ORGANOMETALLICS

FLPNO Nitroxide Radical Formation by a 1,1-Carboboration Route

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S Supporting Information

ABSTRACT: The 1-trimethylsilylethynyl-2-diarylphosphanylethynylbenzene substrates $7\mathbf{a}-7\mathbf{c}$, with the diarylphosphanyl groups = PPh₂, P(*o*-tolyl)₂, or P(mesityl)₂, were reacted with the strong boron Lewis acid B(C₆F₅)₃ at ambient conditions. The starting materials $7\mathbf{a}$ and $7\mathbf{b}$, featuring rather small nucleophilic phosphanyl substituents, underwent selective 1,1carboboration at the C \equiv C-PAr₂ moiety, forming rather



unreactive unsaturated vicinal P/B Lewis pairs 8a and 8b that show a relatively strong internal P···B Lewis base/Lewis acid interaction. In contrast, the PMes₂ system 7c reacted with $B(C_6F_5)_3$ by a reaction sequence which was initiated by 1,1carboboration and involved tandem C_6F_5 and mesityl group migration to yield the unsaturated annulated P/B Lewis pair 9, featuring an electron-withdrawing C_6F_5 group at phosphorus. Compound 9 underwent cooperative P/B addition to the nitrogen atom of nitric oxide to give the persistent FLPNO[•] nitroxide radical 12. Radical 12 was characterized by electron spin resonance spectroscopy and by X-ray diffraction. It showed typical nitroxide radical reactions.

INTRODUCTION

Saturated vicinal phosphane/borane (P/B) frustrated Lewis pairs (FLPs) can undergo cooperative N,N-addition to nitric oxide (NO) to form a new family of persistent FLPNO nitroxide radicals.¹ So far a sizable number of saturated C₂-bridged P/B FLPs like compound **1**, featuring various substituents at the bridge or derived from alicyclic analogues, have undergone this reaction (see Scheme 1).² The parent

Scheme 1



compound 2 was shown to be a slightly more oxygen-centered radical as compared to, e.g., TEMPO. The calculated O–H bond dissociation energy of the corresponding diamagnetic FLPNOH compound 3 is by ca. 10 kcal/mol higher than that of TEMPOH, which renders the FLPNO radical by this value less stabilized and thus slightly more reactive than the TEMPO radical.³

We have recently shown that the unsaturated C₂-bridged P/B systems 5 were easily prepared in a one-step procedure by 1,1carboboration of phosphanyl-substituted acetylenes R¹-C≡C-PAr₂ using strongly electrophilic borane reagents R²-B- $(C_6 F_5)_2$.^{5,6} The reaction can be formulated topologically by alkyne addition to boron followed by 1,2-migration of the phosphanyl group along the acetylene C2-framework and R2migration from boron to the former acetylenic carbon atom C1. The P/B systems 5 show a rather low reactivity in the FLP sense: in contrast to the very reactive FLP 1, they do not cleave dihydrogen. One of the few well-defined reactions some members of this class of FLPs undergo is cooperative 1,1-P/Baddition to some isocyanides, giving the products 4 (see Scheme 1).⁷ So far, none of the described P/B compounds 5 (without additional functional groups) have added to NO to form a respective unsaturated P/B FLPNO nitroxide radical. We have now found the first example of such a reaction of an analogue of 5 with NO, which will be described in this article.

RESULTS AND DISCUSSION

1,1-Carboboration Reactions. For this study we employed three closely related unsymmetrically substituted *o*bis(alkynyl)benzene starting materials. The starting material 7**a** was synthesized by a single deprotonation of 1,2-diethynylbenzene followed by subsequent addition of chlorodiphenylphosphane. A second deprotonation and silylation then led to the product 7**a**. The syntheses of the starting materials 7**b** $(PAr_2 = P(o-tolyl)_2)$ and 7**c** $(PAr_2 = PMes_2)$ started with

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Sonogashira coupling of *o*-iodobromobenzene with trimethylsilylacetylene to give compound **6**, followed by Negishi crosscoupling with the in situ-generated diarylphosphinoethynylzinc chloride reagents to give the products 7 (see Scheme 2).⁸



Each of the three bis(alkynyl)benzenes 7 was reacted with $B(C_6F_5)_3$. The reaction of 7a and 7b took a different course than the one with 7c. Both alkynyl groups in the systems 7 bear substituents at their ends that have previously been shown to serve as good migrating groups in 1,1-carboboration reactions.^{9,10} In the systems 7a and 7b, the PAr₂ substituents became the favored migrating groups under our typical reaction conditions. We isolated the products 8a and 8b formed by selective 1,1-carboboration at the respective C=C-PAr₂ moiety in good yields.

Compound 8a was isolated as a yellowish solid (89%). It was characterized by C,H-elemental analysis, by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis confirmed that a 1,1-carboboration reaction had selectively taken place at the $C \equiv C-PPh_2$ moiety. This resulted in the formation of a 1,2-B(C₆F₅)₂/PPh₂-substituted olefin. Addition of the $B(C_6F_5)_3$ Lewis acid at the alkyne terminal apparently resulted in 1,2-PPh₂ migration along the CC backbone, with concomitant C_6F_5 migration from boron to carbon. This 1,1carboboration is stereoselective. It results in a cis-1,2-arrangement of the phosphanyl Lewis base and the boryl Lewis acid substituent at the newly formed olefinic moiety. The reason for this is probably the formation of the energetically favorable P... B interaction (see Figure 1). Both the phosphorus and the boron atom show pseudotetrahedral coordination geometries $(\sum P1^{CCC} = 334.4^{\circ}, \sum B1^{CCC} = 349.0^{\circ}).$

In solution, compound **8a** features four CH ¹H NMR resonances of the central *o*-phenylene framework [δ 7.23, 7.09, 6.68, 6.60]. The acetylenic ¹³C NMR signals of the intact C \equiv C-SiMe₃ substituent occur at δ 103.2 and 99.7, respectively [SiMe₃: δ -0.6 (¹H), -17.2 (²⁹Si)], and the ¹³C NMR resonances of the newly formed tetrasubstituted alkenyl unit are located at δ 164.9 (\equiv C[B]) and 140.7 (¹J_{pc} = 53.0 Hz). Compound **8a** shows a ³¹P NMR signal at δ 17.2 and a ¹¹B



Figure 1. Molecular structure of the 1,1-carboboration product 8a (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C1-C2 1.339(5), C1-B1 1.652(5), C2-P1 1.794(3), B1-P1 2.034(4), C3-C4 1.209(5), C3-C4-C5 172.1(4), C2-P1-B1 77.7(2), P1-B1-C1 78.8(2), P1-C2-C1-B1 1.1(3), C1-C2-C6-C5 51.7(6).

NMR resonance at δ –5.1, which indicates a marked P…B interaction. Consequently, the B(C₆F₅)₂ unit shows a trio of ¹⁹F NMR signals at δ –128.8 (*o*), –156.7 (*p*), and δ 163.4 (*m*) with a typical $\Delta \delta^{19}$ F_{m,p} = 6.7 ppm shift difference. The carbon-bonded single C₆F₅ substituent shows the respective ¹⁹F NMR resonances at δ –136.8 (*o*), –154.5 (*p*), and –162.2 (*m*). The P(*o*-tolyl)₂-substituted 1,1-carboboration product **8b** shows very similar NMR features [e.g., δ 20.1 (³¹P), –3.6 (¹¹B), and –17.2 (²⁹Si)] (for details see the Supporting Information).

The reaction of the PMes₂-substituted starting material 7c with $B(C_6F_5)_3$ took a different course (see Scheme 3). The

Scheme 3



reaction was carried out in toluene solution at 80 °C. It took 3 h to go to completion. Workup with precipitation by pentane eventually gave the product 9 as a colorless solid in 82% yield. The X-ray crystal structure analysis showed that a benz-annulated heterobicyclic compound had been obtained. It is apparently formed by initial 1,1-carboboration of the C \equiv C-SiMe₃ moiety. The resulting C3–C4 carbon–carbon double bond (1.360(3) Å, see Figure 2) has the SiMe₃ substituent



Figure 2. A view of the molecular structure of compound 9 in the crystal (thermal ellipsoids are shown with 15% probability).

attached at C4 (C4–Si1 1.922(2) Å) and the single C_6F_5 substituent at C3 (C3–C61 1.495(3) Å). The boron atom at C3 is found attached at the second carbon–carbon double bond, which was apparently formed by a subsequent attack of the boron Lewis acid at the remaining $C \equiv C$ -PMes₂ group followed by a series of rearrangement steps.¹¹ The boron atom B1 contains only a single C_6F_5 substituent. The remaining third C_6F_5 group had been shifted to the phosphorus atom, which in turn has shifted one of its mesityl substituents to the adjacent former acetylene carbon atom (C1). In the crystal we note some P…B interaction (P1–B1 2.130(2) Å).

We assume a reaction pathway as it is sketched in Scheme 3. The reaction sequence is probably initiated by a 1,1-carboboration reaction at the C \equiv C-SiMe₃ group, which proceeds by 1,2-SiMe₃ migration along the alkynyl framework and C₆F₅ migration from boron to carbon to generate Z-10. This is set up for boron Lewis acid attack at the adjacent alkynyl group,¹² which seems to take a carbenium ion-specific reaction course, similar to that previously been observed in other multifunctionalized carboboration systems. In this course ring-closure seems to be followed by shifting of a C₆F₅ group from boron to phosphorus and 1,2-mesityl migration from phosphorus to carbon.¹¹

The colorless crystalline product **9** dissolves in toluene to give deeply red solutions. Upon cooling these solutions, a marked thermochromic behavior is observed: at -80 °C they are yellow. The exact nature of this effect has still to be disclosed, but we assume opening of the weak P…B interaction in solution with increasing temperature. In accord with this interpretation, we have observed a shifting of the ¹¹B NMR resonance of compound **9** from δ -4.3 at -80 °C to δ 16.4 at room temperature. The ³¹P NMR resonance of **9** occurs at δ 18.0 at -80 °C (in d_8 -toluene), which is shifted to δ 11.0 at room temperature.

At room temperature compound **9** shows three separate sets of ¹⁹F NMR signals for three different C_6F_5 groups in solution (C_6D_6) . We find the four CH ¹H NMR signals of the central *o*-phenylene moiety of compound **9** at δ 7.52, 6.94, 6.90, and 6.71. Compound **9** shows a ¹H NMR resonance of the SiMe₃ group at δ –0.02. We have monitored the CH ¹H NMR signals

for the carbon-bound mesityl substituent at δ 6.66 and for the mesityl group at phosphorus at δ 6.49 (⁴J_{PH} = 3.3 Hz).

Reactions with Nitrogen Monoxide. Compound 9 reacts rapidly with nitric oxide at ambient temperature with N,N-addition of the P/B-FLP. We exposed a dark red solution of 9 in benzene to NO (1.5 bar) at room temperature. Within minutes the color of the solution changed to yellow. Workup after 2 h reaction time resulted in isolation of the NO cycloaddition product 12 in <70% yield (see Scheme 4). The compound was obtained as an orange-red solid.



Single crystals of the compound 12 were obtained from dichloromethane/pentane at -40 °C by the diffusion method. The X-ray crystal structure analysis confirms that the reaction of 9 with NO has resulted in the formation of a P/B FLPNO nitroxide radical (see Figure 3). It shows the presence of a five-



Figure 3. A projection of the molecular structure of the persistent P/B FLPNO nitroxide radical **12** in the crystal (thermal ellipsoids are shown with 15% probability).

membered heterocycle newly formed by P–N and B–N bond formation (P1–N1 1.707(3) Å, B1–N1 1.569(5) Å). Both these bonds are in the typical element–N σ -bond range. The coordination geometry of the nitrogen atom in compound **12** is trigonal planar ($\sum N1^{POB} = 359.8^{\circ}$). The newly formed fivemembered ring is close to planar [dihedral angle P1–N1–B1–

C2 2.5(3)°]. The N1–O1 bond length amounts to 1.300(3) Å. which is much longer than the N–O distance in free NO (1.15 Å);¹³ it is in the typical range of P/B FLPNO¹⁴ radicals (and of typical organic persistent nitroxides), which indicates considerable delocalization of the unpaired electron along the N-O vector. The five-membered ring in compound 12 still contains the distal C=C double bond $(C1-C2\ 1.345(5)\ \text{Å})$. We note that there is only one diastereomer of compound 12 present in the crystal. It features the pair of C_6F_5 substituents at phosphorus and boron in a trans-arrangement at the newly formed five-membered heterocyclic ring. This is different from the arrangement of these two groups at the weakly P...B bound four-membered ring of the starting material 9, where the respective pair of C₆F₅ substituents was found *cis*-orientated (see Figure 2). This probably indicates involvement of the open form of the FLP 9 in the NO addition reaction, which would allow for free rotation around the P-C vector.

The persistent nitroxide radical **12** was characterized by EPR spectroscopy (see Figure 4).¹⁴ In benzene at room temperature.



Figure 4. X-band EPR spectrum and simulation of 12 in benzene at room temperature.

12 displays a multi-line pattern centered at g = 2.0081. Quite similar to other P/B-FLPNO adducts, coupling to the ¹⁴N ($A(^{14}N) = 18.5 \text{ MHz}$), ³¹P ($A(^{31}P) = 48.9 \text{ MHz}$), and ¹¹B/¹⁰B ($A(^{11}B) = 9.7 \text{ MHz}$) nuclei is observed. The magnitude of coupling to N is much lower than in organic nitroxides such as TEMPO (43.5 MHz), ¹⁵ consistent with the greater degree of O-centered unpaired electron density found in P/B FLPNO species.¹⁴

Reactions of the New Persistent P/B FLPNO Radical. The persistent P/B FLPNO radical undergoes reactions typical of persistent nitroxide radicals.^{3,16} It cleanly reacts with 1,4cyclohexadiene at room temperature (overnight) by H-atom abstraction to yield the diamagnetic P/B FLPNOH product **13** (isolated as a colorless solid in 94% yield). It was characterized by C,H,N-elemental analysis, by spectroscopy, and by X-ray diffraction (see Figure 5).

The X-ray crystal structure analysis shows that the P/B FLPNO radical **12** forms the diamagnetic P/B FLPNOH product **13** upon treatment with the cyclohexadiene H-atom donor. This was evident by a number of marked changes of characteristic structural parameters. The N1–O1 bond in **13** (1.429(3) Å) is much longer than the one in **12**, which indicates the "loss" of the delocalized unpaired electron. At the same time, the P1–N1 bond in **13** (1.625(3) Å) is markedly shorter than the corresponding P–N linkage in **12**.¹⁷ This probably indicates a pronounced participation of the phosphinimime/borane adduct resonance structure (**13**') for the description of the P/B FLPNOH product (see Scheme 4 and



Figure 5. Molecular structure of the P/B FLPNOH product 13 (thermal ellipsoids are shown with 15% probability).

Figure 5). The stereochemical arrangement of the substituents at P and B at the five-membered heterocyclic core of 13 was, of course, retained in the H-atom abstraction reaction.

Nitroxide radicals have extensively been used as the essential controlling reagents in NMP radical polymerization reactions of some olefinic monomers.¹⁸ We wanted to learn if our new P/B FLPNO system 12 would behave as a typical controlling NMP reagent in the radical polymerization of styrene. For that purpose we prepared the diamagnetic P/B FLPNO-1-phenylethyl reagent 14 as a suitable precursor for the thermally induced generation of a benzylic radical starter and a controlling persistent nitroxide radical. In a close variation of a typical procedure,¹⁹ we oxidatively coupled the P/B FLPNO radical 12 with 1-phenylethyl bromide in a copper-induced reaction using 1.7 molar equiv of Cu powder with a catalytic quantity of $Cu(OTf)_2$ and a bipyridyl ligand (0.4 equiv). Heating for 2 days at 70 °C in benzene and chromatographic workup eventually gave the expected product 14 as a 3:2 mixture of diastereoisomers $(14/14' \text{ in } C_6D_6)$ (see Scheme 5).





We could not achieve a reliable relative assignment of the diastereoisomers by NMR spectroscopy in solution but monitored some characteristic pairs of resonances, such as the [N]-O-CH ¹H NMR quartets at δ 4.71/4.82 (major/minor) or the Me₃Si ¹H NMR signal pair at δ 0.01/-0.06. The major isomer shows a ³¹P NMR signal at δ 48.3, whereas the minor diastereomer features a corresponding resonance at δ 52.7. We observed only a single broad ¹⁰B NMR resonance at δ -2.3 ($\nu_{1/2} \approx 250$ Hz) jointly for both isomers.

Slow crystallization of 14/14' from benzene eventually gave single crystals suited for the X-ray crystal structure analysis. In the crystal we found two diastereoisomers, namely one with the relative stereochemistry of *rac*-(R^P, R^C, S^B) (85%) and the *rac*-(R^P, S^C, S^B) diastereoisomer (15%) (see Figure 6). The structure



Figure 6. A view of the molecular structure of the benzylic P/B FLPNO derivative rac- (R^P, R^C, S^B) -14 (thermal ellipsoids are shown with 15% probability). [rac- (R^P, S^C, S^B) -14 is depicted in the Supporting Information.]

shows that the 1-phenylethyl unit became [N]-O-attached (O1–C14 1.446(4) Å) to give the O-benzylated heterohydroxylamine derivative. In compound 14, the P1–N1 bond (1.657(3) Å) is again rather short (similar as in the [N]–OH derivatives 13, see above) and the N1–O1 bond (1.454(3) Å) is long. The B1–N1 linkage (1.626(5) Å) is in a similar range in all three FLPNO derivatives (12, 13, 14).

The mixture of diastereoisomers 14/14' was used for nitroxide-mediated radical polymerization of styrene.²⁰ Styrene polymerization was typically carried out at 110 °C in benzene solution using 1 mol % of the 14/14' mixture of diastereoisomers as initiator/controlling reagents. This gave polystyrene with a polydispersion index of around 1.6, which indicates only a low efficiency of these alkoxyamines as NMP initiators/ regulators.

CONCLUSION

We used the tandem 1,1-carboboration sequence of 1,2bis(trimethylsilylethynyl)benzenes and related systems for benzannulation.²¹ The unsymmetrically functionalized 1trimethylsilylethynyl-2-diarylphosphanylethynylbenzene derivatives 7 show a remarkably different behavior upon treatment with the strong boron Lewis acid $B(C_6F_5)_3$. The pair of compounds 7a and 7b that contain the rather small and markedly nucleophilic PPh₂ or P(*o*-tolyl)₂ substituents undergo a single 1,1-carboboration reaction selectively at the C \equiv C-PAr₂ alkynyl moiety. This reaction gives the vicinal P/B systems 8 that feature a strong Lewis acid/Lewis base interaction. Such unsaturated phosphane/borane Lewis pairs have been known to be rather unreactive.

The bulkier PMes₂-substituted analogue 7c shows a markedly different behavior toward $B(C_6F_5)_3$. In this case a reaction

sequence takes place that is apparently initiated by $B(C_6F_5)_3$ attack at the C=C-SiMe₃ alkynyl functional group. We assume that initially the respective 1,1-carboboration product **10** is generated, which then undergoes a subsequent internal borane attack at the remaining adjacent carbon–carbon triple bond. This seems to initiate a domino-type sequence of steps¹¹ that eventually results in the formation of the unusually substituted unsaturated vicinal P/B Lewis pair (9) found annulated with the newly formed six-membered heterocyclic structure.

The system 9 is structurally and chemically remarkable. The $B \cdots P$ distance in 9 is rather long, indicating a somewhat reduced Lewis acid/Lewis base interaction as compared to other conventionally substituted unsaturated vicinal P/B pairs. We assume that this is caused by the presence of the $P-C_6F_5$ substituent at phosphorus,^{22,23} resulting in a decreased Lewis basicity. Nevertheless, the combined Lewis acid/Lewis base strength in 9 is sufficient to observe a typical cooperative FLP reaction, namely the N.N-addition of nitric oxide to the P/B pair with formation of the new persistent FLPNO nitroxide radical 12. This behavior is uncommon: such FLPNO radical formation had previously only been observed by reacting NO with the reactive saturated vicinal P/B FLPs.^{1,2} The FLPNO system 12 undergoes typical nitroxide radical reactions, including H-atom abstraction from suitable substrates. The unsaturated FLPNO system 12 is a more oxygen-centered persistent radical as compared to, e.g., TEMPO. However, it shows reactivities very similar to those previously found for the closely related saturated FLPNO nitoxide radicals such as, e.g., 2. This study underlines the high potential that the advanced version of the 1,1-carboboration reaction has for offering pathways to unusual new chemical systems, in this case the formation of a rather unusual FLP system²⁴ for nitroxide radical formation by cooperative addition to NO.

EXPERIMENTAL SECTION

For general information and details of the characterization of the compounds, see the Supporting Information.

Preparation of Compound 9. Compound 7c (325 mg, 0.7 mmol, 1 eq)equiv) and $B(C_6F_5)_3$ (356 mg, 0.7 mmol, 1 equiv) were dissolved separately in toluene (each ~3 mL). The solutions were combined at room temperature and then stirred for 3 h at 80 °C. The resulting deep red solution was cooled to room temperature, and the solvent was removed *in vacuo*. *n*-Pentane (~5 mL) was then added and directly removed *in vacuo* (to remove remaining toluene). The residue was redissolved in *n*-pentane (~8 mL) and stored at -40 °C overnight to give a suspension. The supernatant was removed using a pipet and the colorless residue dried *in vacuo* to give compound 9 (564 mg, 0.58 mmol, 82%) as a colorless solid. Single crystals suitable for the X-ray diffraction were obtained by storing a diluted solution of compound 9 in *n*-heptane for several days at -40 °C. Anal. Calcd for $C_{49}H_{35}BF_{15}PSi: C, 60.14$; H, 3.60. Found: C, 60.36; H, 3.56. Mp = 109 °C.

Preparation of Compound 12. Compound 9 (288 mg, 0.29 mmol, 1 equiv) was dissolved in C_6H_6 (~5 mL), and the solution was exposed to 1.5 bar of NO gas. The color of the solution changed from red to yellow within a couple of minutes, and the resulting solution was stirred for 2 h at room temperature. After that, all volatiles were removed *in vacuo*, and the resulting residue was redissolved in *n*-pentane (~5 mL). The solvent was directly removed *in vacuo* (this procedure was repeated one more time to remove remaining C_6H_6). The residue was then redissolved in *n*-pentane (~5 mL) and sonicated for 10 min. The supernatant was removed and the residue washed with *n*-pentane (2× ~3 mL). Drying of the orange solid *in vacuo* gave compound **12** (190 mg, 0.19 mmol). The washing solution was kept at -40 °C for 3 days to give more orange material (**12**, 22.0 mg, 0.02 mmol), which was combined with the previous isolated material. In

total compound **12** (212 mg, 0.21 mmol, 72%) was isolated as an orange solid. Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of **12** in CH₂Cl₂ at -40 °C. Anal. Calcd for C₄₉H₃₅BF₁₅NOPSi: C, 58.35; H, 3.50; N, 1.39. Found: C, 58.57; H, 3.62; N, 1.41. Mp (decomp) = 151 °C.

Preparation of Compound 13. Compound 12 (101 mg, 0.1 mmol, 1 equiv) was dissolved in C_6H_6 (~3 mL), and 1,4-cyclohexadiene (20 μ L, 0.2 mmol, 2 equiv) was added. The resulting solution was stirred at room temperature overnight, and then all volatiles were removed *in vacuo*. *n*-Pentane (~5 mL) was added and directly removed *in vacuo* (to remove remaining C_6H_6). The residue was purified by flash chromatography (SiO₂, CH₂Cl₂: *n*-pentane = 1:4). After drying *in vacuo*, compound 13 (94.0 mg, 0.09 mmol, 94%) was isolated as a colorless solid. Single crystal suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound 13 in C_6D_6 at room temperature. Anal. Calcd for $C_{49}H_{36}BF_{15}NOPSi: C, 58.29; H, 3.59; N, 1.29.$ Found: C, 58.16; H, 4.08; N, 1.24. Mp (decomp) = 227 °C.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00886.

Detailed description of the experiments and characterization of the new compounds (PDF)

Crystal structure data for 8a, 9, 12, 13, and 14 (CIF)

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Notes

The authors declare no competing financial interest.

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