only one example of a ruthenium–benzylidene catalyst sporting a benzimidazolylidene ligand has been reported so far. Thus, in 2007 Grubbs *et al.* disclosed the synthesis of complex **1c** featuring the 1,3-diphenylbenzimidazol-2-ylidene ligand (Scheme 1).[32] This compound was highly unstable and decomposed rapidly into metathetically inactive species in air. More detailed investigations led to the isolation of degradation products **3** and **4**, whose molecular structures were determined by X-ray diffraction analysis.[33] The mechanism postulated to rationalize their formation is illustrated in Scheme 1. It involves the activation of *ortho* C–H bonds on both phenyl substituents of the NHC ligand with the assistance of the dissociated phosphine present in solution and is supported by DFT calculations performed independently by the groups of Suresh[34] and Cavallo.[35]

We reasoned that protecting the *ortho*-positions of the *N*-phenyl substituents in complex **1c** with alkyl groups would alleviate its tendency to decomposition and should result in a new, promising second-generation catalyst for olefin metathesis. Therefore, we launched a research program to investigate the ligand properties of benzimidazol-2-ylidene derivatives bearing bulky aromatic substituents on their nitrogen atoms. Several attempts to synthesize suitable precursors for these compounds had met with failure,[36] and we are only aware of a single report that describes the synthesis of pentacarbonylchromium(0) complex **6** bearing the 1,3-dimesitylbenzimidazol-2-ylidene ligand (nicknamed BMes).[37] In this case, the NHC was assembled directly on the metal upon reaction of the lithium 1,2-phenylenediamide derived from **5** with [$Cr(CO)_6$] in the presence of 12-crown-4, followed by treatment with chlorotrimethylsilane (Scheme 2). Given the limited scope of this ingenious strategy and the poor yield attained, we searched for a more satisfactory entry to the chemistry of the BMes ligand. Eventually, we managed to prepare 1,3-dimesitylbenzimidazolium tetrafluoroborate (**8**) *via* the intermediacy of dihydrophenazine **7** formed upon oxidation of *N*,*N*′-dimesityl-1,2-benzenediamine (**5**) with sodium periodate on wet silica gel, followed by electrocyclic ring closure (Scheme 3).[38]

In this contribution, we first assess the steric and electronic properties of the 1,3-dimesitylbenzimidazol-2-ylidene ligand (BMes) using rhodium complexes. Then, we report on the synthesis of the second-generation ruthenium–benzylidene complex [$RuCl_2(PCy_3)$(BMes)(=CHPh)] (**1d**) and we probe its catalytic activity in ring-closing metathesis (RCM) using benchmark reactions.



Scheme 3 Synthesis of 1,3-dimesitylbenzimidazolium tetrafluoroborate (**8**). *Reaction conditions*: (a) $MesNH_2$, $Pd(OAc)_2$, $P(Bu^t)_3$, $NaOBu^t$, $PhCH_3$, 110 °C, overnight; (b) $NaIO_4$, SiO_2, H_2O, CH_2Cl_2, RT, 24 h; (c) $^tBuCO_2CH_2Cl$, AgOTf, KOAc, CH_2Cl_2, 50 °C, 48 h; (d) HBF_4, H_2O, RT, 1 h.



Scheme 4 Synthesis of [RhCl(COD)(BMes)] (**9**) and *cis*-[RhCl-$(CO)_2$(BMes)] (**10**).

Table 1 Steric and electronic parameters of mesityl-based NHC ligands coordinated to rhodium

NHC	$\%V_{Bur}$ [a]	δ_{Rh-C} [b]/ppm	$\bar{\nu}_{CO}$ [c]/cm^{-1}	TEP[d]/cm^{-1}
IMes	31.7[e]	183.6[f]	2038.5[f]	2051.0
BMes	30.0	196.4	2040.0	2052.2
SIMes	32.7[g]	212.8[f]	2040.5[f]	2052.6

[a] Computed using the web-based application Samb*V*ca[46] from the XRD structures of the corresponding [RhCl(COD)(NHC)] complexes. [b] ^{13}C NMR chemical shift of the carbene carbon in [RhCl(COD)(NHC)] complexes. [c] Average wavenumber for the stretching vibration of CO ligands in [RhCl$(CO)_2$(NHC)] complexes. [d] Tolman electronic parameter calculated using eqn (1). [e] Based on the data from ref. 47. [f] Taken from ref. 40. [g] Based on the data from ref. 48.

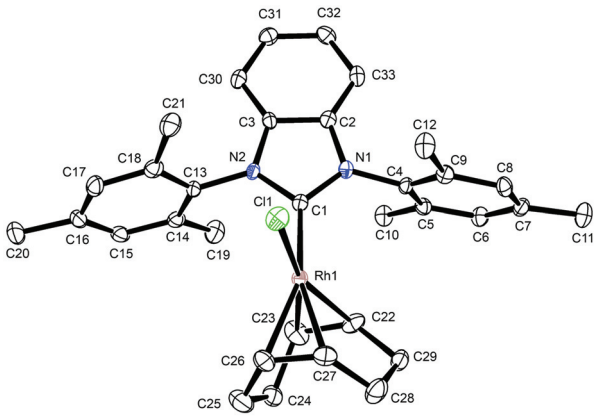


Fig. 2 ORTEP representation of [RhCl(COD)(BMes)] (**9**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen and disordered atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–C1 2.029(3), Rh1–Cl1 2.3556(9), Rh1–C22 2.096(3), Rh1–C23 2.118(3), Rh1–C26 2.180(4), Rh1–C27 2.197(3), C1–Rh1–Cl1 87.52 (8), N1–C1–N2 104.1(2), C1–N1–C4–C5 93.1(3), C1–N2–C13–C14 −84.3(4).

Results and discussion

Evaluation of the steric and electronic properties of BMes

Over the past few years, several distinct methods were developed to quantify the steric and electronic properties of NHC ligands.[39–41] Among them, the study of [RhCl(COD)(NHC)] (COD is 1,5-cyclooctadiene) and *cis*-[RhCl$(CO)_2$(NHC)] derivatives to probe steric parameters and electronic factors, respectively, is perhaps the most popular one, owing to the straightforward preparation, high stability, and low toxicity of the rhodium complexes involved. Hence, we first synthesized [RhCl(COD)(BMes)] (**9**) by deprotonating benzimidazolium salt **8** with potassium *tert*-butoxide to generate the BMes carbene *in situ*, followed by cleavage of the $[RhCl(COD)]_2$ dimer (Scheme 4). The desired product was isolated in 91% yield after purification by column chromatography.

^{13}C NMR analysis of complex **9** in CD_2Cl_2 revealed the presence of a highly deshielded doublet, whose chemical shift (196.4 ppm) and multiplicity ($^1J_{Rh-C}$ = 52.4 Hz) left little doubt about the successful coordination of a carbene ligand to the metal center. It is noteworthy that this chemical shift is almost exactly average between those recorded for [RhCl(COD)(IMes)] and [RhCl(COD)(SIMes)] (Table 1).‡ This trend is not unprecedented in the literature. For example, the chemical shifts of the carbenoid centers in chromium complexes with the general formula $[(NHC)Cr(CO)_5]$ increase in the following order: imidazol-2-ylidenes (186–200 ppm)[42,43] < benzimidazol-2-ylidenes (200–210 ppm)[37,43] < imidazolin-2-ylidenes (217–225 ppm).[44] This evolution was explained by a parallel decrease in the π-charge density on C^2 when aromatic conjugation in the 6π-electron imidazole ring is shared with the benzannulated moiety or disrupted by saturation of the $C^4{=}C^5$ double bond.[45]

Bright yellow crystals of [RhCl(COD)(BMes)] (**9**) were grown by evaporating a dichloromethane solution and subjected to X-ray diffraction analysis (Fig. 2).† As expected, a square-planar arrangement of the ligands around the metal center was observed, with the NCN plane of the carbene approximately perpendicular to the coordination plane of rhodium. The cyclooctadiene ring presented a little disorder, with two different

‡(183.6 + 212.8)/2 = 198.2 ppm.

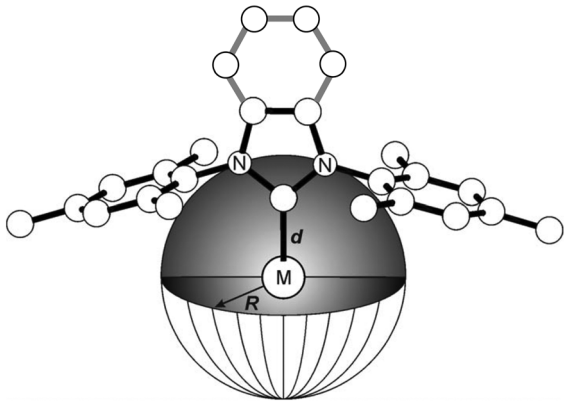


Fig. 3 Graphical representation of the sphere used to calculate the $\%V_{Bur}$ parameter for the mesityl-based NHC ligands IMes, BMes and SIMes.

orientations in a *ca.* 65/35 ratio for the C–C single bonds linking the C=C double bond *trans* to the halogen. Altogether, the various bond lengths and angles were in line with those reported previously for other complexes of the same family,[49] including [RhCl(COD)(IMes)][47] and [RhCl(COD)(SIMes)].[48]

In order to quantify the steric demand of NHC ligands, Cavallo and Nolan have defined a parameter called the "percentage of buried volume" ($\%V_{Bur}$), which gives a measure of the space occupied by a ligand in the first coordination sphere of a metal center (Fig. 3).[50,51] The bulkier an NHC ligand is, the greater its $\%V_{Bur}$. Several refinements were brought to the set of atom radii and sphere radius used for the calculations and the resulting algorithm can now be run *via* a user-friendly interface on the internet.[46] We have used this front-end to compute the $\%V_{Bur}$ parameter of BMes based on the crystal structure of [RhCl(COD)(BMes)] (**9**). The default processing parameters were kept unchanged (sphere radius: 3.5 Å; distance from the center of the sphere: 2.10 Å; mesh spacing: 0.05 Å; Bondi radii scaled by 1.17).

Because only a small area around the nitrogen atoms is mainly responsible for the value of $\%V_{Bur}$ (*cf.* Fig. 3), rather similar behaviors were expected for BMes and the other mesityl-based NHCs, IMes and SIMes. We were surprised, however, to find out that the "aromatic" backbone led to a slightly *lower* value of $\%V_{Bur}$ than its "unsaturated" or "saturated" counterparts (Table 1).[52] Indeed, given that the N–C–N angle of the carbene ligand in complex **9** (104.1(2)°) lies in-between those recorded for IMes (103.50(14)°)[47] and SIMes (107.29(12)°)[48] in the respective [RhCl(COD)(NHC)] complexes, one would have expected an intermediate $\%V_{Bur}$ value for BMes compared to its "unsaturated" and "saturated" analogues. It is noteworthy that our experimental results fit nicely with earlier theoretical calculations based on DFT optimized geometries, which had already predicted a slightly *lower* $\%V_{Bur}$ parameter for BMes (31.2) compared to IMes (31.6) and SIMes (32.7).[46] Crystal structures obtained for ruthenium catalysts were therefore examined to further probe the tendency observed with rhodium complexes (*vide infra*).

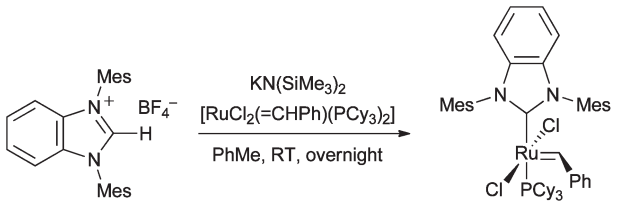
Dissolving the [RhCl(COD)(BMes)] complex **9** in dichloromethane and bubbling carbon monoxide for 15 min led to the displacement of the COD ligand and afforded the *cis*-dicarbonyl complex **10** in 63% yield (Scheme 4). The IR spectrum of this compound was recorded in CH_2Cl_2 to allow a direct comparison of the $\bar{\nu}_{CO}$ values with previous measurements carried out in the same way on [RhCl(CO)$_2$(IMes)] and [RhCl(CO)$_2$(SIMes)] by Wolf and Plenio (Table 1).[40] The Tolman electronic parameter (TEP) was then computed using the linear regression proposed by Dröge and Glorius to correlate data obtained for Rh and Ni complexes (eqn (1)).[41] For the series of *N*,*N*′-dimesityl substituted NHCs under scrutiny, the electron-donating character increased in the order SIMes < BMes < IMes. This sequence is in good agreement with the evolution of ^{13}C NMR chemical shifts discussed above for the C^2 carbenic center and further supports the idea that benzimidazole-derived NHCs have intermediate electronic properties compared to imidazole and imidazoline derivatives.

$$\mathrm{TEP}/\mathrm{cm}^{-1} = 0.8001\bar{\nu}_{CO}{}^{\mathrm{Rh,average}}/\mathrm{cm}^{-1} + 420 \qquad (1)$$

It is important to stress that the steric and electronic parameters under investigation differed only marginally when switching from IMes to BMes or SIMes ($\Delta\%V_{Bur}$ = 2.7%, $\Delta\bar{\nu}_{CO}$ = 2.0 cm^{-1}). Electrochemical measurements could help further refine this analysis as they are often more sensitive than TEP determinations for probing the donor properties of NHC ligands,[40,53] especially in ruthenium catalysts for olefin metathesis.[54] From the data gathered here, it is nonetheless obvious that changes in the hydrocarbon backbone of an NHC ligand have only a limited influence on its steric and electronic properties, as long as the core heterocycle remains a five-membered ring with two nitrogen atoms. Likewise, introduction of methyl or halogen substituents on the C^4 and C^5 positions of IMes had only a minor impact on the $\%V_{Bur}$ and TEP parameters.[22] Expanding the heterocycle to a 6, 7 or 8-membered ring is a better option to alter more substantially the $\%V_{Bur}$ parameter.[55] Modulation of the N^1 and N^3 substituents provides another suitable approach to adjust the steric properties of NHC ligands, due to their proximity to the metal center. Unless they bear strong electron-donating or withdrawing functional groups,[56] exocyclic alkyl or aryl groups do not, however, have a strong electronic impact, because of the lack of conjugation with the donor C^2 atom. Arguably, the most convenient approach developed so far to broadly tune the donor properties of imidazole-based NHC ligands involves the derivatization of an enolate group as a reactive C^4–C^5 backbone.[57]

Synthesis of [RuCl$_2$(PCy$_3$)(BMes)(=CHPh)] (1d)

Deprotonation of benzimidazolium salt **8** with potassium bis(trimethylsilyl)amide followed by ligand exchange with the Grubbs first-generation catalyst [RuCl$_2$(PCy$_3$)$_2$(=CHPh)] led to the mixed complex **1d** featuring the BMes ligand (Scheme 5). This product was isolated in 82% yield after removal of the accompanying free phosphine by column chromatography under an inert atmosphere. It was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and its crystal structure was determined by X-ray diffraction analysis (Fig. 4).† The ^{1}H and ^{13}C NMR spectra were recorded at 223 K to allow the observation of the signals due to the *meta*-hydrogen atoms on the mesityl substituents, which



Scheme 5 Synthesis of $[RuCl_2(PCy_3)(BMes)(=CHPh)]$ (**1d**).

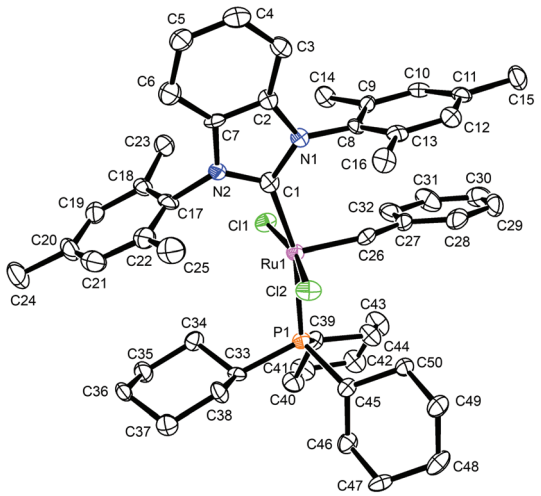
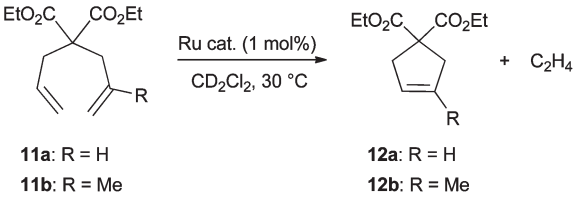


Fig. 4 ORTEP representation of $[RuCl_2(PCy_3)(BMes)(=CHPh)]$ (**1d**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–C1 2.060(6), Ru1–C26 1.835(6), Ru1–Cl1 2.3781(16), Ru1–Cl2 2.3920(16), Ru1–P1 2.4252(16), C1–Ru1–P1 163.98(17), Cl1–Ru1–Cl2 168.35(6), C1–Ru1–C26 97.8(2), Cl1–Ru1–C26 102.6(2), N1–C1–N2 103.7(5), C2–N1–C8 120.6(5), C7–N2–C17 121.3(4), C1–N1–C8–C9 82.3(7), C1–N2–C17–C22 103.3(7).

completely disappeared in the baseline at room temperature. In the solid state, complex **1d** exhibited a distorted square pyramidal geometry with the benzylidene moiety occupying the apical position. No significant deviations were observed between the spectroscopic data acquired for this new compound and those reported previously for the analogous second-generation ruthenium–benzylidene catalysts **1a**[58] and **1b**.[24]

We were particularly interested in extracting the $\%V_{Bur}$ parameter of BMes from the crystal structure of **1d** in order to determine whether the steric pressure exerted by the benzimidazolylidene ligand was indeed slightly inferior to those displayed by IMes and SIMes, as observed in the [RhCl(COD)(NHC)] complexes (*vide supra*). In the $[RuCl_2(PCy_3)(NHC)(=CHPh)]$ series, however, the $\%V_{Bur}$ computed for BMes (30.3) was intermediate between those obtained from the molecular structures of complex **1b** (30.1) and the Grubbs second-generation catalyst **1a** (31.3). These fluctuations confirm the structural flexibility of mesityl-based NHCs and their ability to fit with the crowding around the metal center.[29,51] They also show that changes between "saturated", "aromatic", and "unsaturated" backbones have only a subtle, unpredictable influence on the buried volume.



Scheme 6 Ruthenium-catalyzed RCM of diethyl 2,2-diallylmalonate (DEDAM, **11a**) and diethyl 2-allyl-2-(2-methylallyl)malonate (**11b**).

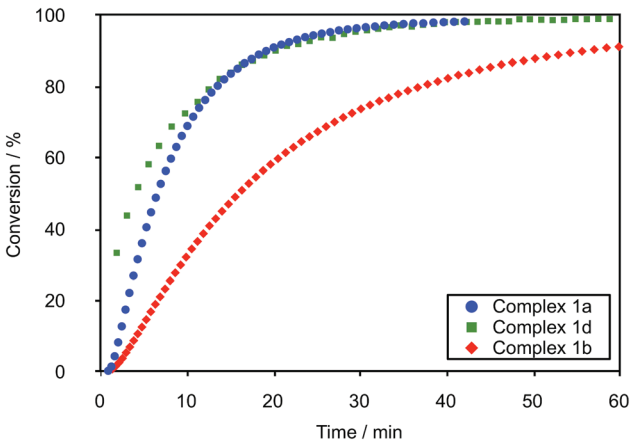


Fig. 5 Time course of the RCM of diethyl 2,2-diallylmalonate (**11a**) using ruthenium catalysts **1a**, **1b**, and **1d** (1 mol%) in CD_2Cl_2 at 30 °C.

Catalytic tests

The catalytic efficiency of complex **1d** was evaluated in the ring-closing metathesis (RCM) of four model α,ω-dienes and compared to the activities of second-generation catalysts **1a** and **1b** using standard experimental procedures defined by Grubbs and co-workers.[26] We first investigated the RCM of diethyl 2,2-diallylmalonate (DEDAM, **11a**) in CD_2Cl_2 at 30 °C (Scheme 6). Reactions were carried out using 1 mol% of ruthenium initiator and monitored by ^1H NMR spectroscopy. Under these conditions, an almost quantitative conversion of the substrate into cyclopentene diester **12a** took place in *ca.* 40 min with $[RuCl_2(PCy_3)(BMes)(=CHPh)]$ (**1d**) (Fig. 5). This new compound even displayed a slightly higher activity than the Grubbs second-generation catalyst **1a** at the beginning of the reaction. As reported previously, replacement of the SIMes ligand with IMes led to a slower reaction.[26] Thus, with catalyst precursor **1b** the conversion after 40 min was 82% and it took about 90 min to reach completion.

Our second benchmark was the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate (**11b**) to form the trisubstituted cycloolefin **12b** (Scheme 6). In this reaction, complex **1d** displayed catalytic activity intermediate between those recorded by Grubbs *et al.* with catalyst precursors **1a** and **1b** (Fig. 6).[26] Indeed, with the "saturated" ancillary ligand the reaction was complete in 75 min, whereas conversions of 93 and 83% were obtained within the same period of time with the "aromatic" and "unsaturated" NHCs, respectively.

Last but not least, we have also compared the metathetical activities of complexes **1a**, **1b**, and **1d** in the RCM of diethyl

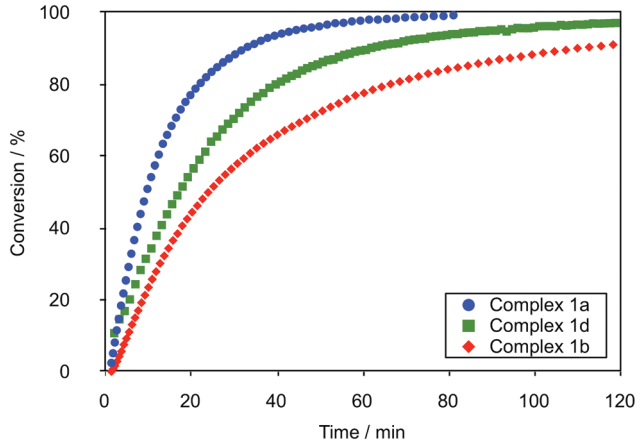
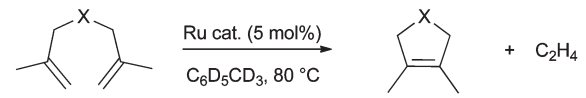


Fig. 6 Time course of the RCM of diethyl 2-allyl-2-(2-methallyl)malonate (**11b**) using ruthenium catalysts **1a**, **1b**, and **1d** (1 mol%) in CD_2Cl_2 at 30 °C.



11c: X = $C(CO_2Et)_2$
13: X = NTs

12c: R = $C(CO_2Et)_2$
14: X = NTs

Scheme 7 Ruthenium-catalyzed RCM of diethyl 2,2-bis(2-methylallyl)malonate (**11c**) and *N*,*N*-bis(2-methylallyl)tosylamide (**13**).

Table 2 RCM of α,ω-dienes catalyzed by complexes **1a**, **1b**, or **1d** (5 mol%) in toluene-d_8 at 80 °C

Substrate	Catalyst	Time/h	Yield/%	Ref.
11c	**1a**	5	57	12
11c	**1b**	5	47	12
11c	**1d**	5	19	This work
13	**1a**[a]	7	90	59
13	**1b**	24	95	10
13	**1d**	24	41	This work

[a] 3.5 mol%.

2,2-bis(2-methylallyl)malonate (**11c**) and *N*,*N*-bis(2-methylallyl)-tosylamide (**13**) (Scheme 7). Because the formation of tetrasubstituted double bonds is one of the most difficult reactions to achieve *via* olefin metathesis, these experiments were performed in toluene-d_8 at 80 °C using 5 mol% of ruthenium initiator. Under these conditions, none of the catalysts under examination afforded a quantitative yield of diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (**12c**) after 5 h (Table 2). Nevertheless, complexes **1a** and **1b** bearing, respectively, the SIMes and IMes ligands significantly outperformed catalyst **1d** in this transformation. This tendency was confirmed in the more facile cyclization of tosylamide **14**. Once again, much higher yields were obtained with catalyst precursors **1a** and **1b** than with complex **1d**. Moreover, monitoring the time course of the reaction by ^1H NMR spectroscopy revealed that conversion of the two substrates stopped increasing already after 10 min using catalyst precursor **1d**, whereas the second-generation ruthenium–alkylidene **1b** remained active over much longer periods.[10] Hence, the presence of mesityl substituents on the nitrogen atoms of BMes did not prevent the rapid decomposition of compound **1d** when heated at 80 °C.

Conclusion and perspectives

Upon deprotonation with a strong base, benzimidazolium salt **8** afforded the carbene ligand BMes, which was further reacted *in situ* with rhodium or ruthenium complexes to afford a small, albeit representative, selection of new organometallic products. The rhodium compounds, [RhCl(COD)(BMes)] (**9**) and *cis*-$[RhCl(CO)_2(BMes)]$ (**10**), were used to probe the steric and electronic features of 1,3-dimesitylbenzimidazol-2-ylidene. Comparison of the $\%V_{Bur}$ and TEP parameters of BMes with those determined previously for IMes and SIMes revealed that the three mesityl-based NHCs had very similar profiles. Nonetheless, changes between "saturated", "aromatic", and "unsaturated" backbones in the central heterocyclic part of these ligands subtly affected their stereoelectronic properties.

Accordingly, the corresponding $[RuCl_2(PCy_3)(NHC)(=CHPh)]$ complexes displayed different catalytic behaviors in the ring-closing metathesis of α,ω-dienes. In the benchmark cyclization of diethyl 2,2-diallylmalonate (**11a**), the new $[RuCl_2(PCy_3)(BMes)(=CHPh)]$ compound (**1d**) performed slightly better than the Grubbs second-generation catalyst (**1a**), which was in turn significantly more active than the related $[RuCl_2(PCy_3)(IMes)(=CHPh)]$ initiator (**1b**). For the formation of trisubstituted cycloolefin **12b**, complex **1d** ranked in-between catalyst precursors **1a** and **1b**, whereas in the RCM of tetrasubstituted cycloalkenes **12c** and **14** it lost its catalytic efficiency much more rapidly.

Altogether, this study underlines how difficult it is to predict the activity of closely related metathesis initiators based on structural information. It also confirms that an optimization of the catalytic system is required for each individual substrate in order to reach the highest possible efficiency.[13] In this respect, the successful introduction of a bulky 1,3-diarylbenzimidazol-2-ylidene ligand instead of the more common imidazol-2-ylidene or imidazolin-2-ylidene derivatives offers additional options to fine-tuning the steric and electronic properties of ruthenium–alkylidene catalyst precursors, and we are currently pursuing further investigations in this direction.

Experimental

General information

All the reactions were carried out using standard Schlenk techniques under a dry argon atmosphere. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. 1,3-Dimesitylbenzimidazolium tetrafluoroborate (**8**)[38] and the substrates for RCM reactions[12,60] were prepared according to the literature. Petroleum ether refers to the hydrocarbon fraction of bp 40–60 °C and was purchased from Labotec. Chromatography was performed on silica gel 60 (60 Å nominal pore diameter, 0.063–0.200 mm particle size) supplied by Biosolve. All the other chemicals were purchased from Aldrich and used as

received. Unless otherwise specified, ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 298 K with a Bruker DRX 400 or a Bruker Avance 250 spectrometer. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Synthesis of [RhCl(COD)(BMes)] (9)

In a 50 mL Schlenk flask, $[RhCl(COD)]_2$ (50.7 mg, 0.1 mmol) and potassium *tert*-butoxide (25.3 mg, 0.23 mmol, 2.3 equiv.) were stirred for 45 min at room temperature in THF (25 mL). Next, 1,3-dimesitylbenzimidazolium tetrafluoroborate (**8**) (100 mg, 0.23 mmol, 2.3 equiv.) was added and the reaction mixture was stirred overnight at room temperature. It was brought back to air and filtered on a 0.45 μm membrane. The filtrate was evaporated *in vacuo*. The residue was dissolved in dichloromethane–pentane and purified by column chromatography on silica gel using petroleum ether–ethyl acetate (3 : 1 v/v) as eluents to afford the title compound (R_f = 0.39) as a yellow powder (113 mg, 91%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.16 (2 H, dd, J = 3.1 and 6.1 Hz), 7.15 (2 H, s), 7.12 (2 H, s), 6.84 (2 H, dd, J = 3.1 and 6.0 Hz), 4.63–4.41 (2 H, m, CH COD), 3.54–3.42 (2 H, m, CH COD), 2.44 (6 H, s), 2.26 (6 H, s), 1.98 (6 H, s), 1.91–1.80 (4 H, m, CH_2 COD), 1.68–1.53 (4 H, m, CH_2 COD). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ = 196.4 (d, J_{Rh-C} = 52.4 Hz), 139.2, 138.3, 135.43, 135.40, 135.39, 133.4, 129.8, 128.7, 123.2, 110.5, 97.8 (CH COD), 97.7 (CH COD), 68.4 (CH COD), 68.3 (CH COD), 32.8 (CH_2 COD), 28.3 (CH_2 COD), 21.0 (CH_3 Mes), 19.4 (CH_3 Mes), 18.0 (CH_3 Mes). Calc. for $C_{33}H_{38}ClN_2Rh$: C, 66.0; H, 6.4; N, 4.7%. Found: C, 66.3; H, 6.6, N, 4.6%.

Synthesis of *cis*-[RhCl(CO)$_2$(BMes)] (10)

Carbon monoxide was bubbled in a solution of [RhCl(COD)-(BMes)] (**9**) (50 mg, 0.08 mmol) and CH_2Cl_2 (10 mL) for 15 min at room temperature. The solvent was evaporated and the residue was washed with a minimal amount of *n*-pentane at 0 °C, leaving a light yellow solid (29 mg, 63%).

IR (NaCl, CH_2Cl_2): $\bar{\nu}_{CO}$ = 2082 (*trans*) and 1998 (*cis*) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.32 (2 H, dd, J = 3.1 and 6.1 Hz), 7.12 (4 H, s), 7.01 (2 H, dd, J = 3.1 and 6.1 Hz), 2.43 (6 H, s), 2.10 (12 H, s). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ = 187.6 (d, J_{Rh-C} = 44.5 Hz), 185.2 (d, J_{Rh-C} = 53.8 Hz), 182.9 (d, J_{Rh-C} = 73.9 Hz), 139.9, 136.3, 134.8, 132.4, 129.6, 124.5, 111.5, 21.1, 18.2.

Synthesis of [RuCl$_2$(=CHPh)(PCy$_3$)(BMes)] (1d)

1,3-Dimesitylbenzimidazolium tetrafluoroborate (**8**) (81 mg, 0.18 mmol, 1.5 equiv.) was weighed in a Schlenk tube and placed under an argon atmosphere. Toluene (3 mL) and a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (0.43 mL, 0.22 mmol, 1.8 equiv.) were added and the mixture was stirred for 30 min at room temperature. After a rapid decantation, the supernatant carbene solution was cannulated under argon into a second flask containing a solution of $[RuCl_2(=CHPh)(PCy_3)_2]$ (100 mg, 0.12 mmol, 1 equiv.) in toluene (7 mL). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography under argon. Tricyclohexylphosphine was first eluted with *n*-pentane. The desired product was then eluted as a dark orange band with *n*-pentane–diethyl ether (9 : 1 v/v) as eluents. The solvents were evaporated and the solid dried under high vacuum to yield a dark-orange powder (89 mg, 82%).

^{1}H NMR (250 MHz, CD_2Cl_2, 223 K): δ = 19.01 (1 H, s, Ru=C*H*Ph), 8.87 (1 H, d, J = 8.0 Hz, CH_{Ph}), 7.39 (1 H, dd, J = 7.2 Hz, CH_{Ph}), 7.14 (1 H, s, CH_{Mes}), 7.10 (4 H, m, 2 CH_{Ph} + 2 $CH_{Benzimid}$), 7.05 (1 H, s, CH_{Mes}), 6.97 (1 H, d, J = 7.4 Hz, CH_{Ph}), 6.87 (1 H, s, CH_{Mes}), 6.70 (1 H, d, J = 7.0 Hz, $CH_{Benzimid}$), 6.57 (1 H, d, J = 8.0 Hz, $CH_{Benzimid}$), 5.79 (1 H, s, CH_{Mes}), 2.42 (3 H, s, CH_3), 2.34 (3 H, s, CH_3), 2.21 (3 H, s, CH_3), 2.07 (3 H, s, CH_3), 1.96 (3 H, s, CH_3), 1.54 (3 H, s, CH_3), 1.6–0.6 (33 H, m, Cy). $^{13}C\{^{1}H\}$ NMR (62.5 MHz, CD_2Cl_2, 223 K): δ = 294.8 (Ru=*C*HPh), 203.6 (J_{P-C} = 82.2 Hz, $C2_{NHC}$), 150.3, 139.2, 138.63, 138.55, 137.5, 136.6, 135.8, 135.30, 135.25, 135.21, 135.18, 132.7, 131.4, 131.1, 129.6, 129.1, 128.9, 128.4, 128.20, 128.15, 127.8, 126.9, 122.5, 110.0, 109.0, 30.2, 29.9, 29.5, 28.8, 28.0, 27.4, 27.3, 25.5, 20.7 (CH_3), 20.6 (CH_3), 18.76 (CH_3), 18.71 (CH_3), 17.8 (CH_3), 17.2 (CH_3). $^{31}P\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 31.9. Calc. for $C_{50}H_{65}Cl_2N_2PRu$: C, 67.0; H, 7.3; N, 3.1%. Found: C, 67.2; H, 7.9, N, 3.3%.

X-Ray diffraction studies

Crystal data were collected on a Bruker APPEX II (for **1d**) or a Bruker Smart-CCD-1000 diffractometer (for **9**) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube source at 100 K. Computing data and reduction was made with the APPEX II software.[61] The structure of **1d** was solved using DIRDIF2008[62] and the structure of **9** with SIR2004.[63] They were refined by full-matrix, least-squares based on F^2 by SHELXL.[64] An empirical absorption correction was applied using SADABS.[65] All non-hydrogen atoms were anisotropically refined and the hydrogen atom positions were calculated and refined using a riding model.

Crystal data for [RhCl(COD)(BMes)] (9). Bright yellow crystals were obtained by slow evaporation of a concentrated solution in dichloromethane under an inert atmosphere. $C_{33}H_{38}ClN_2Rh$, M = 601.01, crystal dimensions: 0.33 × 0.14 × 0.10 mm, monoclinic, a = 13.077(3), b = 11.325(3), c = 19.269(4) Å, β = 99.374(3)°, V = 2815.5(11) Å^3, T = 100 K, space group $P2_1/n$, Z = 4, 23 108 measured reflections, 5540 independent reflections, R_{int} = 0.05, final R_1 values [$I > 2\sigma(I)$] = 0.034, final w$R(F^2)$ = 0.082.

Crystal data for [RuCl$_2$(=CHPh)(PCy$_3$)(BMes)] (1d). Dark orange crystals were obtained by slow evaporation of a *n*-pentane solution under an inert atmosphere, $C_{50}H_{65}Cl_2N_2PRu$, M = 896.98, crystal dimensions: 0.21 × 0.06 × 0.05 mm, monoclinic, a = 9.7323(5), b = 37.4221(19), c = 12.4794(5) Å, β =

90.151(2)°, V = 4545.0(4) Å^3, T = 100 K, space group $P2_1/n$, Z = 4, 46 648 measured reflections, 6516 independent reflections, R_{int} = 0.143, final R_1 values [$I > 2\sigma(I)$] = 0.057, final w$R(F^2)$ = 0.112.

RCM of α,ω-dienes 11a and 11b

A 2 mL volumetric flask capped with a septum was charged with a ruthenium complex (3.2 μmol) under argon. Dried and degassed dichloromethane-d_2 (2 mL) was added with a dried syringe under argon. An NMR tube capped with a septum was charged with this stock solution (0.50 mL, 0.8 μmol of catalyst) and dichloromethane-d_2 (0.3 mL) under argon. The sample was thermostated at 30 °C in the NMR probe before the substrate (**11a**: 19.3 μL or **11b**: 20.5 μL, 0.08 mmol, 0.1 M) was added with a dried microsyringe under argon. Experimental data points were collected using the Bruker automation software. The conversion of diethyl 2,2-diallylmalonate (**11a**) was computed from the integrals of the allyl methylene protons in the starting material (δ = 2.53, d) and the product (δ = 2.90, s). The conversion of diethyl 2-allyl-2-(2-methylallyl)malonate (**11b**) was determined similarly from the signals of the allyl methylene protons in the starting material (δ = 2.59, s and 2.56, m) and the product (δ = 2.79, m and 2.85, m).

RCM of α,ω-dienes 11c and 13

An NMR tube capped with a septum was charged with a ruthenium complex (4 μmol, 5 mol%) under argon. Dried and degassed toluene-d_8 (0.8 mL) was then introduced under argon. The sample was thermostated at 80 °C in the NMR probe before the substrate (**11c**: 21.6 μL or **13**: 22.3 μL, 0.08 mmol, 0.1 M) was added with a dried microsyringe under argon. Experimental data points were collected using the Bruker automation software. The conversion of diethyl 2,2-bis(2-methylallyl)malonate (**11c**) and 4-methyl-*N*,*N*-bis(2-methylallyl)benzenesulfonamide (**13**) was computed from the integrals of the allyl methylene protons in the starting material (δ = 2.65, s or 3.68, s, respectively) and the product (δ = 2.81, s or 3.88, s, respectively).

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