

# Dinitrogen Activation by Dihydrogen and a PNP-Ligated Titanium Complex

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**S** Supporting Information

**ABSTRACT:** The hydrogenolysis of the PNP-ligated titanium dialkyl complex  $\{(\text{PNP})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\}$  (**1**, PNP =  $\text{N}(\text{C}_6\text{H}_3\text{-}2\text{-P}^i\text{Pr}_2\text{-}4\text{-CH}_3)_2$ ) with  $\text{H}_2$  (1 atm) in the presence of  $\text{N}_2$  (1 atm) afforded a binuclear titanium side-on/end-on dinitrogen complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2\eta^1, \eta^2\text{-N}_2)(\mu_2\text{-H})_2\}$  (**2**) at room temperature, which upon heating at 60 °C with  $\text{H}_2$  gave a  $\mu_2$ -imido/ $\mu_2$ -nitrido/hydrido complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2\text{-NH})(\mu_2\text{-N})\text{H}\}$  (**3**) through the cleavage and partial hydrogenation of the  $\text{N}_2$  unit. The mechanistic aspects of the hydrogenation of the  $\text{N}_2$  unit in **2** with  $\text{H}_2$  have been elucidated by the density functional theory calculations.

Dinitrogen ( $\text{N}_2$ ) is an abundant and easily accessible resource, but it is highly inert under ordinary conditions. The activation and functionalization of  $\text{N}_2$  has therefore been a long-standing important research subject. Industrially, the cleavage and hydrogenation of  $\text{N}_2$  is achieved by reaction with  $\text{H}_2$  at high temperatures (350–550 °C) and high pressures (150–350 atm) on solid catalysts to afford ammonia ( $\text{NH}_3$ ) (the Haber–Bosch process).<sup>1</sup> This is the only commercially successful process using  $\text{N}_2$  gas as a feedstock. To have a better understanding of the  $\text{N}_2$  activation mechanism and thereby achieve ammonia synthesis under milder conditions, extensive studies on the activation of  $\text{N}_2$  by molecular organometallic complexes have been carried out over the past decades.<sup>2–13</sup> It has been reported that the reduction and cleavage of  $\text{N}_2$  could be achieved at ambient temperature and pressure by using a combination of transition metal complexes and strongly reducing metal reagents such as  $\text{KC}_8$ , Na/Hg, Mg, and  $\text{Cp}_2\text{Co}^{3-6}$  or by using multimetallic transition metal polyhydrides.<sup>7,8</sup>

In view of the fact that  $\text{H}_2$  is the only source of both electrons and protons in the industrial Haber–Bosch ammonia synthesis, the activation of  $\text{N}_2$  by  $\text{H}_2$  in the presence of a transition metal complex is particularly of interest. However, studies on the activation and hydrogenation of  $\text{N}_2$  by  $\text{H}_2$  at the molecular level remained scarce. Fryzyk and co-workers reported the hydrogenation of a bis(phosphine)diamido-ligated zirconium dinitrogen complex  $\{[(\text{P}_2\text{N}_2)\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)\}$  generated by the reaction of  $\text{N}_2$  with a combination of  $\{(\text{P}_2\text{N}_2)\text{ZrCl}_2\}$  and  $\text{KC}_8$  ( $\text{P}_2\text{N}_2 = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{-CH}_2)_2\text{PPh}$ ), which led to N–H formation without inducing

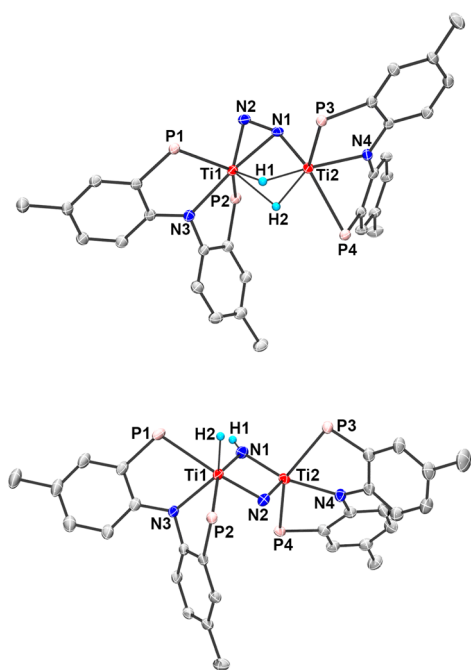
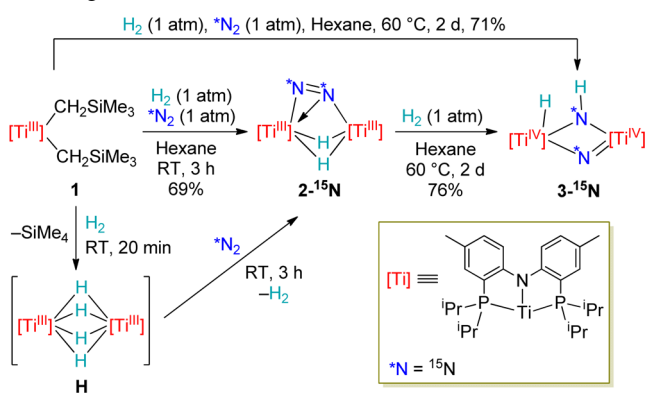
N–N cleavage.<sup>11a</sup> Chirik and co-workers investigated the hydrogenolysis of a zirconocene dinitrogen complex  $\{[(\text{C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)\}$  obtained by the reaction of  $\{(\text{C}_5\text{Me}_4\text{H})_2\text{ZrCl}_2\}$  with Na/Hg under an  $\text{N}_2$  atmosphere, and observed the formation of a zirconocene diazenido/dihydrido complex  $\{[(\text{C}_5\text{Me}_4\text{H})_2\text{ZrH}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2\text{H}_2)\}$  at room temperature, which upon heating at 85 °C gave a mixed amide/nitride complex  $\{[(\text{C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2\text{-N})(\mu_2\text{-NH}_2)\}$  with release of  $\text{H}_2$ .<sup>11d</sup> We recently reported the cleavage and hydrogenation of  $\text{N}_2$  by a combination of  $\text{H}_2$  and a half-sandwich titanium trialkyl complex  $\{(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}(\text{CH}_2\text{SiMe}_3)_3\}$ , which yielded a tetranuclear diimido/tetrahydrido complex  $\{[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{-Ti}]_4(\mu_3\text{-NH})_2(\mu\text{-H})_4\}$  via a trinuclear titanium polyhydride complex.<sup>8a</sup> The cleavage and hydrogenation of  $\text{N}_2$  by  $\text{H}_2$  in a well-defined molecular system without preactivation using other reducing agents has not been reported previously. We report here the formation and hydrogenation of a side-on/end-on dinitrogen complex by the reaction of  $\text{N}_2$  with  $\text{H}_2$  and a bis(phosphinophenyl)amido (PNP)-ligated titanium complex.

The hydrogenolysis of the PNP-ligated titanium dialkyl complex  $\{(\text{PNP})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\}$  (**1**, PNP =  $\text{N}(\text{C}_6\text{H}_3\text{-}2\text{-P}^i\text{Pr}_2\text{-}4\text{-CH}_3)_2$ )<sup>14</sup> with  $\text{H}_2$  (1 atm) in the presence of  $\text{N}_2$  (1 atm) at room temperature afforded a binuclear titanium dinitrogen complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu\text{-H})_2\}$  (**2**) in 70% isolated yield in 3 h. The analogous hydrogenolysis of **1** in the presence of  $^{15}\text{N}_2$  afforded the  $^{15}\text{N}$  analog **2-<sup>15</sup>N** (Scheme 1). Single crystals of **2** suitable for X-ray crystallographic studies were grown from a hexane solution at –35 °C. It was revealed that **2** adopts a binuclear structure, in which the two Ti atoms are bridged by two hydride ligands and one  $[\text{N}=\text{N}]^{2-}$  species in a side-on/end-on fashion (Figure 1, top). The  $\eta^1$  Ti1–N2 bond distance (1.887(2) Å) is significantly shorter than that of the  $\eta^2$  Ti1–N1 bond (2.057(2) Å), but comparable with that of the  $\eta^2$  Ti2–N1 1.850(2) bond, showing that the  $\mu_2$ -N1 bridge is highly asymmetric. The N1–N2 bond distance (1.301(3) Å) is comparable with that of the  $[\text{N}=\text{N}]^{2-}$  unit in  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Dy}\}(\mu_2, \eta^2, \eta^2\text{-N}_2)$  (1.305(6) Å),<sup>3c</sup> and is slightly shorter than that of the  $[\text{N}=\text{N}]^{4-}$  unit in  $\{[(\text{NPN})\text{-Ta}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu_2\text{-H})_2\}$  (1.319(4) Å, NPN =  $\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$ ).<sup>9</sup> The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **2** (or **2-<sup>15</sup>N**) showed broad signals, which were not informative. The

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Scheme 1. Activation and Hydrogenation of  $^{15}\text{N}_2$  by  $\text{H}_2$  at a PNP-Ligated Titanium Platform

**Figure 1.** ORTEP drawings of **2** (top) and **3** (bottom) with 30% thermal ellipsoids. Hydrogen atoms (except H1 and H2) and the  $i\text{Pr}$  groups on the P are omitted for clarity.

$^{15}\text{N}\{^1\text{H}\}$  NMR spectrum of **2- $^{15}\text{N}$**  at  $-10\text{ }^\circ\text{C}$  showed two broad multiplets centered at  $\delta_{\text{N}}$  351.0 and 57.9 (using  $\text{MeNO}_2$  as a standard reference), respectively, which could be assigned to the two nitrogen atoms in the  $[\text{N}=\text{N}]^{2-}$  moiety.

Complex **2** represents a rare example of side-on/end-on dinitrogen complexes,<sup>9</sup> as well as a rare example of dinitrogen complexes formed by  $\text{N}_2$  activation with  $\text{H}_2$  or  $\text{H}_2$ -derived transition metal hydrides.<sup>2b,9,10</sup> To gain more information on the formation of **2**, the hydrogenolysis of **1** in the absence of  $\text{N}_2$  was carried out to obtain an  $\text{N}_2$ -free titanium hydride complex.<sup>8a,9,15</sup> The  $^1\text{H}$  NMR monitoring of the reaction in cyclohexane- $d_{12}$  at room temperature showed complete disappearance of **1** within 20 min, with release of  $\text{SiMe}_4$  and formation of a hydride species plausibly assignable to a binuclear titanium(III) tetrahydride complex like **H** (Scheme 1). However, the hydride species **H** was not stable, and decomposed to a complicated product mixture in several hours. When a pentane solution of the reaction mixture was left at  $-35\text{ }^\circ\text{C}$  for 2 months, several single crystals of a new

compound were precipitated, which was revealed by an X-ray diffraction analysis to be a PNP-ligated binuclear titanium trihydrido/diisopropylphosphido complex  $\{[(\text{PNP})\text{Ti}]_2(\text{P}^i\text{Pr}_2)(\mu_2\text{-H})_3\}(\text{H}')$  (see Supporting Information). The formation of the  $\text{P}^i\text{Pr}_2$  unit in **H'** may suggest that the initially generated hydride species **H** is highly reactive and could break a C—P bond of the PNP ligand. This is in sharp contrast with the analogous NPN-ligated binuclear tantalum tetrahydride complex  $\{[(\text{NPN})\text{Ta}]_2(\mu_2\text{-H})_4\}$  (NPN =  $\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$ )<sup>9</sup> as well as with the  $\text{C}_5\text{Me}_4\text{SiMe}_3$ -ligated trinuclear titanium heptahydride complex  $\{[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3(\mu_3\text{-H})(\mu_2\text{-H})_6\}$ ,<sup>8a</sup> either of which was isolable without apparent reaction with the ancillary ligands.<sup>16</sup>

In spite of this instability, when the hydride **H**-containing reaction mixture (prepared from **1**+ $\text{H}_2$  within 20 min) was exposed to an  $\text{N}_2$  atmosphere at room temperature for 3 h, the dinitrogen complex **2** was isolated in 45% yield, suggesting that the hydride species **H** could be trapped by  $\text{N}_2$  and this  $\text{N}_2$ -activation reaction could be even faster than the decomposition reactions such as the C—P bond cleavage of a PNP ligand. Monitoring of the reaction of **1** with a 1:1  $\text{H}_2$ : $^{15}\text{N}_2$  mixture (2 atm) in cyclohexane- $d_{12}$ /hexane by the  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{15}\text{N}$  NMR spectroscopy showed complete disappearance of **1** within 20 min and simultaneous formation of some unidentified  $^{15}\text{N}_2$ -incorporated titanium species, which after 3 h at room temperature afforded **2- $^{15}\text{N}$**  as a major product (Scheme 1). The hydride species **H** was not observed in this case. These results again demonstrate that the hydride species **H** generated in situ from the reaction of **1** with  $\text{H}_2$  could rapidly react with  $\text{N}_2$ .<sup>8,9</sup>

The dinitrogen complex **2** or **2- $^{15}\text{N}$**  was quite stable at room temperature under an inert atmosphere. When heated at  $60\text{ }^\circ\text{C}$  under argon for 2 days, about 10% of **2- $^{15}\text{N}$**  decomposed into unidentified products. In contrast, when **2- $^{15}\text{N}$**  was heated under an  $\text{H}_2$  atmosphere (1 atm) at  $60\text{ }^\circ\text{C}$  for 2 days, a  $\mu_2$ -imido/ $\mu_2$ -nitrido/hydrido titanium complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2\text{-}^{15}\text{NH})(\mu_2\text{-}^{15}\text{N})\text{H}\}$  (**3- $^{15}\text{N}$** ) was formed in 76% yield through the cleavage and partial hydrogenation of the  $[\text{N}=\text{N}]^{2-}$  unit (Scheme 1). Alternatively, **3- $^{15}\text{N}$**  could also be obtained by the reaction of **1** with a 1:1  $\text{H}_2$ : $^{15}\text{N}_2$  mixture (2 atm) in hexane at  $60\text{ }^\circ\text{C}$  for 2 days (Scheme 1), and this transformation could be achieved even at room temperature though a longer reaction time (2 weeks) was needed.

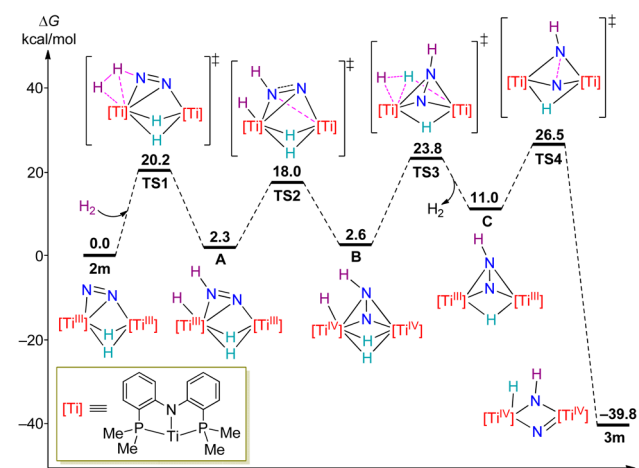
Single crystals of  $\{[(\text{PNP})\text{Ti}]_2(\mu_2\text{-NH})(\mu_2\text{-N})\text{H}\}$  (**3**), which was synthesized by the reaction of **1** with  $\text{H}_2$  and  $\text{N}_2$ , were grown from a hexane solution at  $-35\text{ }^\circ\text{C}$ . An X-ray diffraction study established that **3** adopts a binuclear structure, in which the two Ti atoms are bridged by an imide nitrogen atom (N1) and a nitride atom (N2) (Figure 1, bottom). One (Ti1) of the two Ti atoms is bonded to a terminal hydride ligand (H2), whereas both Ti atoms each bear a PNP pincer ligand in a similar bonding mode. Therefore, one Ti atom (Ti1) in **3** is six-coordinated to three N atoms, two P atoms, and one H atom in a distorted octahedral fashion, while the other Ti atom (Ti2) is five-coordinated to three N atoms and two P atoms in a distorted triangular bipyramidal form, in which the P3, P4, and N2 atoms are located at the equatorial positions and the N1 and N4 atoms occupy the axial positions. The bond length of the Ti1—N1(imide) bond (2.031(4) Å) is significantly longer than that of the Ti2—N1(imide) bond (1.856(4) Å), suggesting that the Ti—imide bridge is asymmetric. Similarly, the Ti—nitride bridge is also asymmetric, with the bond length

of the Ti1—N2(nitride) bond (1.874(3) Å) being much longer than that of the Ti2—N2(nitride) bond (1.768(3) Å).

The  $^1\text{H}$  NMR spectrum of **3** in THF- $d_8$  showed two sets of signals in an almost 1:1 ratio. The imide NH unit appeared as two doublets at  $\delta_{\text{H}}$  13.04 (d,  $^3J_{\text{P-H}} = 10.4$  Hz) and 12.66 (d,  $^3J_{\text{P-H}} = 10.4$  Hz), respectively. The Ti—H hydride gave two signals as a doublet of doublet located at  $\delta_{\text{H}}$  8.63 (dd,  $^2J_{\text{P-H}} = 35.0$ , 34.8 Hz) and 8.45 (dd,  $^2J_{\text{P-H}} = 35.4$ , 44.2 Hz), respectively. The  $^{31}\text{P}$  NMR spectrum of **3** showed eight resonances in a chemical shift range of  $\delta_{\text{P}}$  8.8–20.9. Similarly, the  $^{15}\text{N}$  NMR spectrum of **3**- $^{15}\text{N}$  showed two peaks for the  $^{15}\text{N}$ -imido unit at  $\delta_{\text{N}}$  70.5 (s) and 74.3 (s), and two peaks for the  $^{15}\text{N}$ -nitrido unit at  $\delta_{\text{N}}$  544.0 (s) and 547.0 (d,  $^2J_{\text{P-N}} = 4.3$  Hz), respectively. The VT (variable temperature) NMR spectrum of **3** or **3**- $^{15}\text{N}$  did not show much difference in a temperature range of  $-60$  to  $+60$  °C. These results suggest that complex **3** could exist in two rather stable stereoisomers, which are distinguishable on the NMR time scale in solution.<sup>17</sup>

The formation of the imide/nitride complex **3** from **2** is in sharp contrast with what was observed previously in the case of the analogous binuclear transition metal dinitrogen complexes generated by  $\text{N}_2$  activation with  $\text{H}_2$  or  $\text{H}_2$ -derived metal hydrides, such as  $\{[(\text{NPN})\text{Ta}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu_2\text{-H})_2\}$  (NPN =  $\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$ ),<sup>9</sup>  $\{[(\text{Me}_2\text{Si}(\text{Cp}')_2\text{Zr})_2(\mu_2, \eta^2, \eta^2\text{-N}_2)]\}$  (Cp' =  $\text{C}_5\text{H}_2\text{-2-SiMe}_3\text{-4-}^t\text{Bu}$ ),<sup>10a</sup> and  $\{[(\text{C}_5\text{H}_2\text{-1,2,4-Me}_3\text{-Ti})_2(\mu_2, \eta^2, \eta^2\text{-N}_2)]\}$ ,<sup>10b</sup> which either did not react with  $\text{H}_2$  or regenerated the hydride species with release of  $\text{N}_2$  upon reaction with  $\text{H}_2$ .

To gain information on the mechanistic aspect of the transformation of **2** to **3**, we then performed the density functional theory (DFT) calculations. The computed energy profile of the most favorable pathway is shown in Figure 2 (see



**Figure 2.** Computed energy profile for the transformation of **2m** (a model of **2**) to **3m** (a model of **3**) in the presence of  $\text{H}_2$ .

Supporting Information for more details). Addition of  $\text{H}_2$  across to a Ti—N bond in **2m** (a model of **2**) could take place via a transition state **TS1** with an energy barrier of 20.2 kcal/mol to give intermediate **A**. The isomerization of the  $\mu_2, \eta^1, \eta^2\text{-(HN=N)}$  unit in **A** to a  $\mu_2, \eta^2, \eta^2\text{-(HN=N)}$  unit accompanied by the reduction of the  $\text{HN=N}$  double bond to a  $\text{HN-N}$  single bond and the oxidation of the two Ti(III) sites to Ti(IV) could give intermediate **B**. Release of one molecule of  $\text{H}_2$  from **B** by the reductive elimination of two hydride ( $\text{H}^-$ ) ligands from the Ti(IV) sites then takes place via **TS3** to give

intermediate **C**, in which the two titanium sites are formally reduced to Ti(III). Finally, cleavage of the N—N bond accompanied by the oxidation of Ti(III) to Ti(IV) affords the thermodynamically stable imide/nitride product **3m**, which is equivalent to **3** observed experimentally. The whole transformation of **2m** to **3m** is exergonic by 39.8 kcal/mol. The overall energy barrier is 26.5 kcal/mol, which is reasonable in view of the experimental conditions (60 °C, 2 days).

To see if the transformation of **2** to **3** could take place without the aid of external  $\text{H}_2$ , the intramolecular hydrogen migration from titanium to the dinitrogen unit in **2m** was also computed. It was found that this process requires overcoming an energy barrier of more than 32 kcal/mol (see Supporting Information), suggesting that an intramolecular hydrogen migration would be difficult under the current experimental conditions (60 °C). This is in contrast with what was observed in the dinitrogen activation by the trinuclear titanium polyhydride complex  $\{[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3(\mu_3\text{-H})(\mu_2\text{-H})_6\}$ , in which N—N bond cleavage and N—H bond formation occurred in an intramolecular fashion without need for external  $\text{H}_2$ .<sup>8a</sup>

In summary, we have demonstrated that a PNP-ligated titanium complex can serve as a unique platform for dinitrogen activation. The hydrogenolysis of the dialkyl complex **1** with  $\text{H}_2$  in the presence of  $\text{N}_2$  easily yielded the side-on/end-on dinitrogen complex **2** possibly via a tetrahydride species like **H**. The reaction of **2** with  $\text{H}_2$  at 60 °C or room temperature enabled the hydrogenation and cleavage of the dinitrogen unit, leading to formation of the mixed imido/nitrido/hydrido complex **3**. The DFT calculations revealed that the transformation of the dinitrogen unit in **2** to the imido/nitrido species in **3** is initiated by the hydrogenation of the dinitrogen unit with an external  $\text{H}_2$ , followed by release of another molecule of  $\text{H}_2$  from the titanium framework and the subsequent cleavage of the N—N bond. This work constitutes the first example of dinitrogen cleavage and hydrogenation by  $\text{H}_2$  in a well-defined molecular system without the preactivation of  $\text{N}_2$  by other reducing agents.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13323.

Experimental details, spectroscopic and analytical data, crystallographic data and DFT calculation (PDF)

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### Notes

The authors declare no competing financial interest.

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