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Decomposition of Vanadium(V) Alkylidenes Relevant to Olefin Metathesis

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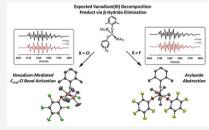
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ABSTRACT: Vanadium alkylidenes can be highly active initiators for ring-opening metathesis polymerization of cyclic olefins; however, attempts to expand their use to cross metathesis have been unsuccessful due to catalyst decomposition. Detailed knowledge of the decomposition reaction is imperative to guide future catalyst design. Herein, we demonstrate that β -hydride elimination is the dominant decomposition pathway during cross metathesis. The isolated vanadium decomposition products [N-2,6-(CH₃)₂C₆H₃]- $(OC_6Cl_5)[P(CH_3)_3]_2VCl$ (10) and $[N-2,6-(CH_3)_2C_6H_3]V(OC_6F_5)_2[P(CH_3)_3]_2$ (11), generated from two separate catalysts, agree with this pathway. Compounds 10 and 11 were shown computationally to form via bimolecular routes after β -hydride elimination from the metallocyclobutane and reductive elimination of propylene, which was itself



demonstrated to be exergonic with low thermodynamic barriers to metallocyclobutane formation. Relative conversions in the selfmetathesis of 1-hexene with the series of variadium alkylidenes of various sterics and electronics (N-2,6-X₂C₆H₃)(OC₆Y₅)[P- $(CH_3)_3$ $V[CHSi(CH_3)_3]$ [X = CH₃, Y = Cl (1); X = CH(CH₃)₂, Y = Cl (6), X = CH(CH₃)₂, Y = F (7)] were determined. It was found that bulkier, yet more electron-donating ligands decreased conversions, indicating that β -hydride elimination is favored over bimolecular decomposition. Analysis of organic reaction products demonstrated that reductive elimination of propylene occurs before insertion of ethylene into the newly formed vanadium-hydrogen bond.

INTRODUCTION

Olefin metathesis (OM) plays a critical role in synthetic chemistry through the formation of C=C bonds with high precision. The reaction is useful in small molecule synthesis, with implications for natural product and drug discovery chemistry^{2,3} via cross metathesis (CM), ring-closing metathesis (RCM), and ring-opening cross metathesis (ROCM),⁴ as well as polymer synthesis via ring-opening metathesis polymerization (ROMP), 5-7 acyclic diene metathesis polymerization (ADMET),⁷⁻¹² and ring-expansion metathesis polymerization (REMP). 13 Since the initial reports of Schrock 14 and Grubbs 15 on well-defined OM catalysts, the field has been dominated by myriad catalysts based on molybdenum and ruthenium. 16,17 Variation in ligands has allowed for remarkably high activity and selectivity, and low catalyst loadings (as low as 1 ppm in the case of cyclic alkyl amino carbene supported ruthenium catalysts). 18 Incorporation of substrates once thought beyond the scope of OM, such as alkenyl halides or others bearing functional groups directly on the olefinic carbon, is also now possible due to advancements with group 6 catalysts. 15

Recently, Nomura and co-workers reported efforts to add the more earth-abundant and inexpensive vanadium to the OM toolbox. Vanadium(V) alkylidenes demonstrated impressively high activity in ROMP of cyclic olefins. 6,23,24 In the case of highly strained norbornene, both living and Z-selective polymerization were achieved. 25,26 When low-strain cyclopentene, cycloheptene, and cis-cyclooctene were employed, high molar mass polyalkenemers of moderately narrow

dispersity were obtained.²⁷ Our group has sought to expand upon the foundational work of Nomura, specifically through expansion in the use of vanadium to include CM. This reaction was selected as a target due to the fact that success will have implications for future possibilities of ADMET, RCM, and ROCM with vanadium, as all require the ability for transient methylidenes ([V]=CH₂, [V] = vanadium-ligand complex) to exist, even fleetingly. Although Nomura reported the use of terminal olefins in low concentrations as chain transfer agents in ROMP,²⁸ systematic investigations into this reaction are lacking. Thus far, we disclosed that the vanadium(V) alkylidenes $(N-2,6-X_2C_6H_3)(OC_6Cl_5)[P(CH_3)_3]_2V[CHSi (CH_3)_3$ [X = CH₃ (1), F (2)] (Chart 1) can in fact catalyze the self-metathesis (SM) of various terminal olefins; however, premature catalyst death prevents the reaction from achieving high conversions.²⁹

One can consider three species present during SM as the sources of decomposition, as depicted in Scheme 1. Alkylidene A appeared unlikely to be the culprit for decomposition, given its similarity to alkylidenes generated during polymerization of

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Chart 1. Vanadium(V) Alkylidenes Screened in Self-Metathesis

Scheme 1. Mechanism and Intermediates of Self-Metathesis

monomers such as cyclopentene, cycloheptene, and ciscyclooctene, which proceed to extremely high conversions with no indication of catalyst decomposition. 27 On the other hand, methylidene B was considered the species most prime for decomposition. Within group 5, decomposition of methylidenes is well-known, usually occurring through a bimolecular mechanism. Schrock first demonstrated this bimolecular process with the tantalum(V) complex Cp2Ta- $(CH_3)(CH_2)$ (Cp = cyclopentadienyl), which decomposed to form Cp₂Ta(CH₃)(η²-CH₂CH₂).³⁰ Rothwell later demonstrated spectroscopically that tantalum(V) methylidenes may be generated photolytically from the tantalum(V) trimethyl precursors $(OAr)_2Ta(CH_3)_3$ $\{Ar = 2,6-[C(CH_3)_3]C_6H_3, 2,6 [C(CH_3)_3]$ -4- $(OCH_3)C_6H_2$, but that these compounds decomposed in a unimolecular fashion through cyclometalation of a tert-butyl group on an aryloxide ligand. 31,32 Arnold reported the synthesis of the amidinate-supported tantalum(V) methylidene complexes $(Am)_2Ta(CH_2)(CH_3)$ $\{Am = \eta^2 - \eta$ $ArC[NSi(CH_3)_3]_2$, Ar = phenyl, tolyl} which were not reported to undergo bimolecular decomposition,³³ but did demonstrate methylidene group transfer to pyridine N-oxides, yielding tantalum(V)-oxo and methyl-substituted pyridine products.³⁴ Presumably, the larger amidinates (relative to Cp)³⁵ prevented bimolecular decomposition. Additional reactivity of these species was later demonstrated with nitriles, isocyanides, aldehydes, thiols, and propylene sulfide.³⁶ Other examples of stable tantalum methylidenes were reported by Ozerov and Mindiola, also supported by sterically demanding ligands (e.g., PNP-pincers and aryloxides). 37,38 Bulky aryloxides were also employed to support niobium methylidenes immune to bimolecular decomposition. 39,40

Given that bulky ligands are certainly needed to stabilize group 5 methylidenes and prevent bimolecular decomposition, and that a vanadium methylidene has yet to be isolated, it would not be surprising to learn that bimolecular decom-

position of transient methylidenes was at play during the SM previously reported. Indeed, Fogg demonstrated that the sterics of the substituents on the alkylidene carbon greatly influence the rate of bimolecular decomposition in ruthenium catalysts, with methylidenes decomposing the fastest. Nomura also showed that reaction of the ketimide containing vanadium(V) alkylidene $[N-2,6-(CH_3)_2C_6H_3]\{N=C[C-(CH_3)_3]_2\}[P(CH_3)_3]V[CHSi(CH_3)_3]$ (3) with 1 equiv of styrene yielded the metallocyclopropane species $[N-2,6-(CH_3)_2C_6H_3]\{N=C[C(CH_3)_3]_2\}[P(CH_3)_3]V[\eta^2-CH_2CH-(C_6H_5)]$ (4) in 24.5% isolated yield (Scheme 2). The

Scheme 2. Decomposition of Vanadium(V) Alkylidenes

authors reported that while mechanistic investigations were not performed, bimolecular decomposition was likely at work. Lastly, and with these examples in mind, the observation of fast decomposition in SM but not in ROMP also leads one to consider bimolecular decomposition as the most likely scenario.

In our previous work, the assumption of bimolecular decomposition was challenged upon observing that the reaction of vanadium(V) alkylidenes 1 and 2 with ethylene produced propylene and unidentified paramagnetic vanadium products, as demonstrated by ¹H nuclear magnetic resonance (NMR) spectroscopy (Scheme 2).²⁹ This observation strongly indicated that rather than bimolecular decomposition, β hydride elimination from the metallocyclobutane intermediate C (Scheme 1) was the cause of decomposition. Propylene was also observed in decomposition of both tungsten and molybdenum molecular alkylidenes upon treatment with ethylene, likely via β -hydride elimination from the metallocyclobutane, although the authors in these cases simply referred to the process as rearrangement of the metallocyclobutane. 43,44 Products associated with β -hydride elimination were observed with heterogeneous rhenium, 45 molybdenum, 46 and tungsten alkylidenes as well. 47 In these cases, computations demonstrated low barriers to decomposition in square pyramidal metallocyclobutane intermediates via β hydride elimination. 48 Lastly, propylene generation via β hydride elimination was shown to occur within ruthenium olefin metathesis catalysts upon treatment with ethylene. 49,50

The conflict between the previous report that decomposition of a vanadium(V) alkylidene upon treatment with a terminal olefin occurs through a bimolecular pathway⁴² and our own observations²⁹ led us to examine the decomposition more thoroughly, as knowledge of which decomposition pathway is present and dominant is imperative to guide future catalyst design. Specifically, we sought to isolate and characterize the

paramagnetic vanadium products in order to shed light on the decomposition mechanism, aiming to determine if they are consistent with β -hydride elimination from the metallocyclobutane rather than bimolecular decomposition of the methylidene (Scheme 3) and, if so, what the subsequent

Scheme 3. Possible Decomposition Routes Considered

reactivity of these products are. This latter point is of great importance given computational and empirical evidence that after β -hydride elimination in rhenium, molybdenum, and tungsten metallocyclobutanes, the subsequent hydride species may insert ethylene to form bis(alkyl) compounds, which can then undergo α -hydride abstraction to regenerate alkylidenes, which would be catalytically active (infra).⁴⁸ If reductive elimination of propylene follows β -hydride elimination, however, catalytically inactive vanadium(III) species would be expected. The first vanadium(V) alkylidene was prepared from a vanadium(III) precursor,⁵¹ so one could imagine regeneration of catalytically active species if no further reaction takes place. This would be unlikely, however, given the known instability of coordinatively unsaturated vanadium(III)-imido species. The first stable example of such a compound was reported by Teuben and co-workers, in which a vanadium(III) alkylidene complex bearing the relatively large Cp ligand was treated with tert-butylnitrile, generating the imido ligand. 52 Teuben then reported a more direct synthesis of a similar vanadium(III) imido species, also bearing a Cp ligand.⁵¹ Galindo and co-workers demonstrated the synthesis of a Cpfree vanadium(III) imido complex bearing carbon monoxide (CO) and phosphine ligands; however, decomposition could not be prevented, even when under a CO atmosphere.⁵³ More recently, Bouwkamp reported the generation of a vanadium-(III) imido complex bearing a Cp ligand via thermolysis of a vanadium(V) precursor.54

Herein, we report the results of our investigation into the decomposition of vanadium(V) alkylidenes 1 and [N-2,6- $(CH_3)_2C_6H_3[OC_6F_5)[P(CH_3)_3]_2V[CHSi(CH_3)_3]$ (5) upon treatment with excess ethylene gas. Density functional theory (DFT) calculations indicated that β -hydride elimination is exergonic with low (≤13.4 kcal/mol) thermodynamic barriers to metallocyclobutane formation. Analysis of the organic products indicated that reductive elimination occurs before insertion of ethylene into the newly formed [V]-H bond. Conversions for SM of 1-hexene with 1 are reported and compared to the less electron deficient, more sterically hindered isopropyl-substituted complexes {N-2,6-[CH- $(CH_3)_2 C_6H_3 (OC_6X_5) [P(CH_3)_3]_2 V [CHSi(CH_3)_3] [X = CI$ (6), F (7)], providing additional experimental support for β hydride elimination being the dominant decomposition pathway, rather than bimolecular routes. Reductive elimination and release of propylene yielded the unobserved vanadium(III)

species $[N-2,6-(CH_3)_2C_6H_3](OC_6X_5)V[P(CH_3)_3]_2$ [X = Cl(8), F(9)]. In both cases, oxidation to the isolated and fully characterized vanadium(IV) compounds $[N-2,6-(CH_3)_2C_6H_3](OC_6Cl_5)[P(CH_3)_3]_2VCl$ (10) and $[N-2,6-(CH_3)_2C_6H_3]V(OC_6F_5)_2[P(CH_3)_3]_2$ (11), respectively, (Scheme 4) occurred. Mechanisms for the formation of both species are proposed and supported by DFT calculations.

Scheme 4. Synthesis of Decomposition Products 10 and 11

$$(H_3C)_3P \bigvee_{P(CH_3)_3} Si(CH_3)_3 \qquad \underbrace{C_2H_4 \ (10 \ psi)}_{\text{benzene-d_6, toluene or DCM Yield < 50%}} (H_3C)_3P \bigvee_{P(CH_3)_3} or \ (H_3C)_3P \bigvee_{P(CH_3)_3}$$

■ RESULTS AND DISCUSSION

Isolation of Decomposition Products. In order to determine the identity of the products of decomposition during OM with vanadium catalysts, compound 1 was treated with ethylene in benzene- d_{6i} and the reaction was monitored by ¹H NMR (Scheme 4). Immediately after the addition of ethylene, no vanadium species were observed; however, vinyltrimethylsilane (vinyl-TMS) and propylene were present, as previously reported.²⁹ After removal of the solvent and volatile byproducts products in vacuo, the resulting crude oily material was dissolved in minimal dichloromethane (DCM), layered with pentane, and cooled to 0 °C. Deep red crystals suitable for single crystal X-ray diffraction were obtained, which conclusively demonstrated the paramagnetic product to be the 13 electron, vanadium(IV) chloride complex 10 (Figure 1a).55 Compound 10 is distorted trigonal bipyramidal, with a P1-V1-P2 angle of 171.4(5)°. The sum of all bond angles in the trigonal N-O-Cl plane is 359.8° [N1-V1-O1 100.1(3)°, $N1-V1-O1 \ 109.2(4)^{\circ}$, and $O1-V1-Cl1 \ 150.7(5)^{\circ}$]. The V=N and V-O bond lengths to the imido and aryloxide ligands are longer in 10 than in 1, 1.692(11) Å vs 1.687 Å and

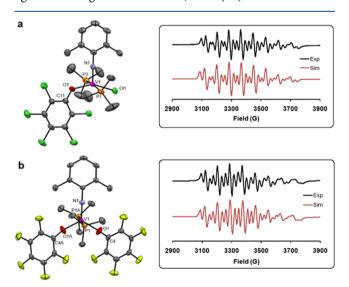


Figure 1. Molecular structures (50% thermal ellipsoids), EPR spectra (black trace, 25 $^{\circ}$ C in toluene, frequency = 8.993584 GHz, power = 2.00 mW, Mod Width = 0.2 mT, time-constant = 0.03 s), and simulated EPR spectra (red trace) for (a) **10** and (b) **11**. Hydrogen atoms have been omitted from structures for sake of clarity.

Scheme 5. \(\theta\)-Hydride Elimination from Vanadium(V) Metallocyclobutanes to Yield Vanadium(III) Complexes

$$(H_3C)_3P = Si(CH_3)_3 = Si(C$$

Figure 2. Free energy profile and mechanism for formation of 10. All values reported in kcal/mol at 25 °C at the B3P86/6-311+G(d) level of theory.

2.044(7) Å vs 1.983 Å, respectively.²⁷ When synthesized on a preparative scale with DCM as the reaction solvent (Scheme 4), **10** was isolated in 33% crystalline yield. The X-band electron paramagnetic resonance (EPR) spectrum of compound **10** recorded at 25 °C in toluene displayed an overall isotropic multiline spectrum due to hyperfine coupling to multiple neighboring nuclei. The simulated EPR spectrum showed $g_{iso} = 1.881$, which is lower than g factor of a free electron ($g_e = 2.0023$) due to spin—orbit coupling as observed for early transition metal complexes (electronic configurations: d^1-d^4).⁵⁶ The hyperfine contributions from five distinct nuclei: $A_{iso}(V) = 218$ MHz, $A_{iso}(N) = 40$ MHz, $A_{iso}(P1$ and P2) = 75 MHz, and $A_{iso}(C1) = 5$ MHz (Figure 1a).⁵⁵

Initially, we presumed that compound **10** formed via abstraction of a chlorine atom from DCM by an unobserved vanadium(III) compound **8**, which resulted from the initial decomposition via β -hydride elimination (Scheme 5). Chlorine abstraction from chlorinated solvents (or other aliphatic chlorides) is not uncommon, and has been observed with copper, ^{57,58} rhenium, ⁵⁹ manganese, ⁵⁹ iron, ^{60–62} silver, ⁶³ cerium, ⁶⁴ and titanium. ⁶⁵ The reaction of **1** with ethylene was repeated in toluene on a preparative scale in the absence of DCM in an attempt to isolate **8**. Compound **10** was isolated again, however, as determined by elemental analysis, in 32% crystalline yield (Scheme 4). This nearly identical yield strongly suggested that the chlorine atom must have originated from the chlorinated aryloxide ligand of another molecule after decomposition, rather than the chlorinated solvent. Chlorine atom abstraction from aryl chlorides is far less common than

from aliphatic chlorides, but has been observed, 60,61,66,67 although not for vanadium.

In order to prevent the undesired chlorine atom abstraction and possibly isolate the proposed vanadium(III) decomposition product, compound 5,25 bearing a fluorinated aryloxide ligand, was prepared and subjected to identical reaction conditions in the absence of DCM (Scheme 4). Rather than the anticipated vanadium(III) product 9 (Scheme 5), the 13 electron, vanadium(IV) bis(aryloxide) complex 11 was produced, as confirmed by single crystal X-ray diffraction (Figure 1b) and elemental analysis, again in <50% crystalline yield. Similar to compound 10, 11 exhibits distorted trigonal bipyramidal geometry, with a P1-V1-P1A angle of 177.09(2)°, and the sum of all angles in the trigonal N-O-O plane is 360.00° [N1-V1-O1 119.53(4)°, N1-V1-O1A $119.53(4)^{\circ}$, O1-V1-O1A $120.94(9)^{\circ}$]. Compound 11 displayed a broad resonance in the ¹H NMR spectrum centered at -5.81 ppm, and one signal in the ¹⁹F NMR spectrum at -167.9 ppm. No resonances were observed by ^{31}P nor ⁵¹V NMR. EPR for compound 11 also displayed an overall isotropic multiline spectrum, with simulations providing g_{iso} = 1.877 ($\langle g_e \rangle$) with hyperfine contributions from four distinct nuclei: $A_{\rm iso}({\rm V})$ = 225 MHz, $A_{\rm iso}({\rm N})$ = 40 MHz, and $A_{\rm iso}({\rm P1}$ and P2) = 74 MHz (Figure 1b). S In order to probe whether exposure to a chlorine atom source would lead to a vanadium(IV) chloride species similar to 10, compound 11 was treated with 2 equiv of DCM. After 12 h at room temperature, no changes were observed by ¹H and ¹⁹F NMR. An EPR spectrum of compound 11 prepared in situ from 5 with DCM as the solvent provided a similar multiline spectrum

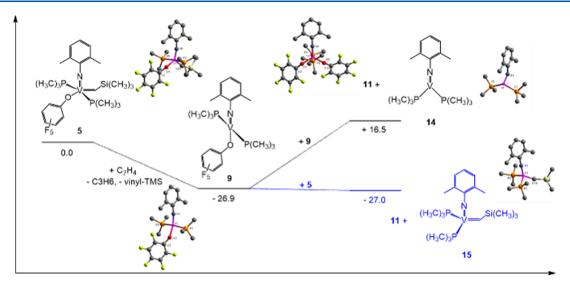


Figure 3. Free energy profile and mechanism for formation of 11. All values reported in kcal/mol at 25 $^{\circ}$ C at the B3P86/6-311+G(d) level of theory.

Scheme 6. Synthesis of Sterically Hindered Vanadium(V) Alkylidenes

to the isolated product, with distinct hyperfine coupling (Figure S20).⁵⁵ When prepared with DCM as the solvent, single crystals of 11 were isolated, and single crystal X-ray diffraction again confirmed its identity.

Mechanisms. With the identity of the decomposition products established, we next sought to determine if they are consistent with β -hydride elimination being the main mode of decomposition. For both compounds 1 and 5, DFT calculations demonstrated that treatment with ethylene generates the expected methylidene species, which then undergo [2 + 2] cycloaddition with another equivalent of ethylene to generate metallocyclobutanes. β -Hydride elimination and reductive elimination then follow to form a coordinated propylene species reminiscent of the styrene complex 4 reported by Nomura, ⁴² followed by release of propylene to generate the vanadium(III) complexes 8 and 9 (Scheme 5, Figure S22 and S23). ⁵⁵

In the proposed vanadium(III) intermediate 8, bearing the chlorinate aryloxide ligand, DFT revealed that coordination of an orthochlorine to vanadium may occur with little energetic cost (1.1 kcal/mol) (Chart S4). This is reminiscent of the ruthenium alkylidene complex bearing a brominated aryloxide ligand $(OC_6Br_5)(IMes)(py)Ru(Cl)[CH(C_6H_5)]$ (IMes = 1,3dimesitylimidazol-2-ylidene, py = pyridine), in which DFT analysis revealed a ruthenium-bromine interaction.⁶⁸ In the case of 8, the chlorine coordination allows for facile oxidative addition to generate the vanadium(V) chloride species 12 (Figure 2). Compound 12 may then act as the source of the chlorine atom observed in the product, 10, via a comproportionation reaction with another equivalent of the vanadium(III) species 8 (Figure 2). The fact that yields of <50% are observed in the preparation of 10 are in agreement with half of the vanadium present serving in a sacrificial

manner to donate a chlorine atom to form the final product. After delivery of the chlorine atom, the vanadium(IV) compound 13 is also proposed to form; however, it was not detected (Figure 2).

In the case of the fluorinated catalyst, no such coordination of a fluorine to the vanadium center after decomposition was found in the proposed intermediate 9. Two possible routes for the generation of 11 from 9 were explored. In the first possibility, reaction occurs between 2 equiv of 9, leading to the observed product 11 and the vanadium(II) complex 14. The second possibility, which is more likely and overall lower in energy, involves the abstraction of an aryloxide ligand from unreacted starting material 5, producing the product 11 and the unobserved vanadium(IV) alkylidene complex 15 (Figure 3). Compound 15 then likely decomposes further, as vanadium(IV) alkylidenes are quite rare, with the only examples reported by Mindiola. These complexes were supported by sterically encumbering β -diketiminate ligands, and decomposed upon gentle heating.⁶⁹ Preferential abstraction of an aryloxide from 5 over 9 was in agreement with the calculated V-OAr bond dissociation free energies calculated as well: 65.8 and 105.7 kcal/mol for 5 and 9, respectively. Again, the yield of <50% is consistent with half of the vanadium species serving in a sacrificial manner.

Taken together, the generation of compounds 10 and 11 with the computationally supported mechanisms provide strong support for β -hydride elimination, followed by reductive elimination of propylene, being the dominant decomposition pathway.

Synthesis of New Catalysts and Relative Conversions in SM. In order to further probe the favored decomposition pathway, compounds 6 and 7 bearing isopropyl groups on the arylimido ligand were prepared. Similar niobium species were

shown by Nomura to polymerize cyclic olefins by ROMP, while Murphy described the synthesis and reactivity of vanadium(V) trialkyl complexes bearing the same arylimido ligand. If β -hydride elimination is the dominant decomposition pathway, as described above, one would expect 6 and 7, bearing the more electron donating arylimido ligand, to decompose more readily, resulting in decreased conversion during SM relative to methyl-substituted 1, which we have previously disclosed as a catalyst for the SM of various terminal olefins. If, however, bimolecular decomposition occurred, higher conversions would be expected for 6 and 7, given the increased steric bulk.

Compounds 6 and 7 were prepared from the vanadium(V) trichloride complex 16^{72} as summarized in Scheme 6, following well-established procedures. The molecular structures determined by single crystal X-ray diffraction are depicted in Figure 4. Compound 6 is distorted trigonal

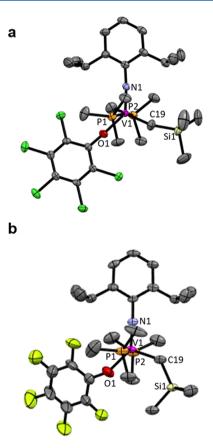


Figure 4. Molecular structures (50% thermal ellipsoids) for (a) 6 (chlorinated aryloxide) and (b) 7 (fluorinated aryloxide). Hydrogen atoms have been omitted from structures for sake of clarity.

bipyramidal with a P1–V1–P2 bond angle of 168.92(3)°, similar to 168.66(4)° in 1.²⁷ The trigonal O–N–C plane has a sum of all bond angles totaling 359.67° [N1–V1–C19 111.30(12)°, N1–V1–O1 133.37(15)°, and O1–V1–C19 115.0(2)°], again nearly identical with those in 1.²⁷ The *syn* isomer for the alkylidene is observed in the solid state structure, and is the dominant species in solution (95% by ¹H NMR).⁵⁵ For 7, the structural features are rather similar to those in 6; however, the *anti* isomer is observed for the alkylidene ligand. In solution, the *anti* isomer is dominant (70% by ¹H NMR).⁵⁵ The structure for the analogous 2,6-

dimethylaryl imido species $[N-2,6-(CH_3)_2C_6H_3](OC_6F_5)[P-(CH_3)_3]_2V[CHSi(CH_3)_3]^{25}$ has not been reported, so no comparisons may be made at this time.

SM with 1-hexene was performed under identical conditions with compounds 1, 6, and 7, as summarized in Scheme 7. The

Scheme 7. Self-Metathesis of 1-Hexene with Vanadium(V) Alkylidenes

C₃H₇

$$\begin{array}{c} \text{catalyst (5 mol \%)} \\ \text{benzene-}d_6, \text{ 25 °C} \\ \text{- C2H4} \end{array}$$

Table 1. Self-Metathesis of 1-Hexene Using Catalysts 1, 6, and 7^a

entry	catalyst	conversion (%) ^b
1	1	15.6
2	6	13.0
3	7	9.1

^aAll runs performed with 5 mol % catalyst in a J. Young NMR tube equipped with a Teflon seal at 25 °C. [Catalyst]₀ = 10.1 mM, [1-hexene]₀ = 199.9 mM. ^bDetermined by 1 H NMR analysis, average of two separate experiments.

conversions determined by ¹H NMR are reported in Table 1. Conversions are not high, and are not meant to imply that these catalysts may be effectively used for SM in synthetic procedures. Rather, their relative values help shed light on the decomposition pathway. In this way, these values may be viewed as a proxy for rate of decomposition, which occurs too quickly to measure through standard means. Complex 1, bearing the less electron-donating and less sterically hindered dimethyl arylimido ligand, showed higher conversion than complex 6, containing the more electron-donating and more sterically demanding isopropyl-substituted imido ligand. Both species are identical aside from this difference. Complex 7, in which a fluorinated aryloxide is employed, demonstrated the lowest conversion. One may initially predict that 7 would provide conversions higher than the chlorinated analogue 6, given the fact that the fluorinated aryloxide should be more electron-withdrawing. In comparing the solid state structures of these species, however, it is apparent that the increased bulk of the chlorine atoms of the aryloxide in 6 result in a longer V-O bond length than in 7 [1.969(4) Å and 1.949(4) Å, respectively]. This decreases the amount of π -donation from the aryloxide in 6 relative to 7, a trend that has been observed in other vanadium alkylidenes bearing this chlorinated aryloxide ligand,²⁷ making it less electron-donating. Overall, faster decomposition (and therefore lower conversions) was observed as the ligands became more electron-donating and sterically demanding, providing evidence that β -hydride elimination is the dominant decomposition pathway, rather than bimolecular decomposition.

Analysis of Organic Decomposition Products. On the basis of reports for the treatment of OM catalysts based on rhenium, molybdenum, and tungsten with ethylene, in which 1-butene and 2-butene are observed along with propylene, ⁴⁸ it is worthwhile to consider similar reactions in the present system. The dominant decomposition path is clearly the one depicted in Scheme 5, as evidenced by propylene being the

Scheme 8. Possible Reaction Pathways after β -Hydride Elimination

$$(H_3C)_3P$$

$$P(CH_3)_3$$

$$A-Hydride Abstr$$

$$C_3H_6$$

$$A-Hydride Abstr$$

$$C_3H_6$$

$$A-Hydride Abstr$$

$$C_3H_6$$

$$C_1H_3C)_3P$$

$$C_2H_4$$

$$C_2H_4$$

$$C_2H_4$$

$$C_2H_4$$

$$C_1H_3C)_3P$$

$$C_1H_3C)_3P$$

$$C_1H_3C)_3P$$

$$C_1H_3C)_3P$$

$$C_1H_3C)_3P$$

$$C_2H_4$$

$$C_1H_3C)_3P$$

$$C_$$

major organic product by ¹H NMR. The other possible routes reminiscent of those reported for rhenium, molybdenum, and tungsten, are illustrated in Scheme 8. In these reactions, insertion of ethylene into the newly formed [V]-H bond after β -hydride elimination but before reductive elimination of propylene leads to an ethyl complex, [V](C2H5)(CH2CH= CH_2), which may undergo α -hydrogen abstraction by the propenyl ligand, generating a new ethylidene complex. This ethylidene may reenter productive catalysis, or also decompose via β -hydride elimination after addition of another equivalent of ethylene, yielding 2-butene. On the other hand, another insertion of ethylene may occur, followed by another α hydrogen abstraction to yield 1-butene or 2-butene. In order to determine if such decomposition paths were at all present in SM with vanadium, the gaseous reaction products of catalyst 1 with ethylene were examined by gas chromatography with flame-ionization detection (GC-FID). Propylene was observed; however, no other gaseous organic products (e.g., 1butene and 2-butene) were detected, indicating that insertion of ethylene into the [V]-H bond does not occur. Rather, reductive elimination and release of propylene is the exclusive decomposition route.

CONCLUSION

We demonstrated previously that vanadium(V) alkylidenes are capable of catalyzing SM; however, decomposition prevented complete conversion. In this work, we provided additional thorough evidence that the primary mode of decomposition is β -hydride elimination from the metallocyclobutane intermediate, rather than bimolecular routes as was previously reported. This was accomplished computationally, and through the isolation of the downstream vanadium products, which form via bimolecular routes after decomposition by β -

hydride elimination. Similar decomposition is likely not observed in ROMP²³ given that cycloreversion of the metallocyclobutane to generate a new alkylidene is highly favored over β -hydride elimination, given that cycloreversion involves the release of ring-strain in the cyclic monomer. More systematic investigations into the possibility of β -hydride elimination in ROMP with vanadium alkylidenes are warranted, and will be investigated in subsequent work by our group. Insertion of ethylene into the newly formed [V]-H bond after β -hydride elimination is not competitive with reductive elimination of propylene, as evidenced by the absence of butenes in the product mixture. Lastly, SM of 1hexene with three catalysts of varying sterics and electronics demonstrated that bulkier and more electron-donating ligands result in decreases in conversion, which strongly indicated that β -hydride elimination is the dominant decomposition pathway. Therefore, in order to effectively employ vanadium in OM beyond ROMP, catalysts more immune to β -hydride elimination must be prepared and/or employed. Possible candidates for such compounds should be increasingly electron-poor relative to the species employed in this study. Some potential compounds have recently been described in the literature, such as $[N-2,6-Cl_2C_6H_3](OC_6Cl_5)[P(CH_3)_3]_2V$ $[CHSi(CH_3)_3]^{27}$ $[N-C_6F_5](OC_6F_5)[P(CH_3)_3]_2V[CHSi (CH_3)_3$], and $[N-C_6F_5](OC_6Cl_5)[P(CH_3)_3]_2V[CHSi-(CH_3)_3].$ ⁸⁷ These compounds have shown incredibly high activities in ROMP of low ring-strain cyclic olefins due to their electron-poor nature. Decreasing π -donation from the aryloxide ligand through the use of more sterically demanding aryloxides may also be useful in this regard. Previously, the preparation of vanadium compounds bearing large aryloxides was found to be quite challenging; 88 however, recent work with niobium has illuminated new pathways that may be useful in

generating these species.⁸⁹ The synthesis and activity of such compounds is beyond the scope of this work, which sought solely to firmly establish the dominant decomposition pathway. However, we are currently investigating such species, which will be reported in due course in their own dedicated study.

■ EXPERIMENTAL SECTION

General Methods. All air and moisture sensitive manipulations were carried out under nitrogen using standard glovebox or Schlenkline techniques. Pentane and toluene were distilled under nitrogen from sodium/benzophenone. Dichloromethane (DCM) was distilled from calcium hydride under nitrogen. Benzene-d₆ and 1-hexene were stirred over sodium/potassium alloy, degassed, and isolated by transfer under static vacuum. Ethylene (>99.5%) was purchased from Sigma-Aldrich and used as received. Celite was oven-dried for several days before use in the glovebox. Compounds $1,^{27}$ $5,^{25}$ and 16^{72} were prepared as described in the literature. All other reagents were used as received. Elemental analyses were performed by Midwest Microlab, LLC. Nuclear magnetic resonance (NMR) spectroscopy was performed using a JEOL 400 MHz spectrometer. ¹H NMR spectra were referenced to the residual solvent signal (7.16 ppm for benzened₆). ¹³C NMR spectra were referenced to the residual solvent signal (128.1 ppm for benzene- d_6). ¹⁹F and ⁵¹V NMR spectra were referenced to hexafluorobenzene (-164.9 ppm) and VOCl₃ (0.00 ppm), respectively. Electron paramagnetic resonance (EPR) spectra were recorded using a JEOL continuous wave spectrometer JES-FA200 equipped with a cylindrical mode cavity having X-band Gunn oscillator bridge. Experiments were performed at 298 K. Freshly prepared solutions (0.5-2 mM in toluene) were used to measure EPR spectra, except where noted otherwise. Overall the instrument features for spectral measurements for compounds 1 and 2 were: Frequency = 8.993584 GHz, power = 2.00 mW, Mod Width = 0.2 mT, timeconstant = 0.03 s. Pure toluene was used to measure background spectra at the same measurement conditions. Spectral simulations were carried out using QCMP 136 program by Prof. Dr. Frank Neese from the Quantum Chemistry Program Exchange as used by Neese et al. 73 The "chi by eye" approach was used for fitting using collinear g and A tensors (see Figure S19). CG-FID was performed on a Shimadzu GC-2010 Plus Gas Chromatograph instrument with a Restek Rt-Alumina BOND/Na₂SO₄, 30 m, 0.32 mmID column (Cat# 19757), with flame-ionization detection. The temperature was held constant at 130 °C, and a flow rate of 51 cm/s was used. The injection and detector temperatures were held constant at 200 °C. Retention times were compared to quality assurance reports provided by Restek.

Synthesis of [N-2,6-(CH₃)₂C₆H₃](OC₆Cl̄₅)[P(CH₃)₃]₂VCl (10) in Toluene. Compound 1 (0.1045 g, 0.1678 mmol) was dissolved in 3.0 mL toluene in a J. Young NMR tube equipped with a Teflon seal ([1] = 56 mM). The headspace was evacuated and charged with ethylene (10 psi). The tube was sealed and agitated for 10 min, at which point the contents were transferred to a vial, and volatiles were removed in vacuo. ¹H NMR revealed the presence of 1. The crude material was redissolved in 3.0 mL toluene, and treated with ethylene again in the same fashion, before again removing volatiles in vacuo. The resulting red oil was dissolved in minimal toluene and filtered through Celite/Kimwipe in a pipet. The solution was concentrated, layered with pentane, and cooled to -30 °C, furnishing 10 as a deep red crystalline material (0.0332 g, yield = 34%). For 10: Anal. Calcd for VNOP₂Cl₆C₂₀H₂₇: C, 38.56; H, 4.37; N, 2.25. Found: C, 38.24; H, 4.37; N,2.03. EPR: See Figure S19.

Synthesis of 10 in DCM. Compound 1 (0.0502 g, 0.0745 mmol) was dissolved in 1.0 mL DCM in a J. Young NMR tube equipped with a Teflon seal ([1] = 75 mM). The headspace was evacuated and charged with ethylene (10 psi). The tube was sealed and agitated for 30 min, at which point the contents were transferred to a vial, and volatiles were removed in vacuo. The resulting red oil was dissolved in minimal toluene layered with pentane, and cooled to -30 °C, furnishing 10 as a deep red crystalline material (0.0154 g, yield = 33%).

Synthesis of $[N-2,6-(CH_3)_2C_6H_3]V(OC_6F_5)_2[P(CH_3)_3]_2$ (11) in **Toluene.** Compound 5 (0.1266 g, 0.2144 mmol) was dissolved in 4.0 mL toluene and distributed across two J. Young NMR tubes equipped with Teflon seals ([5] = 54 mM). The headspaces were evacuated and charged with ethylene (10 psi). The tubes were sealed and agitated for 10 min, at which point the contents were transferred to a vial, and volatiles were removed in vacuo. ¹H NMR revealed the presence of 5. The crude material was redissolved in 4.0 mL toluene, and treated with ethylene again in the same fashion, before again removing volatiles in vacuo. The resulting material was dissolved in minimal toluene and filtered through Celite/Kimwipe in a pipet. Volatiles were removed in vacuo, and then dissolved in minimal toluene, layered with pentane, and cooled to −30 °C, furnishing 11 as a bright red crystalline material (0.0612 g, yield = 42%). For 11: Anal. Calcd for VNO₂P₂F₁₀C₂₆H₂₇: C, 45.36; H, 3.95; N, 2.03. Found: C, 45.11; H, 3.92; N, 2.08. 1 H (400 MHz, benzene- d_{6} , 25 $^{\circ}$ C) NMR -5.18 (br). 19 F (376.5 MHz, benzene- d_{6} , 25 °C) NMR –169.6. EPR: See Figure

Synthesis of $[N-2,6-(CH_3)_2C_6H_3]V(OC_6F_5)_2[P(CH_3)_3]_2$ (11) in DCM for XRD Analysis. Compound 5 (0.0196 g, 0.0332 mmol) was dissolved in 1.0 mL DCM in a J. Young NMR tube equipped with a Teflon seal ([5] = 33 mM). The headspace was evacuated and charged with ethylene (10 psi). The tube was sealed and agitated for 20 min, at which point the contents were transferred to a vial, and volatiles were removed in vacuo. The crude material was redissolved in minimal DCM, layered with pentane, and cooled to $-30\,^{\circ}$ C, furnishing single crystals which were analyzed by XRD, confirming the identity as compound 11.

Synthesis of {N-2,6-[CH(CH₃)₂]₂C₆H₃}V[CH₂Si(CH₃)₃]₃ (17). Compound 16 (2.0781 g, 6.248 mmol) was dissolved in 100 mL n-hexane and cooled to -30 °C, at which point 1.0 M LiCH₂Si(CH₃)₃ in hexane (19.0 mL, 19.0 mmol) was added dropwise. After addition was complete, the flask was sealed, allowed to warm to room temperature, and stirred overnight (13 h). The resulting solution was filtered through Celite, and volatiles were removed in vacuo to yield a reddish-brown oil (2.8669 g, yield = 94%). Freshly prepared 17 was used as the precursor for the synthesis of the alkylidenes described below. 1 H (400 MHz, benzene- d_6 , 25 °C) NMR 7.11 (d, 2H, J = 8.0 Hz), 7.00 (t, 1H, J = 8.0 Hz), 4.46 (sp, 2H, J = 7.2 Hz), 1.97 (br, 6H), 1.38 (d, 12H, J = 6.8 Hz), 0.17 (s, 27H). 51 V (105 MHz, benzene- d_6 , 25 °C) NMR 1074.15.

Synthesis of {N-2,6-[CH(CH₃)₂]₂C₆H₃}(OC₆Cl₅)[P(CH₃)₃]₂V [CHSi(CH₃)₃] (6). Compound 17 (1.3743 g, 2.817 mmol) was dissolved in 100 mL n-hexane and cooled to -30 °C, at which point pentachlorophenol (0.7796 g, 2.927 mmol) was added as a suspension in 10 mL n-hexane. The flask was sealed, and the reaction was allowed to warm to room temperature and stir overnight (14.5 h). Volatiles were removed in vacuo, yielding the dialkyl species 18 as a brownish-red oil (1.7425 g, yield = 93%) which was identified by its diagnostic ⁵¹V chemical shift.²⁷ ⁵¹V (105 MHz, benzene- d_6 , 25 °C) NMR 669.24. 18 was used in the next step without further purification.

Compound **18** (1.7425 g, 2.616 mmol) was dissolved in 100 mL nhexane and cooled to -30 °C, at which point trimethylphosphine (800 μ L, 7.865 mmol) was added dropwise. The flask was sealed, and the solution was warmed to room temperature and stirred overnight (14 h), at which point an orange precipitate was visible. The solution was filtered through Celite with n-hexane until the filtrate was clear. Volatiles were removed in vacuo, and the resulting reddish-orange solid was cooled to -30 °C in excess pentane. The red supernatant was removed, and additional pentane was added and cooled again. Removal of the red supernatant again yielded alkylidene 6 as an orange crystalline solid (0.6776 g, yield = 35%). For 6: Anal. Calcd for VSiP₂ONCl₅H₄₅C₂₈: C, 46.08; H, 6.21; N, 1.92. Found: C, 46.27; H, 5.98; N, 1.87. ¹H (400 MHz, benzene-d₆, 25 °C) NMR 16.60, 15.49 (br, 1H), 7.08 (m, 2H), 6.93 (t, 1H, J = 6.8 Hz), 4.84 (sp, 2H, J = 6.8Hz), 1.36 (d, 12H, J = 6.8), 0.78 (s, 18H), 0.23 (s, 9H). ¹³C (100 MHz, benzene- d_6 , 25 °C) NMR 146.8, 131.3, 131.1, 124.8, 123.1, 122.4, 121.9, 118.3, 27.2, 25.3, 15.4, 2.2. ⁵¹V (105 MHz, benzene- d_6)

25 °C) NMR 36.58, -130.29 (t, ${}^{1}J_{\rm VP} = 285$ Hz). ${}^{31}{\rm P}$ (162 MHz, benzene- d_6 , 25 °C) NMR -8.08 (oct, ${}^{1}J_{\rm VP} = 293$ Hz). Synthesis of {N-2,6-[CH(CH₃)₂]₂C₆H₃}](OC₆F₅)[P(CH₃)₃]₂V

Synthesis of $\{N-2,6-[CH(CH_3)_2]_2C_6H_3\}\}[OC_6F_5][P(CH_3)_3]_2V$ [CHSi(CH₃)₃] (7). Compound 17 (1.4680 g, 3.009 mmol) was dissolved in 100 mL *n*-hexane and cooled to -30 °C, at which point pentafluorophenol (0.5841 g, 3.173 mmol) was added as a suspension in 10 mL *n*-hexane. The flask was sealed, and the reaction was allowed to warm to room temperature and stir overnight (19.5 h). Volatiles were removed in vacuo, yielding the dialkyl species 19 as a brown oil (1.7481 g, yield = 99%) which was identified by its diagnostic ⁵¹V chemical shift.²⁵ ⁵¹V (105 MHz, benzene- d_6 , 25 °C) NMR 667.45. 19 was used in the next step without further purification.

Compound 19 (1.7041 g, 2.920 mmol) was dissolved in 100 mL nhexane and cooled to -30 °C, at which point trimethylphosphine (900 μ L, 8.849 mmol) was added dropwise. The flask was sealed, and the solution was warmed to room temperature and stirred overnight (12 h). The solution was filtered through Celite with n-hexane until the filtrate was clear. Volatiles were removed in vacuo, and the resulting orange solid and brown oil was cooled to −30 °C in excess pentane. The red supernatant was removed, and additional pentane was added and cooled again. This process was repeated three times, yielding alkylidene 7 as an orange crystalline solid (1.0531 g, yield = 56%). For 7: Anal. Calcd for VSiP₂ONF₅H₄₅C₂₈: C, 51.93; H, 7.00; N, 2.16. Found: C, 52.19; H, 6.77; N, 2.41. The ¹H NMR spectrum exhibited broad resonances for the isopropyl groups for one of the isomers. Both are reported. See Figure \$10 and \$11. 1H (400 MHz, benzene-d₆, 25 °C) NMR 16.42, 15.31 (br. 1H), 7.10 (m, 2H), 6.95 (m, 1H), [5.44 (br), 4.67 (sp, J = 6.4 Hz), 4.373 (br), total = 2H],[1.42 (br), 1.39 (d, J = 6.8 Hz), total = 12H], 0.78 (s, 18H), 0.39,0.26 (s, 9H). ¹³C (100 MHz, benzene-d₆, 25 °C) NMR 147.6, 146.6, 141.3, 140.7, 140.2, 139.0, 138.3, 137.7, 132.7, 130.4, 124.7, 123.1, 123.0, 27.5, 25.1, 24.7, 15.5, 15.2, 2.4, 2.3. ¹⁹F (376 MHz, benzene-d₆, 25 °C) NMR -166.9 (dd), -168.0 (dd), 169.2 (m), -180.1 (m), -180.4 (m). ⁵¹V (105 MHz, benzene- d_6 , 25 °C) NMR -2.87, -87.56(t, ${}^{1}J_{\rm VP}$ = 275 Hz). ${}^{31}{\rm P}$ (162 MHz, benzene- d_{6} , 25 °C) NMR -8.88 (oct, ${}^{1}J_{VP} = 279 \text{ Hz}$).

Computational Details. The Gaussian 16 suite of programs was used for all optimizations and frequency calculations. Visualization and structure analyses were done using CCDC-Mercury.⁷⁴ The B3P86 functional 75 with the 6-311+G(d) basis set $^{76-82}$ was used for all the optimization of geometries and frequency calculations.83the B3P86/6-311+G(d) stationary points, single point energies were ^{7-82,85} basis set, in calculated using B3P86 with the 6-311++G(d,p)⁷⁷ benzene or acetonitrile using the PCM⁸⁶ solvent model. Four small molecules (ethylene, propene, ·OC₆F₅, and vinyl-TMS) and six complexes $\{(OC_6Cl_5)[V](CH-TMS), (OC_6Cl_5)[V](Cl), (OC_6F_5)-$ [V](CH-TMS), $(OC_6F_5)_2[V]$, [V](CH-TMS), and [V], where [V] = $[N-2,6-(CH_3)_2C_6H_3][P(CH_3)_3]_2V$ were calculated to analyze thermodynamics of the reaction mechanism. Two isomers were calculated for six of the complexes {(OC6Cl5)[V](CH2), ((OC6F5)- $[V](CH_2)$, $(OC_6Cl_5)[V](CH_2-CH_2-CH_2)$, $(OC_6F_5)[V](CH_2-CH_2)$ CH2-CH2), (OC6Cl4)[V], and (OC6Cl4)[V]Cl}. Four isomers were calculated for three of the complexes {(OC6Cl5)[V](CH2- $CH-CH_3$), $(OC_6F_5)[V](CH_2-CH-CH_3)$, and $(OC_6F_5)[V]$ }. Five isomers were calculated for complex (OC₆Cl₅)[V]

SM Reactions. A general procedure is provided. 0.60 mL of a 10.1 mM stock solution of compound 6 (6.1 μ mol) was transferred to a J. Young tube equipped with a Teflon seal by syringe. 1-Hexene (15.0 μ L, 0.120 mmol) was added via syringe, and the tube was quickly sealed and immediately shaken. ¹H NMR was recorded after 15 min, demonstrating complete decomposition of 6. Conversion was determined by comparing the integrals of the CH₂ olefinic proton resonances of 1-hexene to the CH olefinic resonances of the target homocoupled product (E and E).

GC-FID Analysis of Organic Products from Decomposition by Reaction with Ethylene. Compound 1 (0.0293 g, 43.5 μ mol) was dissolved in 0.6 mL benzene- d_6 in a J. Young NMR tube equipped with a Teflon seal. The headspace was evacuated, and charged with ethylene (10 psi), and agitated. ¹H NMR confirmed the complete decomposition of 1. The Teflon seal was replaced quickly with a

rubber septum. An aliquot (25 μ L) of the headspace was removed with a syringe and injected in the GC-FID for analysis.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00610.

Computational data and structures, crystallographic data, and supporting spectra and chromatogram (PDF)

Accession Codes

CCDC 2013007–2013008 and 2026031–2026032 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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