Cationic molybdenum oxo alkylidenes stabilized by N-heterocyclic carbenes: from molecular systems to efficient supported metathesis catalysts†

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Cationic d⁰ group 6 olefin metathesis catalysts have been recently shown to display in most instances superior activity in comparison to their neutral congeners. Furthermore, their catalytic performance is greatly improved upon immobilization on silica. In this context, we have developed the new family of molecular cationic molybdenum oxo alkylidene complexes stabilized by N-heterocyclic carbenes of the general formula [Mo(O)(CHCMe₃)(IMes)(OR)][X³] [IMes = 1,3-dimesitylimidazol-2-ylidene; R = 1,3-dimesityl-C₆H₅, C₆F₅Si, X = B(3,5-(CF₃)₂C₆H₃)₄⁻, B(3,5-(CF₃)₂C₆H₃)₄⁻]. Immobilization of [Mo(O)(CHCMe₃)(IMes)(O-1,3-dimesityl-C₆H₅)B(3,5-(CF₃)₂C₆H₃)₄⁻] on silica via surface organometallic chemistry yields an active alkene metathesis catalyst that shows the highest productivity towards terminal olefins amongst all existing molybdenum oxo alkylidene catalysts.

Introduction

Since the discovery of olefin metathesis more than half a century ago,¹ the development of novel catalyst families has been at the core of extensive research efforts, with the goal to increase catalytic performance, from functional group tolerance to increased activities, selectivities and stabilities.² Apart from Ru-based “Grubbs-type” catalysts,³ d⁰ early-transition-metal metathesis catalysts mostly based on group 6 metals (Mo/W), i.e. Schrock-type catalysts of the general formula M[E(CHR)(X)(Y)] with E = oxo or imido and X, Y = anionic ligands of various types (alkyls, alkoxys, amidos), have emerged as a central class of olefin metathesis catalysts.⁴ Besides, the use of surface organometallic chemistry (SOMC)⁵ has enabled to greatly improve their activity and stability through generation of the corresponding well-defined active sites dispersed at the surface of oxide supports like silica.⁶ In parallel, DFT calculations have revealed that the right balance of the σ-donation ability of the X, Y and E ligands is key to these improved catalytic performances.⁷ The concurrent presence of both strong and weaker σ-donating anionic X and Y ligands for instance avoids overstabilization of the metallaacyclobutane intermediates while favouring [2 + 2] cycloaddition and cycloreversion processes as well as suppressing deactivation pathways. N-Heterocyclic carbenes (NHCs) have gained increasing importance as ancillary ligands in transition metal complexes since the 1990s.⁸ In this regard, the introduction of NHCs in overall tetracoordinate, metathesis-active, cationic Mo and W species has illustrated how catalytic performance can be further improved.⁹ Charge delocalization between the NHC and the cationic metal centre renders cationic complexes rather “soft” according to the HSAB principle, which explains the high activity and functional group tolerance in cationic group 6 alkylidene complexes.¹⁰ The combination of both concepts – introduction of the strong σ-donating NHC ligands and weak siloxy ligands provided by the silica surface – has thus enabled the generation of some of the most active and stable olefin metathesis catalysts to date.¹¹,¹²,¹³ For the cationic tungsten-based catalysts, the oxo-bearing complexes outperformed their imido analogues by 1–2 orders of magnitude in activity;¹⁴ this can be attributed to the combination of the smaller E ligand size, allowing for easier access of the incoming olefin to the metal centre, and its strong σ-donating ability, which simultaneously enhances catalyst stability. Previously published immobilized neutral Mo oxo alkylidene complexes proved to possess high activity for internal olefins (Fig. 1a).¹⁵ Consequently, we wanted to investigate whether the activity of molybdenum oxo complexes can be boosted for terminal olefins similar to what was shown for analogous tungsten oxo complexes.¹⁶

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Results and discussion

Synthesis of molecular catalysts

In this context, we developed and herein report the synthesis and characterization of the long-awaited family of molecular and well-defined silica-supported cationic Mo oxo species stabilized by NHC ligands (Fig. 1b) and investigated their activity towards internal and terminal olefins. The synthesis of cationic molybdenum oxo alkylidene NHC complexes was first attempted starting from the 4-methoxybenzylidene precursor Mo-1 (Scheme 1a). Addition of 1 equiv. of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) to Mo-1 resulted in deprotonation of the alkylidene ligand. Through careful choice of a less basic chlorinated NHC, this side-reaction could be vastly circumvented and the desired product was isolated in 34% yield. Single crystals of Mo-2 for X-ray diffraction were grown from a mixture of dichloroethane/n-heptane at −40 °C (Fig. 2). Mo-2 crystallizes in the triclinic space group P1 with a = 1184.11(6) pm, b = 1247.18(7) pm, c = 1537.13(8) pm, α = 80.252(2)°, β = 81.208(2)°, γ = 66.112(3)°, Z = 2. In the solid state, the complex adopts a distorted square pyramidal geometry ($\tau_5 = 0.34$) with a syn alkylidene ($^1J_{CH} = 134$ Hz) in the apical position. The Mo-oxo bond (166.4 pm) is slightly shorter than in five-coordinate W oxo alkylidene NHC complexes (169.0–176.0 pm) whereas the Mo–NHC bond distance of 226.3 pm is well in the expected range of comparable tungsten complexes.

Exchange of the fluorinated alkoxides was achieved by protonation using N,N-dimethylanilinium chloride to furnish complex Mo-3. Due to their electron count of 16 (counting the free electron pair at the oxo ligand, too) and their binding site occupied by an NHC, both, Mo-2 and Mo-3 were not expected to exhibit high activity in olefin metathesis. Therefore, we strived for the synthesis of highly active cationic species. 

![Scheme 1](image)  
**Scheme 1** (a) Synthesis of 4-methoxybenzylidene complexes that could not be further transformed into cationic species; (b) synthesis of cationic molybdenum oxo neopentylidene complexes.
Abstracting one of the X-type ligands using either N,N-dimethylaminium B[Ar\(^+$\)]\(^-$\) or Ag[pivCN]\(_2\)B[Ar\(^+$\)]\(^-$\) in the reaction with Mo-2 in the presence of pivalonitrile (pivCN) or Ag[pivCN]\(_2\)B[Ar\(^+$\)]\(^-$\) in the reaction with Mo-3 resulting in complexes of the formula \{MoO(CH-4-(OMe)C\(_6\)H\(_4\))\_X\}[IMesCl\(_2\)][B[Ar\(^+$\)]\(^-$\)] (X = OC(C\(_2\)F\(_5\))\(_2\), Cl) proved to be successful when conducted in CDCl\(_3\) and monitored by \(^1\)H NMR. However, the cationic species readily decomposed upon workup, which we attribute to the low steric demand of both, the 4-methoxybenzylidene moiety and the oxo ligand. And indeed, so far, all isolated cationic group 6 alkylidene complexes either bear a neophylidene or neo-pentylidene ligand\(^6\) in line with the “almost magic properties” of the neopentylidene ligand contributing to the stability of group 6 complexes.\(^5\)

We consequently shifted our attention to a lately published procedure leading to the Mo oxo neo-pentylidene complex MoO(CHCMe\(_3\))\_Cl(OHMT)(3-Brpy) (OHMT = 2,6-dimesitylphenoxide; 3-Brpy = 3-bromopyridine).\(^6\) 3-Bromopyridine as a relatively weak donor could then be readily replaced by strongly donating IMes (Scheme 1b). In this case, no deprotonation of the alkylidene ligand occurred. The resulting five-coordinate NHC complex was not isolated on account of its poor crystallisation propensity. Nevertheless, the addition of NaB(Ar\(_F\))\(_4\) and lithium tetrais(perfluoro-\(\alpha\)-butyl)aluminate (LiPFTA), respectively, to the crude reaction mixture led to formation of the desired cationic complexes that could be purified by recrystallisation and which were isolated in good yields of 72 and 80%, respectively, over two steps. The stable cationic species served as efficient and general precursors for immobilization but can also be further transformed by exchange of the X-ligand. Thus, upon addition of an excess of HOC\(_4\)F\(_5\) to Mo-7, quantitative protonation of the HMTIO ligand was facilitated to form Mo-8 in a high isolated yield of 84%. The coordination of THF in complex Mo-8 that lacks the sterically demanding alkoxide is imperative for its purification by recrystallization. Single crystals of Mo-8 suitable for X-ray diffraction were grown from 1,2-dichloroethane at \(-40 \degree C\) (Fig. 3). As for Mo-2, the triclinic space group \(P\overline{1}\) was found in Mo-8 with the unit cell dimensions being \(a = 1296.54(8)\) pm, \(b = 1388.76(9)\) pm, \(c = 1930.09(12)\) pm, \(\alpha = 79.898(2)\), \(\beta = 78.994(2)\), \(\gamma = 86.057(3)\) and two molecules in the unit cell. The distorted square pyramidal structure (\(\tau_s = 0.29\)) bears a \(\alpha\)-alkylidene ligand in the apical position and all other ligands in the equatorial plane. All bond lengths and angles are similar to those observed for five-coordinate cationic W oxo alkylidene NHC complexes.\(^17\)

On a final note regarding the synthesis of cationic Mo oxo alkylidene complexes, the synthesis of further species bearing fluorinated alkoxides starting from aryloxide complexes Mo-6 and Mo-7 have been attempted using HOC\(_4\)F\(_5\). Unfortunately, the reactions proved unsuccessful, and no conversion was observed. However, the aryloxide ligand in Mo-6 and Mo-7 was successfully protonated by the action of HCl in Et\(_2\)O in the presence of pivCN to yield a mixture of complexes of the type \{MoO(CHCMe\(_3\))\_Cl(IMes)[pivCN]\}_\(X\) (X = B[Ar\(^+$\)]\(_4\)) or LiPFTA and the protonated OHMT ligand as an inseparable oil. All attempts to isolate the complexes by crystallization or to further convert them \(in\ situ\) using MOC\(_4\)\(\alpha\)-halides (M = Li, Ag) failed.

**Immolization of complexes**

The reaction of Mo-7 with HOC\(_4\)F\(_5\) illustrates that protic functional groups can lead to the very selective exchange of the X-ligand without notable side-reactions. Following the development of the molecular compounds, we also sought to exploit this reactivity for grafting the complex on silica partially dehydroxylated at 700 \(\degree C\) (SiO\(_2\)_700). For comparability with previously published complexes,\(^5\) the B[Ar\(^+$\)]\(_4\)-containing complex Mo-6 was selected for this purpose and yielded the corresponding supported species Mo-6\@SiO\(_2\) (Scheme 2).

Quantification by \(^{19}\)F solution NMR spectroscopy of the remaining B[Ar\(^+$\)]\(_4\) of the complex indicates that \(ca.\) 29% of the surface silanols (0.32 mmol g\(^{-1}\)) reacted with Mo-6, in line with a molybdenum loading of 0.79 wt% as determined by elemental analysis. IR spectroscopy confirms that a significant amount of isolated silanols (\(\tilde{\nu} = 3747\) cm\(^{-1}\)) are consumed upon grafting by protonolysis, although the large size of Mo-6 likely prevents full coverage.

Besides the appearance of CH stretching bands between \(\tilde{\nu} = 3200\) and 2800 cm\(^{-1}\), a broad absorption band appeared at around \(\tilde{\nu} = 3700\) cm\(^{-1}\), typical of the non-covalent interactions of unreacted surface silanols with the aromatic ligands of the grafted complex.\(^{29,30,31}\) Further characterization of Mo-6\@SiO\(_2\)
Catalytic testing of molecular and immobilized complexes

Evaluation of the catalytic activity for **Mo-6** was carried out for both molecular and immobilized complexes in the homo metathesis of the two benchmark substrates cis-4-nonene and 1-nonene at 30 °C (Table 1). While the homogeneous complex **Mo-6** had to be tested in o-dichlorobenzene (DCB) due to solubility requirements, the immobilized analogue **Mo-6@SiO2** was tested in both DCB and toluene, prototypical metathesis solvents used in many studies. In all cases, the metathesis activity towards \( \text{olefin} \) was higher than for internal ones. This behavior was most pronounced for the molecular complex **Mo-6**, where no activity was observed for internal olefins and only 86% conversion after 8 hours was reached with 1-nonene. The lack of reactivity is likely associated with the presence of the large phenoxy (OHMT) ligand, whose steric encumbrance probably hinders the required distortion of the metal complex to a trigonal prism necessary to bind the incoming olefin.\(^7\)

In fact, switching OHMT for the smaller surface siloxy ligand leads to an increase in activity towards both olefins.\(^8,9\) Notably, the initial turnover frequency recorded for the self-metathesis of cis-4-nonene was modest in comparison to other molybdenum oxo allyldienes \( (\text{TOF}_{3\text{min}} = 26 \text{ min}^{-1} \text{ vs. } >500 \text{ min}^{-1}).\)\(^9,11\) This observation is in line with the reported activity difference for the cationic tungsten analogues\(^8,9\) and established trends that show increased activity for internal olefins in Schrock-type metathesis catalysts with decreasing \( \sigma \)-donor strength of the \( X \) ligands [\( X = \text{NHC, pyrrolide, alkoxide}\)].\(^8,9,11-18\) Considering also the activity for terminal olefins, the same correlation can only be observed in few cases.\(^11\) The decisive factor for a high catalytic activity might be rather the right balance of strong and weak \( \sigma \)-donor ligands as outlined above.\(^7\) However, the activity of **Mo-6@SiO2** towards terminal olefins exceeds those previously reported for this family of supported complexes with **TOF\(_{3\text{min}} = 254 \text{ min}^{-1} \text{ at } 0.02\text{ mol}\% \text{ catalyst loading compared to only } 75 \text{ min}^{-1} \text{ and } 170 \text{ min}^{-1} \text{ of their neutral congeners at their optimal loadings (Fig. 4).}\(^9,11\) Indeed, this supports our working hypothesis that the catalytic activity of cationic Mo oxo allyldienes is enhanced for terminal olefins similarly as shown previously for the corresponding tungsten oxo complexes.\(^8,9\) Furthermore, the catalyst remained active (94% after 8 h), when increasing the substrate to catalyst ratio to 10 000 : 1.

The excellent performance of **Mo-6@SiO2** was additionally demonstrated by recycling tests, where maximum conversion was obtained within 8 h three times, albeit accompanied by a constant loss of activity (see ESI†).

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**Table 1** Homocoupling of cis-4-nonene and 1-nonene (toluene, 30 °C)

| Catalyst                  | Mol% | **TOF\(_{3\text{min}}^a\)** | Time to equilibrium/maximum conversion \(^{a}\) |
|---------------------------|------|-----------------------------|--------------------------------------------------|
| Metathesis of cis-4-nonene\(^c\) |      |                             |                                                  |
| Mo-6                      | 0.1  | — (≤1%)                     | 5% after 24 h                                    |
| Mo-6@SiO2\(^e\)           | 0.1  | 18 (6%)                     | 50% after 16 h                                   |
| Mo-6@SiO2                 | 0.1  | 26 (8%)                     | 50% after 4 h                                    |
| Metathesis of 1-nonene\(^d\) |      |                             |                                                  |
| Mo-6                      | 0.1  | 47 (14%/98%)                | 86% after 8 h                                    |
| Mo-6@SiO2\(^e\)           | 0.1  | 124 (37%/97%)               | 98% after 4 h                                    |
| Mo-6@SiO2                 | 0.1  | 118 (36%/98%)               | 98% after 4 h                                    |
| Mo-6@SiO2\(^e\)           | 0.02 | 254 (15%/98%)               | 97% after 8 h                                    |
| Mo-6@SiO2                 | 0.005| 225 (7%/98%)                | 94% after 8 h                                    |

\(^{a}\) **TOF** at 3 min, given in min\(^{-1}\). \(^{b}\) In cases where full conversion was not reached, the maximum conversion measured after a given time is provided. \(^{c}\) Equilibrium conversion is 50%, conversion in brackets. \(^{d}\) Maximum conversion is 100%, conversions/selectivity for the formation of hexadec-8-ene in brackets. \(^{e}\) Experiment performed in o-dichlorobenzene.
In previous studies it was shown that the homometathesis of 1-nonenone using neutral immobilized Mo alkylidene catalysts can lead to low selectivities through isomerization of the position of the double bond. This can result in a selectivity of the desired hexadec-8-ene of only 80–85%, especially in closed vessels and at prolonged reaction times.2m,2b This type of isomerization can be attributed to Mo(n) species resulting from methylidyne complex decomposition that form π-complexes with olefins in the reaction mixture. Subsequently, the π-complexes undergo oxidative addition and reductive elimination processes and, thereby, lead to isomerization.19 Monitoring the selectivity for the formation of the homocoupling product in the metathesis of 1-nonenone using cationic Mo oxo alkylidene complexes, in contrast, demonstrated that neither the homogeneous nor the immobilized catalyst are prone to form structural isomers. Even after long reaction times of 8 h, high selectivities of ca. 98% were obtained.

Conclusions
In conclusion, catalysts belonging to the new family of cationic Mo oxo alkylidenes NHC complexes have been developed. The immobilization on silica yielded a catalyst with preferential activity towards α-olefins over internal olefins. This particular reactivity is attributed to the nature of the NHC ligand, whose steric demand and strong σ-donor ability have an important influence on the formation and reversion of the TBP metalacyclobutane. These results further contribute to the overall understanding on how structural and electronic properties of metal alkylidenes affect the catalytic performance and further highlight the role of the NHC ligand in providing highly active cationic d8-based olefin metathesis catalysts.

Experimental
General considerations
All experiments were carried out under an inert nitrogen or argon atmosphere using Schlenk techniques or an MBraun or GS glove box equipped with a purifier unit. Water and oxygen levels were kept below 0.1 ppm. Diethyl ether, methylene chloride, pentane, toluene and tetrahydrofuran were purified using double MBraun SPS alumina columns. Benzene and benzene-d6 were distilled from Na, degassed by three consecutive freeze-thaw cycles, autoclaved, and distilled over activated Selexsorb CD® and activated 4 Å molecular sieves.

Silica. Silica (Aerosil Degussa, 200 m2 g–1) was compacted with distilled water, sieved, calcined at 500 °C under air for 12 h and treated under vacuum (10–5 mbar) at 500 °C for 8 h and then at 700 °C for 14 h (referred to as SiO2–700).

Synthesis of molecular precursors

[MoO(CH4–O–OMe)2]2+[OC(CF3)3]2][IMesCl2] (Mo-2). A cold (–35 °C) solution of IMesCl2 (112 mg, 0.30 mmol, 0.9 equiv.) in toluene (4 mL) was added dropwise to a cold (–35 °C) solution of [MoO(CH4–O–OMe)2]2+[OC(CF3)3]2][PPh2Me] (Mo-1, 300 mg, 0.33 mmol, 1 equiv.) in toluene (4 mL). The reaction mixture was stirred at room temperature for 30 minutes and then stored at −35 °C for three hours. The solvent was removed under reduced pressure and the residue was triturated with n-pentane.

Chemical shifts are reported in ppm relative to the solvent signal (CDCl3: 7.26 ppm, C6D6 7.16 ppm, CD2Cl2 5.13 ppm).28 Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. The 1H and 13C solid-state NMR spectra were acquired on a Bruker AVANCE III spectrometer operating at 500 MHz. 1H frequency (9.4 T) and equipped with a 3.2 mm proton-heteronucleus magic angle spinning (1H,X MAS) probe (Bruker). Samples were packed into a 3.2 mm MAS NMR zirconia rotor closed with a VESPEL drive cap in an argon-filled glovebox, transferred to the NMR spectrometer in a tightly sealed vial under argon, rapidly inserted into the NMR spectrometer and spun under dry nitrogen. The MAS frequency was set to 16 kHz for all experiments. For the 13C CP MAS measurements, the Hartman–Hahn cross-polarization was performed by making use of a linear ramp from 70% to 100% with the contact time set to 3 ms. For decoupling, SPINAL64 was applied with 100 kHz irradiation on 1H. The acquired solid-state NMR spectra were referenced externally with respect to the downfield signal of adamantane (38.5 ppm). All MAS NMR spectra were acquired at ambient temperature.

Liquid catalytic test aliquots were analysed using a GC/FID (Agilent Technologies 7890 A) equipped with a split–splitless injector heated to 250 °C, injection volume 0.5 μL using hydrogen carrier gas. Chromatographic separations for 1-nonenone and cis-4-nonenone catalytic tests were performed using an HP-5 (Agilent Technologies) column (30 m, 0.32 mm, 0.25 μm stationary phase). Critical data have been deposited with the Cambridge Crystallographic Data Centre (CCDC): Mo-2 CCDC 2151036, Mo-8 CCDC 2151037.

Preparation of precursor reagents. The following reagents were prepared according to literature procedures: IMes,21 IMesCl2,22 NaB[Ar7]4,23 Li[Al(OCP2)]4,24 [MoO(CH4–O–OMe)2 H4][OC(CF3)3]2[PPh2Me]22,25 [MoO(CHCMe3)2(OHMT)][Cl](3-BrPy).25

Substrates and internal standard. 1-Nonenone (TCI ≥ 99.5%), cis-4-nonenone (TCI ≥ 95%) and decaline (Sigma Aldrich 98%) were distilled from Na, degassed by three consecutive freeze-pump-thaw cycles, filtered through activated alumina, and stored for 4 hours over activated Selexsorb CD® and activated 4 Å molecular sieves.

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to give a brown solid. The n-pentane was decanted and diethyl ether (4 mL) was added, which resulted in the formation of a dark brown solution and an orange solid. The solution was decanted and the solid was washed with diethyl ether (1 mL) and dried in vacuo. Yield: 120 mg (34%). Crystals suitable for single-crystal X-ray diffraction were obtained from a mixture of 1,2-dichloroethane and n-heptane.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 13.50 (s, 1H), 6.99 (s, 2H), 6.93–6.13 (m, 6H), 3.87 (s, 3H), 2.24 (s, 6H), 2.13 (s, 6H), 1.92 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 72.15 (d, 0.78 Hz, 2H), 7.04 (s, 2H), 2.43 (s, 6H), 2.34 (s, 6H), 1.90 (s, 6H), 1.87 (s, 6H), 1.85 (s, 6H), 1.56 (s, 6H), 0.89 (s, 9H) ppm.

Elemental analysis (% calcd. for C$_{29}$H$_{30}$Cl$_4$MoN$_2$O$_2$: C 51.50, H 1.30, 1.29, 1.20, 1.13, 0.57, 0.34, 0.21, 0.18, 0.18 ppm. Elemental analysis (% found: C 51.48, H 0.30, 0.29, 0.28, 0.27 ppm.

13C NMR (101 MHz, CDCl$_3$) $\delta$ 303.1, 186.4, 163.9, 141.0, 136.6, 136.0, 133.5, 132.1, 131.0, 130.1, 129.7, 120.0, 113.2, 55.7, 34.1, 21.3, 18.3, 18.3 ppm.

Elemental analysis (calcd.) for C$_{29}$H$_{30}$Cl$_4$MoN$_2$O$_2$: C 51.50, H 1.30, 1.29, 1.20, 1.13, 0.57, 0.34, 0.21, 0.18, 0.18 ppm.
added to a suspension of SiO₂–700 (160.1 mg, 0.051 mmol SiOH, 1.1 equiv.) in o-dichlorobenzene (5 mL) at 25 °C in a nitrogen filled glovebox. The suspension was slowly stirred (120 rpm) over 3 h. The supernatant was removed by decantation and the solid was washed by suspension/decantation cycles in o-
dichlorobenzene (3 × 1 mL), toluene (3 × 1 mL) and pentane (3 × 2 mL). The resulting light-yellow solid was dried thoroughly under high vacuum (10⁻³ mbar) at room temperature for 2 hours to afford 180 mg of the title compound. All filtrate solutions were collected and analysed by ¹⁹F NMR spectroscopy in C₆D₆ using 4,4’-difluorobiphenyl as internal standard, indicating that 0.015 mmol of the molecular complex remained in solution, corresponding to 29% grafting. Mo 0.79%, C 5.85%, H 0.53%, N 0.47%, corresponding to 59 C/Mo (82 expected), 64 H/Mo (71 expected), 4 N/Mo (2 expected).

Data availability
Primary and complementary data are available from https://doi.org/10.18419/darus-3013.

Author contributions
JVM and JDJS contributed equally.

Conflicts of interest
There are no conflicts to declare.

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