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An unusual cationic Ru(II) indenylidene complex and its Ru(III) derivative—efficient catalysts for high temperature olefin metathesis reactions[†]

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The use of a mixed phosphite/N-heterocyclic carbene bearing ruthenium precursor permits the synthesis and characterisation of unprecedented four-coordinate Ru(II) and Ru(III) cationic complexes adopting an unusual sawhorse structure. The cationic Ru(II) complex performs very effectively on challenging substrates at high temperature in very short reaction times and low catalyst loadings.

Olefin metathesis is a powerful and versatile tool for carboncarbon bond formations¹ that has been successfully used for the synthesis of high value products.² Since the initial reports of "first generation" Ru-based complexes,³ numerous strategies have been developed in order to afford ever more active and longer-living catalytic species. Amongst all developments to achieve this goal, the replacement of a phosphine ligand by an *N*-heterocyclic carbene (NHC) represents a landmark in this area (Fig. 1). The enhanced performance of these precatalysts was attributed to the increased electrophilicity of the ruthenium conferred by the NHCs steric and electronic properties.⁴

As an alternative to the widely studied neutral complexes, a relatively small number of research groups have developed catalytic systems focusing on cationic ruthenium architectures (Fig. 2).^{5–9}

We have recently reported on the superior stability and excellent catalytic performance of catalysts bearing mixed ligand systems NHC/P(OR)₃ such as **Caz-1**.¹⁰ Based on these findings and on the seminal reports discussed above, it seemed of interest to develop cationic derivatives of **Caz-1** and study their catalytic activity in alkene metathesis reactions.

Reaction of *cis*-**Caz-1** with one equivalent of silver hexafluoroantimonate provided the mono-cationic complex **Caz-1**⁺



Fig. 1 Commercially available 2nd generation catalysts.

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK. E-mail: cc111@st-andrews.ac.uk; Fax: +44 (0)1334 463808; Tel: +44 (0)1334 463698 † Electronic supplementary information (ESI) available: Experimental details, X-ray data and NMR spectra. CCDC 832820 (Caz-1⁺). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc15903a



Fig. 2 Cationic Ru metathesis catalysts.



Scheme 1 Synthesis of cationic ruthenium pre-catalyst Caz-1⁺.

in 95% yield (Scheme 1). Surprisingly, whilst this reaction proceeds cleanly and in a quantitative yield, reactions carried out with the phosphine or pyridine derivatives **G-II**, **Ind-II** and **Ind-III** (Fig. 1), under similar conditions, led to very complex mixtures of products.¹¹

The ³¹P{¹H}-NMR spectrum of Caz-1⁺ contains a singlet shifted upfield ($\delta_{\rm P}$ 115.6 ppm) compared to the starting material Caz-1 (δ_P 122.0 ppm). The ¹H NMR spectral data of **Caz-1**⁺ show that both the NHC and the phosphite ligands rotate freely, which is in marked contrast with the starting material cis-Caz-1 and its isomer trans-Caz-1 (NHC/P(OR)₃ mutually trans). Indeed, the former shows a static behavior of both the NHC and the phosphite ligands whilst the latter shows that of a static NHC and a fluxional phosphite.^{10a} The ¹³C{¹H}-NMR spectrum of Caz-1⁺ displays a doublet at 202.8 ppm assigned to the carbone carbon atom, with a coupling constant ${}^{2}J_{C-P}$ of 15.1 Hz. The latter is consistent with a mutual cis-orientation of the NHC and phosphite ligands. This value is similar to the one of 13.4 Hz found for cis-Caz-1 ($\delta_{\rm C}$ 208.9) and different from the one found for *trans*-Caz-1 (127.8 Hz with $\delta_{\rm C}$ 217.3 ppm).^{10a} The structure of Caz-1⁺, and therefore the cis disposition of the P- and C-donor ligands were unambiguously determined by X-ray



Fig. 3 Molecular structure of Caz-1⁺ \cdot 0.5EtOAc. Counter-anions (SbF₆⁻) and hydrogens omitted for clarity.

diffraction studies on single crystals (Fig. 3).¹² Unlike the systems reported by Hofmann et al., and presumably due to the steric hindrance of the ancillary ligands and of the indenvlidene fragment, Caz-1⁺ does not dimerise into a 16 electron species.⁸ Instead, the four-coordinate 14 electron complex displays an unusual sawhorse geometry with the phosphite ligand in a cis position to the NHC and trans to the "vacant site". The latter is occupied by an agostic interaction (Ru.-H-C 2.300 Å) with a hydrogen from the NHC (H12b), which undoubtedly contributes to the stability of the low valent sawhorse structure. The agostic interaction leads to a distortion of the NHC, as shown by the angles between the mean planes of the two mesityl rings. Indeed, whilst in Caz-1, the angle between the mesityl rings is 10° , 10^{a} a twist of 30° is observed in **Caz-1**⁺ due to the agostic interaction pulling the ring towards the metal centre. Additionally, a π - π interaction between the mesityl ring not involved in the agostic interaction and the indenylidene moiety seems to be present.

Only a very limited number of four-coordinate Ru(II) complexes has been described in the literature.^{13–15} Such systems often involve two agostic interactions that complete the coordination sphere of the metal centre, leading to an octahedral geometry.¹³ Caulton *et al.* have shown that four-coordinate Ru(II) species bearing bi- or tri-dentate ligands without extra stabilising interaction could be isolated.¹⁴ Grubbs and Piers have disclosed similar systems bearing solely monodentate ligands. In such cases, a distorted trigonal pyramidal geometry was observed.¹⁵ To the best of our knowledge, **Caz-1**⁺ is the first example of a four-coordinate Ru(II) complex which displays a single agostic interaction leading to a square-based pyramidal geometry, the indenylidene group occupying the apex.

The abstraction of the second chloride with an additional equivalent of silver salt was next examined. *cis*-**Caz-1** was reacted with 2 equivalents of AgSbF₆ at room temperature for 15 minutes yielding a green solution. Simple removal of salts by filtration afforded a mixture of two products that rapidly converted to complex 6.¹⁶ The same result was obtained when **Caz-1**⁺ was treated with one equivalent of AgSbF₆ (Scheme 2).



Scheme 2 Synthetic routes leading to the Ru(III) complex 6.



Fig. 4 Molecular structure of the Ru(III) complex 6 EtOAc. Counteranions $(2SbF_6^-)$ and hydrogens omitted for clarity.

The ¹H NMR spectrum of complex 6 displays broad signals that have chemical shifts similar to those obtained for Caz-1⁺. Similarly, the singlet observed in the ${}^{31}P{}^{1}H$ -NMR spectrum of complex 6 is broad, and is shifted upfield ($\delta_{\rm P}$ 105.7 ppm) compared to Caz-1⁺.¹⁷ Reliable ¹³C{¹H} NMR data could not be obtained due to the lack of stability of complex $6^{.18}$ However, single crystals of 6 were obtained and subjected to X-ray diffraction studies that allowed us to establish atom connectivity.¹⁹ These data show that the abstraction of the second chloride had not occurred, but that instead the ruthenium centre has been oxidised. This reactivity can be explained by the presence of silver (1) that can be easily reduced to Ag(0), and by the fact that halide abstraction from a cationic species requires more energy. As Caz-1⁺, complex 6 exhibits a distorted square pyramidal geometry, the apex being occupied by the indenylidene ligand, and a vacant site is occupied by a molecule of ethyl acetate (crystallisation solvent) (Fig. 4).

One interesting feature of the oxidation reaction is the unexpected isomerisation of the chloride at a position trans to the phosphite ligand. As complex 6 was synthesised in the absence of ethyl acetate or any coordinating solvent, we can assume that complex 6, in solution, is, to the best of our knowledge, one of the rare examples of a Ru(III) four-coordinate bis-cationic species, which has only 13 electrons. To further investigate this possibility, EPR experiments were carried out, however, they remained inconclusive due to the degradation of the complex during data acquisition. Nevertheless, NMR and microanalytical data suggest that the 13 electron species is the isolated compound. As mentioned above, cationic Ru complexes proved to be promising systems for olefin metathesis.^{5–9} In this respect, the catalytic potential of Caz-1⁺ was next assessed in the ring closing metathesis (RCM) of the challenging tosylamine derivative 7. Toluene was first examined as it proved to be the solvent of choice for the neutral parent complex cis-Caz-1.^{10a} However, optimisation of reaction conditions (see Table S2 in ESI[†]) proved xylene to be the solvent of choice, as at 0.1 mol% catalyst loading, 79% of 8 was formed, which corresponds to 790 TONs. Under the optimised reaction conditions, the kinetic profile of Caz-1⁺ was compared to that of commercially available neutral complexes in the model reaction (Fig. 5).

At 140 °C, all catalysts except Caz-1⁺ exhibit rapid initiation. At this temperature, decomposition of G-II and Ind-II occurs rapidly (*ca.* 2 min) and these catalysts could not achieve more than 40% conversion. The more thermally stable *cis*-Caz-1 and Hov-II were able to afford, under these conditions, *ca.* 67% conversion. Caz-1 displayed an extremely high activity for 3 minutes followed by rapid decomposition whilst Hov-II displayed a lower rate but with apparently a longer-living active species. An initial thermal treatment of 2 min at 140 °C



Fig. 5 Performance of **Caz-1**⁺ *vs.* **Caz-1**, **Hov-II**, **G-II** and **Ind-II**. Conditions: **7** (0.25 mmol), cat. (0.1 mol%), xylene (1.5 mL), 140 °C.

was necessary to activate $Caz-1^+$ and 80% conversion was reached after only 10 min. Despite the previously reported thermal stability of one cationic Ru complex by Caulton *et al.*,^{13c} the exceptional robustness of $Caz-1^+$ was unexpected. The reasons behind this high thermal stability are still unclear. The unsuccessful attempts to abstract Cl from the non-phosphite based **Ind-II** and **Ind-III** point to an important role of the P(OR)₃ ligand in the complex formation and stabilisation. The exact mechanism at play here is being examined but the necessary thermal activation is in sharp contrast with the reactivity displayed by the distorted trigonal pyramid complex reported by Piers *et al.* that exhibits high activity at rt.^{15a} The catalytic potential of **Caz-1**⁺ was next examined in RCM of a range of dienes and enynes and in cross metathesis (Fig. 6).

The cationic system **Caz-1**⁺ is highly active for a wide range of substrates in RCM as essentially quantitative yields are obtained within 15 min using a catalyst loading of 0.1 or 0.2 mol%. Of note is the fact that sterically hindered substrates are efficiently ring closed leading to 5- and 6-membered rings bearing a tetra-substituted double bond. However, the ring closure of the tetra-substituted malonate derivative proved to be more problematic. **Caz-1**⁺ was also tested in the enyne metathesis of **16** using 0.2 mol% of catalyst. Within 15 minutes, enyne **16** was fully converted to the desired cyclic diene **17**. Finally, the



Reaction conditions: Caz-1⁺ (0.1 mol%), substrate (0.25 mmol), xylene (1 mL), 15 min, 140°C; Average of 2 runs; conversion was determined by GC; isolated yield in parentheses; ^a 0.2 mol%Ru, ^b 2 mol%Ru.

Fig. 6 Catalytic performance of Caz-1⁺ in RCM, enyne metathesis and CM.

cross metathesis reaction of 18 with methyl acrylate was achieved using 0.4 mol% of Caz-1⁺.

We developed the first type of cationic ruthenium complex that was proven to be highly active in RCM, CM and enyne metathesis (0.1–0.4 mol% Ru). The high activity of the catalyst and thermal stability of the active species allowed the full conversion of difficult substrates in only 15 minutes. The synthetic accessibility of **Caz-1**⁺ and its thermal stability are imputed to the presence of the phosphite ligand. This system also led us to the isolation of a very rare example of Ru(III) 13-electron complex. The mechanism by which complexes are obtained remains unclear and studies aiming to shed light on these matters are ongoing in our laboratories.

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- 16 Isolation and characterisation of the intermediates not successful.
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- 18 Decomposition was observed when stored at -25 °C in a glovebox.
- 19 Despite numerous efforts higher quality crystals could not be obtained.