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Design, synthesis and reactivity of *N*-adamantyl cyclometalated cyclic(alkyl)(amino)carbene ruthenium complexes in *Z*-selective olefin metathesis

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The synthesis of a *Z*-selective ruthenium complex featuring a cyclic(alkyl)(amino)carbene (CAAC) ligand is reported. Its preparation proceeds through a selective intramolecular C(sp^3)–H activation at the *N*-adamantyl substituent of the CAAC ligand featuring a key spiro-tetraline moiety. The resulting cyclometalated precatalyst was isolated in good yield and fully characterized by X-ray diffraction analysis. This catalyst displays high *Z*-selectivity (up to 95 : 5 *Z*/*E* ratio) in both self-metathesis (SM) and cross-metathesis (CM) reactions.

Since the introduction of the cyclometalated ruthenium complex **Ru1** by Grubbs and co-workers in 2011 (Fig. 1a),[1] *Z*-selective olefin metathesis[2] has emerged as an efficient and competitive approach to access *Z*-alkenes, which are widely found in pharmaceuticals,[3] fragrances,[4] agrochemicals,[5] and material sciences.[6] In recent years structural refinements of these cyclometalated ruthenium complexes (**Ru2–5**, Fig. 1b) further enhanced catalytic efficiency and expanded the scope of accessible transformations.[7–10] In parallel, the remarkable advances achieved with ruthenium complexes bearing cyclic(alkyl)(amino)carbene (CAAC) ligands[11] in olefin metathesis,[12] naturally motivated Grubbs and co-workers to merge the CAAC framework with these cyclometalated architectures (**Ru6**, Fig. 1c).[13] Unfortunately, the later displayed modest catalytic performances in the SM of allylbenzene (15% conv., 49% *Z*-selectivity). We reasoned that the adamantyl group positioned at the quaternary carbon of the CAAC framework, enforces a rigid and congested environment around the metal centre, limiting the ligand's capacity to adapt during key steps of the metathesis cycle. To address this constraint, we envisaged redirecting the adamantyl substituent to the nitrogen atom, a modification expected to reduce proximal steric pressure, introduce conformational flexibility. With this design principle in mind, herein, we report the synthesis of a CAAC iminium salt precursor ^{Ad}**CAAC**·BF_4 containing the *N*-adamantyl fragment and a spirotetraline moiety (Fig. 1d). The resulting cyclometalated CAAC Ru-complex **Ru7** displays high *Z*-selectivity (up to 95 : 5 *Z*/*E* ratio) across a range of self- and cross-olefin metathesis transformations.

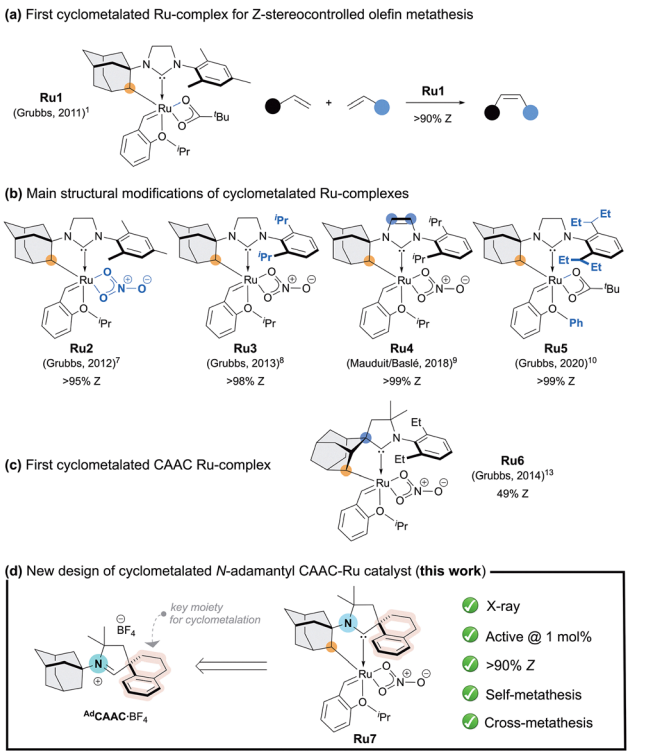

Fig. 1 State of the art of cyclometalated Ru complexes for *Z*-selective olefin metathesis (a)–(c). New design of cyclometalated CAAC–Ru complex featuring a *N*-adamantyl unit and a key spiro-tetraline moiety ((d) this work).

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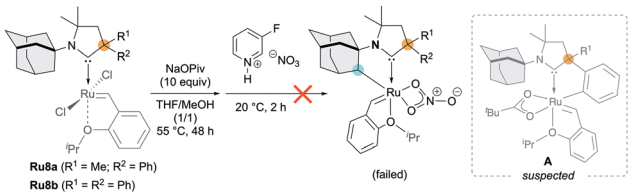


Scheme 1 Failure of the intramolecular cyclometalation process performed on known *N*-adamantyl CAAC Ru-complex **Ru8a,b**.[14b]

We began our study by investigating the Grubbs' cyclometalation protocol[7–10] on CAAC Ru-complexes **Ru8a,b** featuring the *N*-adamantyl unit, which were recently reported by Tuba and coworkers (Scheme 1).[14] Unfortunately, in both cases, the intramolecular cyclometalation of the *N*-Adamantyl fragment using a carboxylate-assisted C–H activation strategy failed. We attribute this behaviour to competing cyclometalation at the phenyl group attached to the quaternary carbon that could led to corresponding species **A**, which are prone to rapidly decompose (Scheme 1).[15]

To address this limitation, we introduced additional steric constraints by introducing a spiro-cycloalkyl backbone into the CAAC framework. Accordingly, CAAC iminium salts ^{Ad}**CAACa–c**·BF_4 featuring respectively spiro-indanyle, -tetraline and -fluorenyl fragments was prepared starting from pre-alkylated aldehydes **1a–c** (Scheme 2a).[16] Condensation of 1-adamantylamine with **1a–c** led to the desired imines **2a–c**, which were directly subjected to hydroiminiumation,[11b] followed by anion metathesis. The desired iminium salt ^{Ad}**CAACa**·BF_4 was obtained with respectable 43% isolated yield (over 3 steps). Unfortunately, despite the accessibility of imines **2b,c**, both failed to cyclise under hydroiminiumation precluding access to corresponding iminium salts **CAACb,c**·BF_4. Next, the Hoveyda-type Ruthenium complexes **Ru8c** was prepared following the standard protocol (Scheme 2b).[12b]

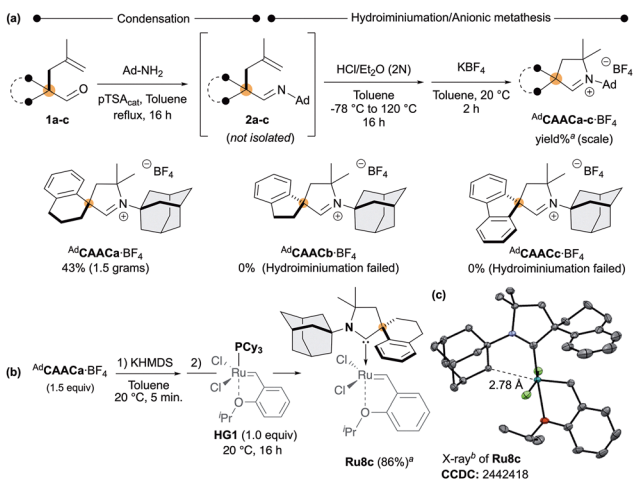
Deprotonation of ^{Ad}**CAACa**·BF_4 with potassium hexamethyldisilazide (KHMDS) followed by the addition of the phosphine-based Hoveyda–Grubbs (**HG1**) afforded the corresponding Ru-complex **Ru8c** in a good 86% yield. X-ray diffraction analyses from a suitable crystal of **Ru8c** established the key proximity between the targeted C–H bond and the ruthenium centre with a distance of 2.78 Å (**Ru8a**) and 2.77–2.78 Å (**Ru8b,c**) (Scheme 2c).

With this complex in hands, we next examined the intramolecular cyclometalation of the *N*-Adamantyl fragment (Scheme 3a).[7–10] In marked contrast to **Ru8a** and **Ru8b** (Scheme 1), **Ru8c** cleanly delivered the desired cyclometalated complex **Ru7** which was isolated in a 35% yield over two steps.

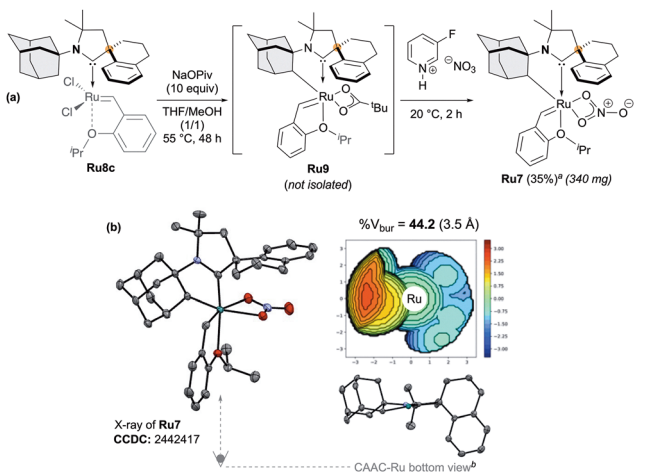
Single-crystal X-ray analysis of the nitrato derivative **Ru7** confirmed the expected chelating architecture. We thus confirm the divergent outcome occurring with **Ru8a** and **Ru8b** (Scheme 1), as the competitive cyclometalation pathway is not accessible in **Ru8c** due to the steric constraints imposed by the spiro-tetraline backbone.

Using the novel cyclometalated complex **Ru7**, we next evaluated its catalytic performance in representative self- and cross-metathesis reactions (Table 1 and Scheme 3). We first examined the self-metathesis of allylbenzene **S1a** (Table 1). Using 1 mol% of **Ru7** at 25 °C in THF (2.1 M), the reaction reached 76% conversion and 68% isolated yield after 28 h. Notably, the catalyst delivered excellent *Z*-selectivity throughout the reaction, with only a minor erosion over time (97 : 3 *Z*/*E* at 6.5 h; 95 : 5 *Z*/*E* at 28 h; entries 2–3). This stereocontrol significantly outperforms the CAAC cyclometalated catalyst **Ru6** which has been reported by Grubbs and colleagues to provide only 49% *Z*-selectivity under analogous conditions (Fig. 1).[13] Increasing the catalyst loading to 1.5 mol% enhanced productivity, affording up to 74% yield after 28 h, while maintaining good *Z*-selectivity (94 : 6 *Z*/*E* ratio; entry 10).

Raising the reaction temperature to 35 °C accelerated the reaction (66–70% yield after 16 h, entries 11 and 12), but at the expense of stereocontrol decreasing to 87 : 13 to 82 : 18 *Z*/*E* ratio.

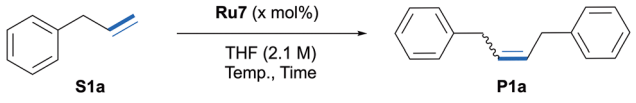


Scheme 2 Synthesis of *N*-adamantyl CAAC precursors containing spiroalkyl fragment (a), the corresponding ruthenium complex **Ru8c** (b) and its solid-state structure determined by single-crystal X-ray diffraction (c). [a] Isolated yield. [b] Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.



Scheme 3 Synthesis of the cyclometalated CAAC–Ru complex **Ru7** (a) and its solid-state structure with corresponding steric map and buried volume analysis (b). Displacement ellipsoids are shown at 30% probability; hydrogen atoms are omitted for clarity. Buried volumes (%V_{bur}) and steric maps (3.5 Å radius) were calculated using SambVca 2.1 (ref. 17). [a] Isolated yield. [b] Styrenyl ether and nitrato ligands omitted for clarity.

Table 1 Catalytic activity of **Ru7** in *Z*-selective SM of allylbenzene **S1a**[a]



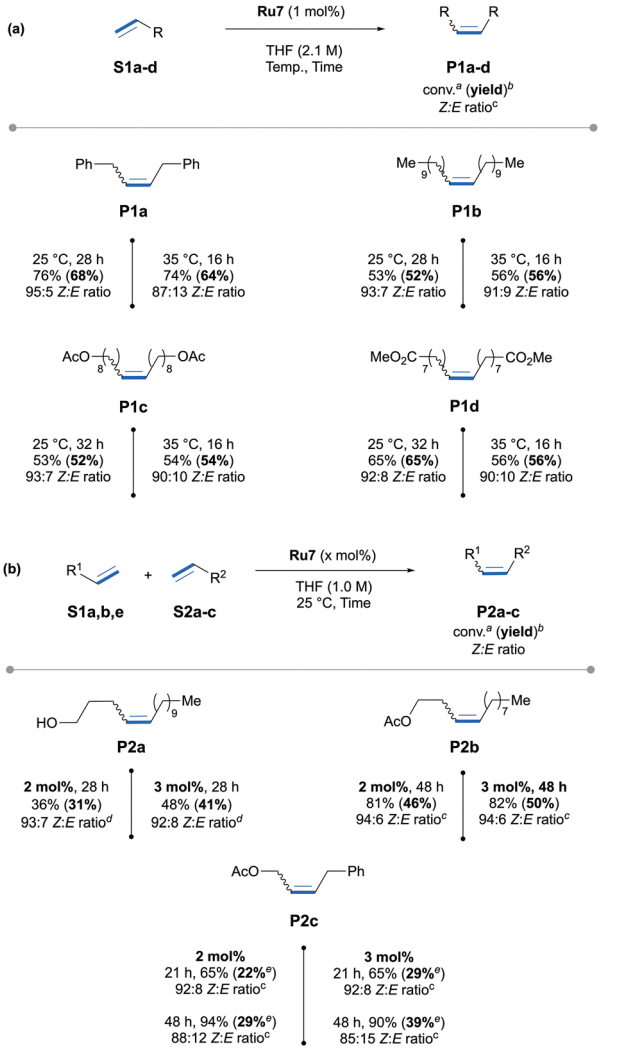
Entry	**Ru7** (mol%)	Temp. (°C)	Time (h)	Conv.[b] (yield)[c] (%)	*Z*/*E* ratio[d]
1			3.5	5 (2)	97 : 3
2			6.5	19 (14)	97 : 3
3	1	25	21	65 (60)	95 : 5
4			24	69 (64)	95 : 5
5			28	76 (**68**)	**95 : 5**
6			3.5	12 (8)	96 : 4
7			6.5	32 (30)	96 : 4
8	1.5	25	21	69 (68)	95 : 5
9			24	74 (72)	94 : 6
10			28	79 (**74**)	**94 : 6**
11	1	35	16	74 (66)	87 : 13
12	1.5	35	16	74 (70)	82 : 18

[a] Reaction conditions: **S1** (0.45 mmol), **Ru7** (0.0045 or 0.00675 mmol), THF (0.215 mL) in Glove-box. [b] Conversions were determined by ^{1}H NMR spectroscopy. [c] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [d] *E*/*Z* ratio was determined by GC analysis (see SI for details).

We then evaluated **Ru7** (1 mol%) in the self-metathesis of 1-dodecene **S1b**, 9-decenyl acetate **S1c** and methyl 1-decenoate **S1d** conduced at 25 and 35 °C (Scheme 4a). In all cases, the corresponding homo-metathesis products **P1b-d** were formed in modest yields (52 to 65%) but high *Z*-selectivity, with *Z*/*E* ratio ranging from 93 : 7 to 90 : 10. Moving to more challenging cross-metathesis reactions, CAAC-**Ru7c** delivered comparable catalytic performance, albeit requiring higher catalyst loading (2–3 mol%, Scheme 4b). The expected cross-metathesis products **P2a–c** were obtained in modest yields (22 to 50%) while maintaining consistently good to high *Z*-selectivity (92 : 8 to 94 : 6 *Z*/*E* ratio).[18] It should be noted that for **P2c**, the increase in reaction time led to a slight improvement in yield but at the expense of *Z*-selectivity (88 : 12 to 85 : 15 *Z*/*E* ratio).

In summary, we have developed the first *Z*-selective cyclometalated ruthenium catalyst **Ru7** bearing an *N*-adamantyl CAAC ligand. Thanks to the introduction of a spiro-tetraline moiety at the quaternary carbon center, the cyclometalation process successfully delivered the targeted complex, which was isolated in 35% yield over two steps and fully characterized, including by single-crystal X-ray diffraction. This catalyst delivers moderate to good yields across a range of self- and cross-metathesis reactions while maintaining consistently high *Z*-selectivity (90 : 10 to 95 : 5 *Z*/*E*). Building on these results and our recent access to enantiopure CAAC ligands, efforts toward new chiral cyclometalated CAAC–Ru catalysts for asymmetric *Z*-selective olefin metathesis are currently underway in our laboratories.[19]

R. J., A. D. and M. M. conceptualized and supervised this work. C. C., F. M and S. C.-R. conducted all the experiments. T. R. accomplished the X-Ray diffraction analysis. The manuscript was written by R. J. and M. M. and was reviewed by all the authors.



Scheme 4 Scope of *Z*-selective SM (a) and CM (b) reactions catalysed by **Ru7**. [a] Conversions were determined by ^{1}H NMR spectroscopy. [b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] *E*/*Z* ratio was determined by GC analysis. [d] *E*/*Z* ratio was determined by ^{13}C NMR analysis. [e] NMR yield of the *Z* isomer determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Conflicts of interest

There are no conflicts to declare.

Data availability

All experimental and crystallographic data associated with this work are available in the supplementary information (SI). Supplementary information: experimental procedures, NMR spectra, and GC analysis. See DOI: https://doi.org/10.1039/d5cc07127e.

CCDC 2442417 and 2442418 contain the supplementary crystallographic data for this paper.[20a,b]

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