ChemComm

COMMUNICATION

View Article Online
View Journal





Cite this: DOI: 10.1039/d5cc03776j

Received 4th July 2025,
Accepted 26th July 2025

DOI: 10.1039/d5cc03776j

rsc.li/chemcomm

# *N*-hydrazine cyclic(amino)(alkyl)carbene ruthenium complexes: synthesis and reactivity in olefin metathesis

Clément Casalta,[a] Thierry Roisnel,[a] Rodolphe Jazzar,*[b] Angelino Doppiu*[c] and Marc Mauduit*[a]

**The synthesis of a ruthenium complex containing an *N*-hydrazine cyclic(amino)(alkyl)carbene (CAAC) ligand is reported. This robust and air-stable complex demonstrates good to excellent catalytic performances under an air atmosphere in various ring-closing metathesis (RCM), ring-closing enyne metathesis (RCEYM), ring-opening cross-metathesis (ROCM), self-metathesis (SM), cross-metathesis (CM) and ethenolysis reactions.**

Olefin metathesis is one of the most efficient catalytic tools for the formation of C=C bonds, which are ubiquitous in many relevant molecules that are widely used in materials science, crop protection, pharmaceuticals, cosmetics and perfumery.[1] Since their first synthesis in 2007,[2] well-defined ruthenium complexes **Ru1** with cyclic (alkyl)(amino)carbene (CAAC)[3] ligands (Fig. 1a) have brought seminal breakthroughs in the field of olefin metathesis,[4] notably with the highest productivity in ethenolysis (TON up to 2 600 000)[5] and in ring-closing metathesis (68 000).[6] Thanks to their high modularity and straightforward synthesis, CAACs are most often tuned at the α-quaternary carbon (alpha to the carbene carbon)[5] or by modification of the heterocyclic backbone (**Ru2–4**)[7–9] (Fig. 1a). Comparatively, structural variation at the nitrogen has seldom been considered and has so far been restricted to aryl and alkyl substituents.[10] Herein, we report the synthesis of CAAC iminium salt precursors containing an *N*-hydrazine fragment, namely $^{Hydraz}$**CAAC**·$BF_4$ (Fig. 1b). This new ligand framework yields a robust and air-stable olefin metathesis complex **Ru5** which has been isolated and fully characterised by X-ray diffraction. Interestingly, this complex displays high thermal stability at 80 °C with good to excellent catalytic performance in olefin metathesis reactions performed in air using ACS grade solvents.

We initiated our study by preparing CAAC iminium salts $^{Hydraz}$**CAAC-1a,b**·$BF_4$ containing an *N*-hydrazine substituent (Scheme 1a). Starting from pre-alkylated aldehydes **1a,b**,[11] condensation with phenylmethylhydrazine **2** led to the desired imines **3a,b**. Subsequent hydroiminiumation[3b] and anionic metathesis afforded the corresponding iminium salts $^{Hydraz}$**CAAC-1a,b**·$BF_4$ which were isolated in 50% and 46% yields, respectively, close to those of previously reported CAACs.[4,11] Using these ligands, we investigated the synthesis

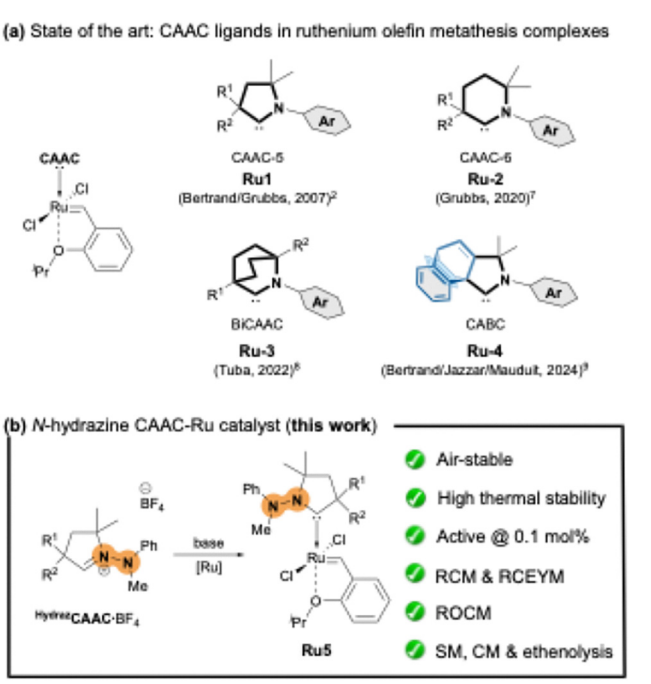
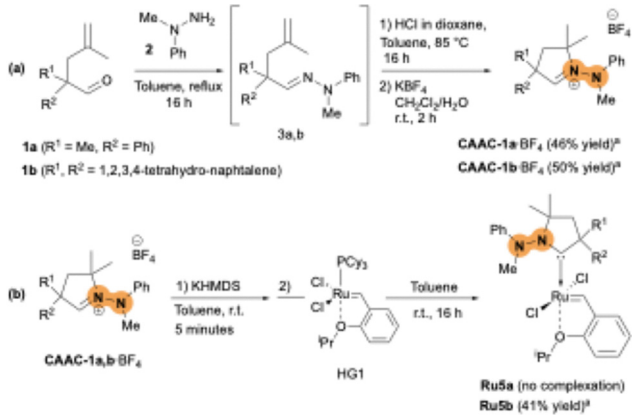



Fig. 1 State of the art of CAAC–Ru complexes for olefin metathesis (a) and the development of a new CAAC–Ru complex featuring an *N*-hydrazine unit (b, this work).

[a] *Univ Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, ISCR UMR 6226, 35000 Rennes, France. E-mail: marc.mauduit@ensc-rennes.fr*
[b] *Department of Chemistry and Biochemistry, San Diego State University, 5500 Campanile Drive, San Diego, California 92182, USA. E-mail: rjazzar@sdsu.edu*
[c] *Umicore AG & Co. KG, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany. E-mail: Angelino.Doppiu@eu.umicore.com*




Scheme 1 Synthesis of *N*-hydrazine CAAC precursors (a) and related ruthenium complexes (b). [a] Isolated yield.

of Hoveyda type Ru-complexes **Ru5a,b** by deprotonation of these salts with potassium hexamethyldisilazide (KHMDS) and *in situ* reaction with first generation Hoveyda–Grubbs (**HG1**) catalyst precursor (Scheme 1b). While no complexation could be observed with $^{Hydraz}$**CAAC-1a** leading to **Ru5a**, we were delighted to isolate **Ru5b** from $^{Hydraz}$**CAAC-1b** in 41% yield.

Gratifyingly a suitable crystal of **Ru5b** allowed us to confirm the structure of this complex by X-ray diffraction which allowed us to gain valuable structural information (Fig. 2). Notably, it revealed that **Ru5b** belongs to the rare class of ''inverted'' CAAC complexes,[4,13] which are characterized by an α-quaternary centre positioned above the isopropoxybenzylidene moiety. The small %buried volume (%$V_{bur}$) of 34.9% observed for **Ru5b** confirmed the low steric hindrance of this ligand framework. We also noted that the *N*,*N*-phenyl substituent and the tetrahydronaphtalene moiety adopt a *cis*-relationship, leading to lower space occupancy in the bottom quadrants (as highlighted in the space filling views).

Next, we evaluated the thermal stability of **Ru5b** in toluene-$d_8$ solution at 80 °C in air (Fig. 3). Interestingly, in this case up to 91% of the remaining complex was observed after 5 hours

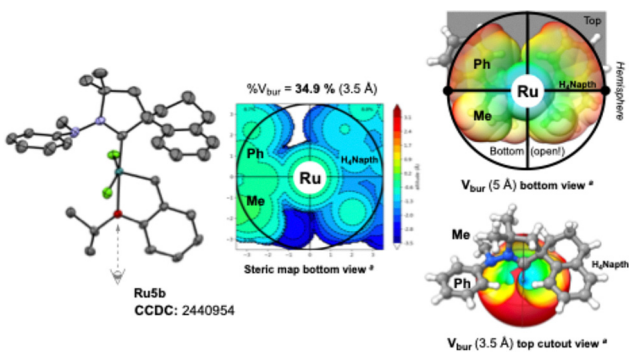



Fig. 2 Solid-state structure and steric map/buried volume of complex **Ru5b** from single-crystal X-ray diffraction. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity. The calculated buried volume (%$V_{bur}$) and steric maps (radii 3.5 and 5 Å) (see ref. 12). [a] Isopropoxybenzylidene ligand and Cl atoms have been omitted for clarity.

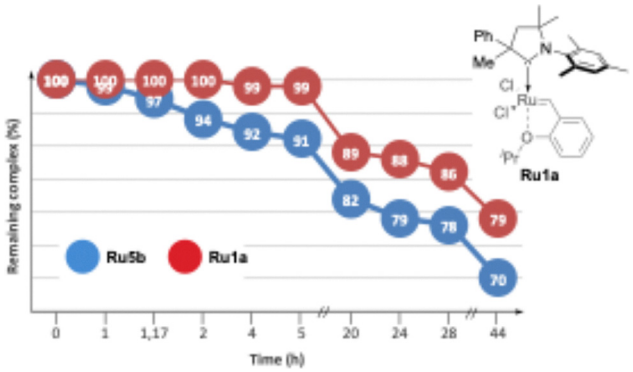



Fig. 3 Thermal stability of **Ru5b** and commercially available **Ru1a** in toluene-$d_8$ at 80 °C under an air atmosphere. 1,3,5-Trimethoxybenzene was used as the internal standard (see the SI for details).

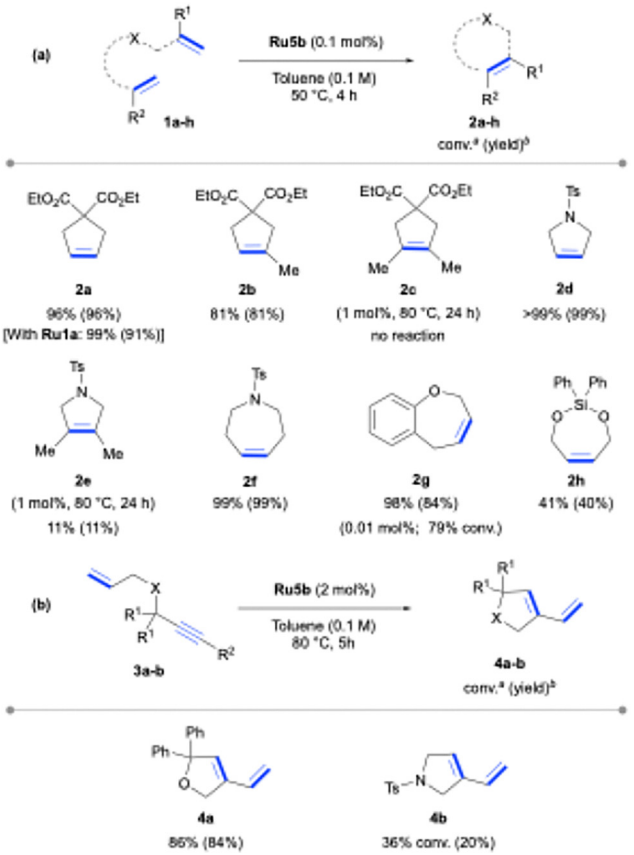
with only 30% decomposition occurring after 2 days. Similar behaviour was also observed with commercially available **Ru1a**,[2b] which decomposed more slowly, with only 1% lost after 5 h (see Fig. 3).

Encouraged by the high stability of **Ru5b** in solution, we next investigated its catalytic performances in olefin metathesis performed in air using ACS grade solvents. First, we evaluated ring-closing metathesis (RCM) using 0.1 mol% catalyst loading at 50 °C (Scheme 2a). Good to excellent yields (81–99%) were obtained for mono-, di- or trisubstituted cyclopentenes **2a**, **2b** and **2d**. However, no or poor conversion was observed for the more sterically hindered tetrasubstituted cyclopentenes **2c** and **2e**, despite higher catalyst loading (1 mol%) and elevated temperature (80 °C). It should be noted that a slightly lower 91% yield was observed with **Ru1a**.

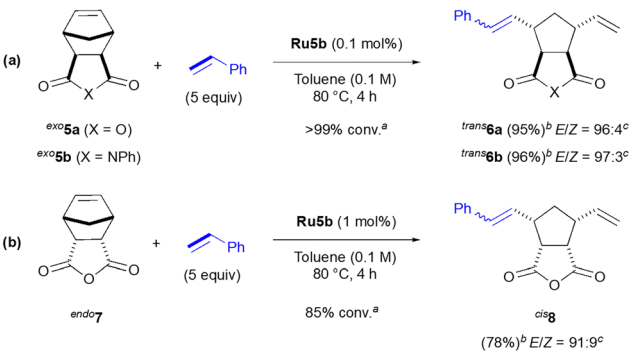
Seven-membered ring products **2f** and **2g** were obtained with excellent yields (99% and 87% yield, respectively) while a moderate 40% yield was obtained for the cyclic silane **2h**. Note that the **Ru5b** remains active at lower catalyst loading with up to 79% conversion of **2g** observed with 0.01 mol% catalyst loading. The ring-closing enyne metathesis (RCEYM) reactions were realized with a higher catalyst loading (2%) at 80 °C (Scheme 2b). While full conversion and good yield (84%) were obtained for product **4a**, a lower reactivity was observed for compound **4b** (20%).

We next considered ring-opening cross-metathesis (ROCM) reactions involving both *endo* and *exo* norbornene derivatives with styrene as a cross-olefin partner. As depicted in Scheme 3, $^{exo}$**5a** and $^{exo}$**5b** displayed excellent reactivity at 0.1 mol% catalyst loading, affording corresponding *trans*-cyclopentanes **6a** and **6b** with a high yield (95–96% respectively) and *E*/*Z* ratio (96 : 4 to 97 : 3). Regarding $^{endo}$**7**, a catalyst loading of 1 mol% was necessary to complete the reaction, leading to expected *cis*-cyclopentanes **8** with 78% yield and 91 : 9 *E*/*Z* ratio.

We also explored self-metathesis reactions using different terminal olefins and a catalyst loading of 0.5 mol% (Scheme 4a). 1-Dodecene **9a** and allylbenzene **9b** gave the corresponding internal alkenes **10a** and **10b** in good yield (73 and 78% respectively), while substrates **9c** and **9d** containing an acetate or an ester moiety afforded the desired homo-metathesis products

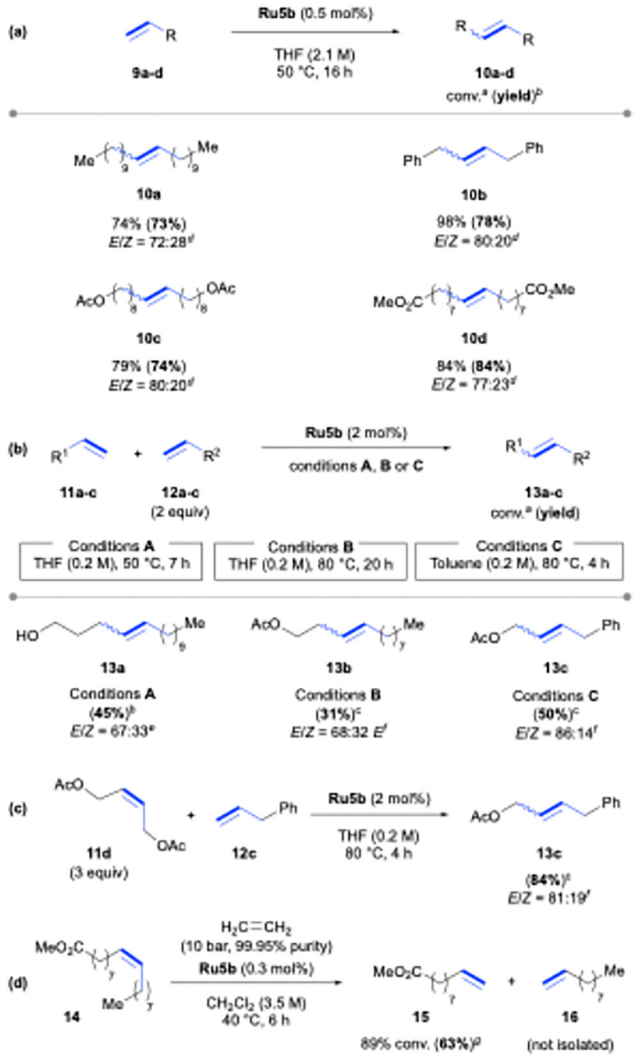



Scheme 2 Scope of RCM (a) and RCEYM (b) catalysed by **Ru5b**. [a] Conversions were determined by $^1$H NMR spectroscopy. [b] Yields were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.




Scheme 3 Scope of ROCM catalysed by **Ru5b**. [a] Conversions were determined by $^1$H NMR spectroscopy. [b] Yields were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] The *E*/*Z* ratio was monitored by GC/MS analysis.

**10c** and **10d** with good to excellent yield (74% and 84% respectively). In comparison, cross-metathesis (CM) performed using various functionalized cross-olefin partners required a higher catalyst loading (2 mol%, Scheme 4b). In this case cross-coupling between 4-penten-1-ol **11a** and 1-dodecene **12a** at 50 °C led to **13a** in 45% yield and a 67 : 33 *E*/*Z* ratio. A lower




Scheme 4 Scope of SM, CM and ethenolysis reactions catalysed by **Ru5b**. [a] Conversions were determined by $^1$H NMR spectroscopy. [b] Yields were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield. [d] The *E*/*Z* ratio was determined by GC analysis. [e] The *E*/*Z* ratio was determined by $^{13}$C NMR analysis. [f] The *E*/*Z* ratio was determined by $^1$H NMR analysis. [g] Conversion and yield determined by GC analysis.

31% isolated yield was observed for product **13b**, despite a higher temperature (80 °C) and a prolongated time (20 h). The reaction between allyl acetate **11c** and allyl-benzene **12c** yielded the corresponding metathesis product **13c** in 50% and a 86 : 14 *E*/*Z* ratio. Replacing **11c** with its dimer counterpart, *i.e. cis*-1, 4-diacetoxy-2-butene **11d** allowed significantly increasing the isolated yield (84%, Scheme 3c) under the same conditions. To complete our catalytic evaluation, we also investigated the performance of **Ru5b** in the ethenolysis of methyl oleate **14** (Scheme 3d).

With a catalyst loading of 0.3 mol% and 10 bar of ethylene pressure (99.95% purity), the expected methyl 9-decenoate **15** was isolated in respectable 63% yield. However, lowering the catalyst loading to 0.1 mol% led to poor conversion (<5%, see the SI for details). Before this, we investigated the stability of **Ru5b** in the

presence of ethylene (10 bar) at 40 °C[13b] in non-degassed and non-distilled $CD_2Cl_2$. We observed a rapid decomposition as only 28% of the remaining precatalyst was observed after 30 min (17% after 6 hours, see the SI for details). Further developments are thus required to improve the efficiency of *N*-hydrazine CAAC Ru complexes for ethenolysis.

In summary, we have reported the synthesis of a new class of CAAC ligands incorporating an *N*-hydrazine motif which has so far remained unexplored. We confirm that these ligands provide a robust architecture for ruthenium olefin metathesis complexes leading to thermal stability up to 80 °C in air. While its performance in cross-metathesis is still modest, the complex excelled in a broad array of transformations including RCM, RCEYM, ROCM, and SM reactions delivering high efficiency at catalyst loadings as low as 0.1 mol%. Advantageously, all reactions can be performed without the need for distilled and degassed solvents. Further developments are underway to explore the scope of its applications, notably in reactions performed under sustainable and industrially relevant experimental conditions.

R. J., A. D. and M. M. conceptualized and supervised this work. C. C. 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.

We are grateful to the CNRS, the ENSC de Rennes and San Diego State University. This work was supported by Umicore AG & Co (grant to C. C.).

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All experimental and crystallographic data associated with this work are available in the SI.

Experimental procedures, NMR spectra, and GC analysis. See DOI: **https://doi.org/10.1039/d5cc03776j**

CCDC 2440954 contains the supplementary crystallographic data for this paper.[14]

## Notes and references

1 (*a*) *Handbook of Metathesis*, ed. R. H. Grubbs, A. G. Wenzel, D. J. O'Leary and E. Khosravi, Wiley-VCH, Weinheim, Germany, 2nd edn, 2015; (*b*) *Olefin Metathesis: Theory and Practice*, ed. K. Grela, John Wiley & Sons, Hoboken, N. J., 2014.
2 (*a*) D. R. Anderson, V. Lavallo, D. J. O'Leary, G. Bertrand and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2007, **46**, 7262; (*b*) V. M. Marx, A. H. Sullivan, M. Melaimi, S. C. Virgil, B. K. Keitz, D. S. Weinberger, G. Bertrand and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2015, **54**, 1919.
3 (*a*) V. Lavallo, Y. Canac, C. Prašang, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2005, **44**, 5705; (*b*) R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 2899; For recent reviews, see: (*c*) M. Soleilhavoup and G. Bertrand, *Acc. Chem. Res.*, 2015, **48**, 256; (*d*) M. Melaimi, R. Jazzar, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2017, **56**, 10046; (*e*) U. S. D. Paul and U. Radius, *Eur. J. Inorg. Chem.*, 2017, 3362; (*f*) R. Jazzar, M. Soleilhavoup and G. Bertrand, *Chem. Rev.*, 2020, **120**, 4141; (*g*) R. K. Singh, T. K. Khan, S. Misra and A. K. Singh, *J. Organomet. Chem.*, 2021, **956**, 122133.
4 For a recent review on CAAC–Ru-complexes, see: J. Morvan, M. Mauduit, G. Bertrand and R. Jazzar, *ACS Catal.*, 2021, **11**, 1714.
5 (*a*) R. Gawin, A. Tracz, P. Krajczy, A. Kozakiewicz-Piekarz, J. P. Martínez and B. Trzaskowski, *J. Am. Chem. Soc.*, 2023, **145**, 25010; see also: (*b*) A. V. Afanaseva, A. A. Vinogradov, A. A. Vinogradov, M. E. Minyaev, D. A. Pyatakov, A. N. Tavtorkin, V. V. Bagrov, P. V. Ivchenko and I. E. Nifant'ev, *ChemSusChem*, 2025, **18**, e202402190.
6 (*a*) R. Gawin, A. Kozakiewicz, P. A. Gunka, P. Dąbrowski and K. Skowerski, *Angew. Chem., Int. Ed.*, 2017, **56**, 981; (*b*) R. Gawin, A. Tracz, M. Chwalba, A. Kozakiewicz, B. Trzaskowski and K. Skowerski, *ACS Catal.*, 2017, **7**, 5443; (*c*) D. L. Nascimento, A. Gawin, R. Gawin, P. A. Gunka, J. Zachara, K. Skowerski and D. E. Fogg, *J. Am. Chem. Soc.*, 2019, **141**, 10626.
7 A. E. Samkian, Y. Xu, S. C. Virgil, K.-Y. Yoon and R. H. Grubbs, *Organometallics*, 2020, **39**, 495.
8 M. Nagyházi, Á. Lukács, G. Turczel, J. Hancsók, J. Valyon, A. Bényei, S. Kéki and R. Tuba, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204413.
9 (*a*) J. Talcik, M. R. Serrato, A. Del Vecchio, S. Colombel-Rouen, J. Morvan, T. Roisnel, R. Jazzar, M. Melaimi, G. Bertrand and M. Mauduit, *Dalton Trans.*, 2024, **53**, 5346; For the previous CABC synthesis, see also ; (*b*) M. R. Serrato, M. Melaimi and G. Bertrand, *Chem. Commun.*, 2022, **58**, 7519.
10 The introduction of *N*-alkyl unit on CAAC was recently reported, see: (*a*) A. Madron du Vigné and N. Cramer, *Organometallics*, 2022, **41**, 2731; (*b*) A. Madron du Vigné and N. Cramer, *Chem. Sci.*, 2024, **15**, 13864; (*c*) Á. Erdélyi, V. Farkas, G. Turczel, M. Nagyházi, A. Bényei, M. L. L. Recta, T. Nagy, S. Kéki, O. Osterthun, J. Klankermayer and R. Tuba, *Chem. – Eur. J.*, 2024, **30**, e202401918.
11 F. Vermersch, L. Oliveira, J. Hunter, M. Soleilhavoup, R. Jazzar and G. Bertrand, *J. Org. Chem.*, 2022, **87**, 3511.
12 (*a*) L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nat. Chem.*, 2019, **11**, 872; (*b*) E. C. Meng, T. D. Goddard, E. F. Pettersen, G. S. Couch, Z. J. Pearson, J. H. Morris and T. E. Ferrin, *Protein Sci.*, 2023, **32**, e4792.
13 Inverted CAAC-complexes were recently reported: (*a*) J. Morvan, F. Vermersch, Z. Zhang, T. Vives, V. Dorcet, T. Roisnel, C. Crévisy, L. Falivene, L. Cavallo, N. Vanthuyne, G. Bertrand, R. Jazzar and M. Mauduit, *Organometallics*, 2023, **42**, 495; (*b*) A. Sytniczuk, A. Kajetanowicz and K. Grela, *Chem. Catal.*, 2023, **3**, 100713.
14 C. Casalta, T. Roisnel, R. Jazzar, A. Doppiu and M. Mauduit, CCDC 2440954: Experimental Crystal Structure Determination, 2025, DOI: **10.5517/ccdc.csd.cc2my0g2**.