Syntheses of Molybdenum Oxo Benzylidene Complexes

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S Supporting Information

ABSTRACT: The reaction between $Mo(O)(CHAr_o)$-$(OR_{F6})_2(PMe_3)$ (Ar_o = *ortho*-methoxyphenyl, OR_{F6} = $OCMe(CF_3)_2$) and 2 equiv of LiOHMT (OHMT = O-2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3) leads to $Mo(O)(CHAr_o)$-$(OHMT)_2$, an X-ray structure of which shows it to be a trigonal bipyramidal *anti* benzylidene complex in which the *o*-methoxy oxygen is coordinated to the metal *trans* to the apical oxo ligand. Addition of 1 equiv of water (in THF) to the benzylidyne complex, $Mo(CAr_p)$-$(OR)_3(THF)_2$ (Ar_p = *para*-methoxyphenyl, OR = OR_{F6} or $OC(CF_3)_3$ (OR_{F9})) leads to formation of $\{Mo(CAr_p)$-$(OR)_2(\mu\text{-}OH)(THF)\}_2(\mu\text{-}THF)$ complexes. Addition of 1 equiv of a phosphine (L) to $Mo(CAr_p)(OR_{F9})_3(THF)_2$ in THF, followed by addition of 1 equiv of water, all at room temperature, yields $Mo(O)(CHAr_p)(OR_{F9})_2(L)$ complexes in good yields for several phosphines (e.g., PMe_2Ph (69% by NMR), $PMePh_2$ (59%), PEt_3 (69%), or $P(i\text{-}Pr)_3$ (65%)). The reaction between $Mo(O)(CHAr_p)$-$(OR_{F9})_2(PEt_3)$ and 2 equiv of LiOHMT proceeds smoothly at 90 °C in toluene to give $Mo(O)(CHAr_p)$-$(OHMT)_2$, a four-coordinate *syn* alkylidene complex. $Mo(O)(CHAr_p)(OHMT)_2$ reacts with ethylene (1 atm in C_6D_6) to give (in solution) a mixture of $Mo(O)(CHAr_p)$-$(OHMT)_2$, $Mo(O)(CH_2)(OHMT)_2$, and an unsubstituted square pyramidal metallacyclobutane complex, $Mo(O)(CH_2CH_2CH_2)(OHMT)_2$, along with ethylene and $Ar_pCH{=}CH_2$. $Mo(O)(CHAr_p)(OHMT)_2$ also reacts with 2,3-dicarbomethoxynorbornadiene to yield *syn* and *anti* isomers of the "first-insertion" products that contain a *cis* C=C bond.

The neopentylidyne ligand in $(t\text{-}BuCH_2)_3M{\equiv}C\text{-}t\text{-}Bu$ (M = W[1] or Mo[2]) complexes is formed through what amounts to an intramolecular deprotonation of an α carbon atom in one alkyl ligand by another in some multialkyl intermediate to give an alkylidene first,[3] followed by a second (more facile) α deprotonation of that alkylidene by an alkyl to give the alkylidyne.[4] Synthesis of M(C-t-Bu)(1,2-dimethoxy-ethane)Cl_3 and M(C-t-Bu)(OR)_3 complexes (OR is a sterically demanding alkoxide or aryloxide) and the demonstration that the latter are initiators for catalytic *alkyne* metathesis[5] led to the development of four-coordinate *alkene* metathesis initiators of the type M(NR′)(CHR″)(OR)_2 (M = Mo or W).[6,7] Synthetic routes to imido alkylidene complexes of Mo and W are based on a single α hydrogen abstraction/deprotonation

reaction in a dineopentyl or dineophyl complex.[8] Syntheses of oxo alkylidenes, which have been proposed to be the type of alkene metathesis catalysts present in "classical" heterogeneous catalyst systems,[9] by analogous methods have been more challenging. Tungsten oxo alkylidene complexes were prepared through α hydrogen abstraction in tungsten dialkyls in 2012,[10] but syntheses of molybdenum oxo alkylidene complexes that are active for metathesis of olefins have remained elusive.[11] Recently we began to explore the synthesis of Mo oxo alkylidene complexes through addition of water to alkylidyne complexes.[7,12]

Addition of 1 equiv of water to $Mo(CAr_o)(OR_{F6})_3(dme)$ (Ar_o = *ortho*-methoxyphenyl) gives the dimeric benzylidyne hydroxo complex, $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}dme)$, in which each bridging hydroxo proton is hydrogen-bonded to the *ortho* methoxy oxygen in the *o*-methoxybenzylidyne ligand. (This is a rare example of a controlled hydrolysis of a high oxidation state alkylidene or alkylidyne.[13,14]) Addition of PMe_3 to $\{Mo(CAr_o)(OR_{F6})_2(\mu\text{-}OH)\}_2(\mu\text{-}dme)$ led to formation of $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$, from which $Mo(O)$-$(CHAr_o)Cl_2(PMe_3)$ and $Mo(O)(CHAr_o)(OHIPT)Cl(PMe_3)$ (OHIPT = O-2,6-(2,4,6-i-Pr_3C_6H_2)_2C_6H_3[15]) were prepared. In the presence of $B(C_6F_5)_3$, $Mo(O)(CHAr_o)(OHIPT)Cl$-(PMe_3) was shown to be active for the stereoselective ring-opening metathesis polymerization of 2,3-dicarbomethoxy-norbornadiene (DCMNBD) and *rac*-2,3-dicarbomethoxy-5-norbornene (DCMNBE), and the homocoupling of 1-decene to 9-octadecene, consistent with analogous reactions that use tungsten-based initiators[16] and with removal of PMe_3 to form active metathesis initiators. Important questions are whether an *ortho*-methoxy group in the benzylidyne and benzylidene ligands is required for a controlled reaction involving water and an alkylidyne complex and whether phosphine-free complexes that are active for olefin metathesis can be prepared and isolated. Some answers to these questions are provided in this communication.

The synthesis and stability of $W(O)(CH\text{-}t\text{-}Bu)(OHMT)_2$ (OHMT = O-2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3 or hexamethyl-terphenoxide[17])[10a] suggested that the phosphine-free target should be $Mo(O)(CHAr_o)(OHMT)_2$ (**1-Ar_o**); it was prepared from $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$ as shown in eq 1. Trimethylphosphine is lost in the process as a consequence of steric hindrance overall in combination with binding of the methoxide oxygen in the Ar_o group in the *anti* alkylidene to the

$$\text{(1)}$$

1-Ar$_o$; 37%
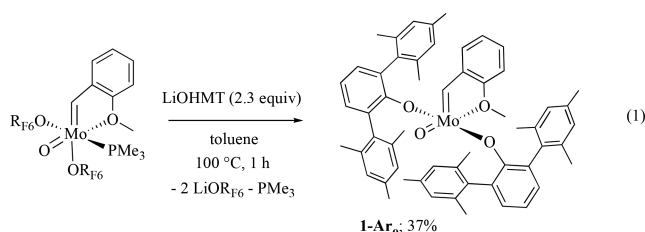
metal *trans* to the oxo ligand, as shown through an X-ray study (Figure 1; see SI). The τ value[18] (0.78) suggests that the
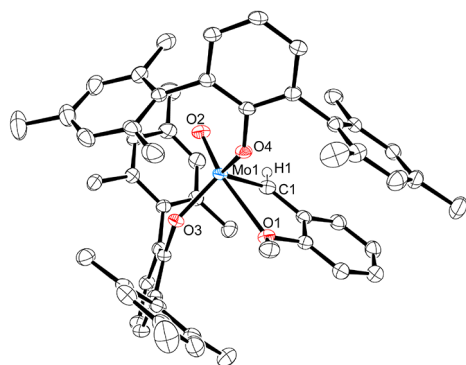

Figure 1. A drawing of the structure of **1-Ar$_o$**; Mo1−C1 = 1.933(2) Å, Mo1−O2 = 1.6698(14) Å, Mo1−O1 = 2.4865(17) Å, Mo1−O3 = 1.915(2) Å, Mo1−O4 = 1.9295(15) Å.

configuration at the metal is closest to a trigonal bipyramid (O2−Mo1−O1 = 166.27(7)°). Alkylidene proton resonances were observed in the initial proton NMR spectrum of **1-Ar$_o$** at 11.92 ppm for the *anti* isomer (97%, J_{CH} = 156 Hz), the isomer found in the solid state (Figure 1), and at 12.02 ppm for the *syn* isomer (J_{CH} = 134 Hz), in which the alkylidene has rotated[19] by 180° and the methoxide is not bound to the metal. After 1 h at 50 °C an 85:15 equilibrium ratio of *anti* to *syn* isomers was observed.

Preliminary studies showed that the rate of reaction of **1-Ar$_o$** with ethylene is slow, perhaps because the lower energy "methoxy-bound" *anti* form only slowly converts to the more reactive *syn* form. We therefore turned to a synthesis of the *p*-methoxybenzylidene analog where intramolecular binding of the methoxy oxygen is not possible.

The *para*-methoxybenzylidyne complex, Mo(CAr$_p$)(dme)-Br$_3$, was prepared by the "low oxidation state" procedure.[20] From it Mo(CAr$_p$)(OR$_{F6}$)$_3$(dme)[21] and Mo(CAr$_p$)-(OR$_{F6}$)$_3$(THF)$_2$[22] were prepared without complications. Addition of 1 equiv of water (in THF, diethyl ether, or dichloromethane) to Mo(CAr$_p$)(OR$_{F6}$)$_3$(THF)$_2$ led to the formation of {Mo(CAr$_p$)(OR$_{F6}$)$_2$(μ-OH)}$_2$(THF)$_3$ (**2-Ar$_p$F$_6$**) in good yield (eq 2). It was crystallized from a mixture of

$$\text{(2)}$$

2-Ar$_p$F$_6$; 70% yield (isolated)
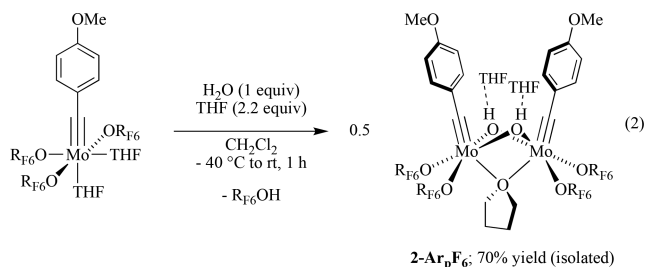
pentane and CH$_2$Cl$_2$ at −40 °C in the presence of several equivalents of THF and isolated in 70% yield as pale red crystals. Similar reactions starting with Mo(CAr$_p$)-(OR$_{F6}$)$_3$(dme) and 1 equiv of water (in THF) also led to **2-Ar$_p$F$_6$**, but in poor yield (~10%), while addition of water in dme to Mo(CAr$_p$)(OR$_{F6}$)$_3$(dme) did not lead to an isolable benzylidyne hydroxo complex. Dme appears to be detrimental and THF beneficial for formation of benzylidyne hydroxo complexes in these circumstances.

An X-ray study of **2-Ar$_p$F$_6$** (Figure 2) shows its structure to be analogous to that of previously reported[12] {Mo(CAr$_o$)-
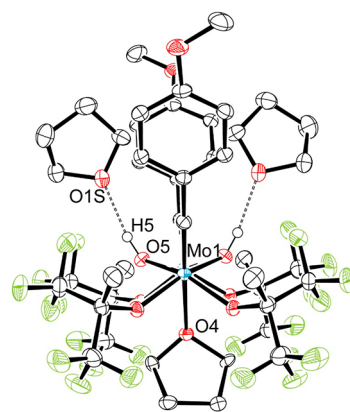

Figure 2. End view of the structure of **2-Ar$_p$F$_6$**.

(OR$_{F6}$)$_2$(μ-OH)}$_2$(μ-dme) with one of the THFs bridging the two Mo centers and one THF hydrogen bonded to each of the two bridging hydroxos. The OH···O angles and O···O distances are consistent with a "classical" hydrogen bond between the bridging hydroxo protons and THF oxygens.[23] The hydroxo proton resonance in **2-Ar$_p$F$_6$** is found at 6.60 ppm in the proton NMR spectrum in CD$_2$Cl$_2$ (cf. 9.30 ppm for the hydroxo protons in {Mo(CAr$_o$)(OR$_{F6}$)$_2$(μ-OH)}$_2$(μ-dme)). The Mo−O distance to the bridging THF is 2.485(2) Å. The Mo−C−C$_{ipso}$ angles are 179.4(2)°, in contrast to 168.57(7)° and 167.33(7)° in {Mo(CAr$_o$)-(OR$_{F6}$)$_2$(μ-OH)}$_2$(μ-dme), which result from the hydroxo protons being hydrogen bonded to the *o*-methoxy oxygens in the Ar$_o$ group instead of to THF, as found in **2-Ar$_p$F$_6$**. Other distances and angles are not unusual (see SI). In solution, proton NMR resonances for the bridging THF are distinct from those for the hydrogen-bonded THFs or THF in solution. The hydrogen-bonded THFs are readily lost from solid samples, especially *in vacuo*, to give {Mo(CAr$_p$)(OR$_{F6}$)$_2$-(μ-OH)}$_2$(μ-THF), and exchange rapidly on the NMR scale with free THF in solution, as shown through proton NMR studies. Addition of dioxane to an NMR sample of {Mo-(CAr$_p$)(OR$_{F6}$)$_2$(μ-OH)}$_2$(μ-THF) led to formation of a mixture of the μ-THF (δ_{OH} at 6.63 ppm) and μ-dioxane (δ_{OH} at 6.51 ppm) complexes.

Addition of 1 equiv of water (in THF) to Mo(CAr$_p$)-(OR$_{F9}$)$_3$(THF)$_2$ in CH$_2$Cl$_2$ led to formation of {Mo(CAr$_p$)-(OR$_{F9}$)$_2$(μ-OH)}$_2$(μ-THF), which could be isolated in 43% yield as lime-green crystals; in the presence of additional THF, it crystallizes as {Mo(CAr$_p$)(OR$_{F9}$)$_2$(μ-OH)(THF)}$_2$(μ-THF) (**2-Ar$_p$F$_9$**). An X-ray structural study showed its structure to be entirely analogous to that for **2-Ar$_p$F$_6$** (see SI for details). The two molecules of hydrogen-bonded THF in **2-Ar$_p$F$_9$** again are lost readily from solid samples, especially *in vacuo*. The μ-OH

resonance is found at 8.21 ppm in **2-Ar$_p$F$_9$** in CD$_2$Cl$_2$ (cf. 6.60 ppm in **2-Ar$_p$F$_6$**).

Reactions between **2-Ar$_p$F$_6$** or **2-Ar$_p$F$_9$** and PMe$_3$ or PEt$_3$ (L) do *not* yield Mo(O)(CHAr$_p$)(OR)$_2$(L) complexes readily and in high yield. However, addition of 1 equiv of L to Mo(CAr$_p$)(OR$_{F9}$)$_3$(THF)$_2$, followed by addition of 1 equiv of water, *all at room temperature in THF*, yields Mo(O)(CHAr$_p$)-(OR)$_2$(L) complexes (**3**) in good yields for several phosphines L (e.g., PMe$_2$Ph (69% by NMR), PMePh$_2$ (59%), PEt$_3$ (69%), or P(*i*-Pr)$_3$ (65%)). For example, Mo(O)(CHAr$_p$)-(OR$_{F9}$)$_2$(PEt$_3$) (**3-PEt$_3$**) can be prepared in this manner (eq 3). These results suggest that in most cases it is best to *avoid*
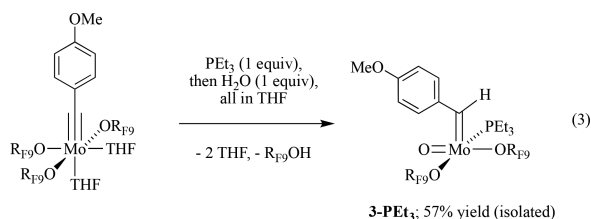
formation of bis(μ-OH) dimers. We propose that THF discourages formation of a hydroxo benzylidyne dimer from monomeric Mo(CAr$_p$)(OR$_{F9}$)$_2$(OH)(THF)$_x$ (*x* unknown). We also propose that the hydroxo proton migrates to the benzylidyne α carbon intramolecularly in intermediate Mo-(CAr$_p$)(OR$_{F9}$)$_2$(OH)(THF)$_x$ to give Mo(O)(CHAr$_p$)-(OR$_{F9}$)$_2$(THF)$_x$, which is then trapped by L to give Mo(O)(CHAr$_p$)(OR$_{F9}$)$_2$(L) complexes. Phosphines can also bind to Mo in Mo(CAr$_p$)(OR$_{F9}$)$_2$(OH)(THF)$_x$ and help prevent formation of μ-OH products and promote (perhaps along with THF itself) migration of the proton from O to C. Formation of OR$_{F6}$ analogs of **3** at room temperature in THF does not appear to be as successful, most likely because the migrating proton is less acidic in OR$_{F6}$ hydroxo benzylidyne complexes. Studies that address multiple mechanistic issues are ongoing.

Mo(O)(CHAr$_p$)(OR$_{F9}$)$_2$(PEt$_3$) (**3-PEt$_3$**) was chosen to proceed further toward the goal of preparing a four-coordinate complex. The reaction between **3-PEt$_3$** and 2 equiv of LiOHMT proceeds smoothly at 90 °C in toluene over a period of 1.5 h to give Mo(O)(CHAr$_p$)(OHMT)$_2$ (**1-Ar$_p$**) which could be isolated as plum-purple needles (eq 4). The
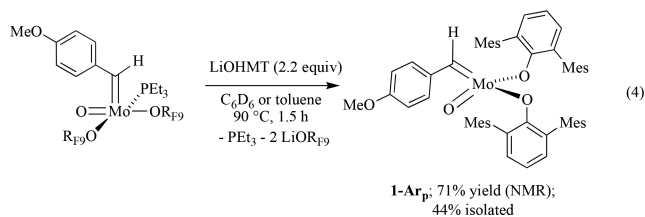
alkylidene proton resonance is found at 11.20 ppm (in C$_6$D$_6$) with J_{CH} = 130 Hz, consistent with the alkylidene being in the *syn* conformation. The corresponding *anti* isomer was not found in solution even upon heating a sample of **1-Ar$_p$** at 100 °C, which suggests that coordination of an *ortho* methoxide in **1-Ar$_o$** (Figure 1) stabilizes the *anti* form. The OHMT ligands in the proton NMR spectrum at 22 °C are equivalent on the NMR time scale through mirror symmetry. The purple color of **1-Ar$_p$** (λ$_{max}$ = 532 nm with ε$_{532}$ ≈ 400) is unusual for a "d^0" complex of this general type. We propose that the purple color arises from a weak LMCT transition that involves the *p*-

methoxybenzylidene ligand. Compound **1-Ar$_p$** also was prepared from **3-PMePh$_2$** in 66% yield on a 500 mg scale at 70 °C in 3.5 h.

An X-ray structural study of **1-Ar$_p$** (Figure 3) reveals that the OHMT terphenyl groups are roughly "interlocked," as they are
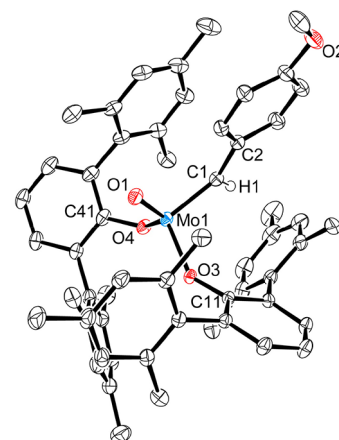

Figure 3. A drawing of the structure of **1-Ar$_p$**; Mo1−C1 = 1.9004(13) Å, Mo1−O1 = 1.6803(10) Å, Mo1−O3 = 1.9064(9) Å, Mo1−O4 = 1.9113(9) Å, Mo1−C1−C$_{ipso}$ = 137.42(10)°, Mo1−O3−C$_{ipso}$ = 143.11(8)°, Mo1−O4−C$_{ipso}$ = 127.58(8)°.

in W(O)(CH$_2$)(OHMT)$_2$,[10b] although they rotate readily around the Mo−O bonds on the NMR time scale in solution at 22 °C. The relevant distances and angles are similar to those in **1-Ar$_o$** (see Figure 1 and SI). Together the two OHMT ligands prevent PEt$_3$ or PMePh$_2$ from remaining bound to the metal in the final product and also provide a significant degree of steric protection against bimolecular decomposition reactions.

Compound **1-Ar$_p$** reacts with ethylene (1 atm in C$_6$D$_6$ at 22 °C) to give an orange solution that contains a mixture of **1-Ar$_p$**, Mo(O)(CH$_2$)(OHMT)$_2$, and an unsubstituted metallacyclobutane complex, Mo(O)(CH$_2$CH$_2$CH$_2$)(OHMT)$_2$, along with Ar$_p$CH=CH$_2$, and ethylene, according to proton NMR studies. At a molybdenum concentration of 17 mM in C$_6$D$_6$, the ratio of Mo=CHAr$_p$:Mo=CH$_2$:Mo(C$_3$H$_6$):Ar$_p$CH=CH$_2$ is 57:5:38:43 (43% conversion) after 1.5 h. The 1:1:2:2 pattern of the four metallacycle proton resonances in Mo(O)-(CH$_2$CH$_2$CH$_2$)(OHMT)$_2$ at 2.92, 2.39, 1.68, and 0.45 ppm suggests that it has a square pyramidal structure.[24] To date, efforts to isolate Mo(O)(CH$_2$CH$_2$CH$_2$)(OHMT)$_2$, an analog of isolable W(O)(CH$_2$CH$_2$CH$_2$)(OHMT)$_2$,[10b] have not been successful.

Compound **1-Ar$_p$** does not react readily with several equivalents of *Z*-5-decene at 22 °C. It does react with 2,3-dicarbomethoxynorbornadiene (4 equiv) to yield a 17:1 mixture of *syn* (δ H$_α$ at 11.63 ppm; eq 5) and *anti* isomers
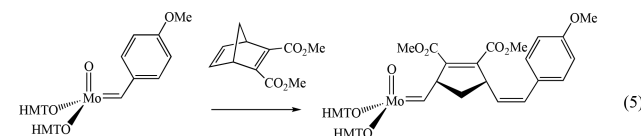
(not shown in eq 5) of the first insertion product, each of which contains a *cis* C=C bond.[25] (The yield (by NMR) is ∼90%; see SI for details.) Both results are consistent with a relatively sterically demanding coordination sphere that limits

access to an alkylidene, in contrast to $Mo(O)(CHAr_o)$-$(OHIPT)Cl$ formed through removal of PMe_3 from $Mo(O)$-$(CHAr_o)(OHIPT)(PMe_3)Cl$, which forms polymers from 2,3-dicarbomethoxynorbornadiene readily.[12]

We conclude that the *o*-methoxy group is not required, either for forming a benzylidene ligand from a benzylidyne ligand or for stabilizing a bis(OHMT) oxo benzylidene complex. The most successful syntheses of oxo alkylidene complexes involve intramolecular α proton migrations from O to C, where C is the benzylidyne α carbon, and are most successful when OR is OR_{F9}, the solvent is THF, and a phosphine is available to trap the oxo benzylidene product and possibly help form it. Several phosphine adducts of molybdenum oxo benzylidene complexes are accessible via reactions between $Mo(CAr_p)(OR)_3(THF)_2$ complexes and water. We can now predict that other metathesis-active molybdenum oxo alkylidene complexes will be observed or isolated under the right circumstances, and look forward to comparing their metathesis reactions with those catalyzed by tungsten analogs.[10,16]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09616.

> Experimental details of the syntheses of all compounds, NMR and spectral data, and details of the metathesis experiments (PDF)
> Crystallographic data for **2-Ar_pF_6**·1.5(C_5H_{12}) (CIF)
> Crystallographic data for **1-Ar_o**·HMDSO (CIF)
> Crystallographic data for **2-Ar_pF_9** (CIF)
> Crystallographic data for **1-Ar_p** (CIF)

Accession Codes

CCDC 1865865−1865868 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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