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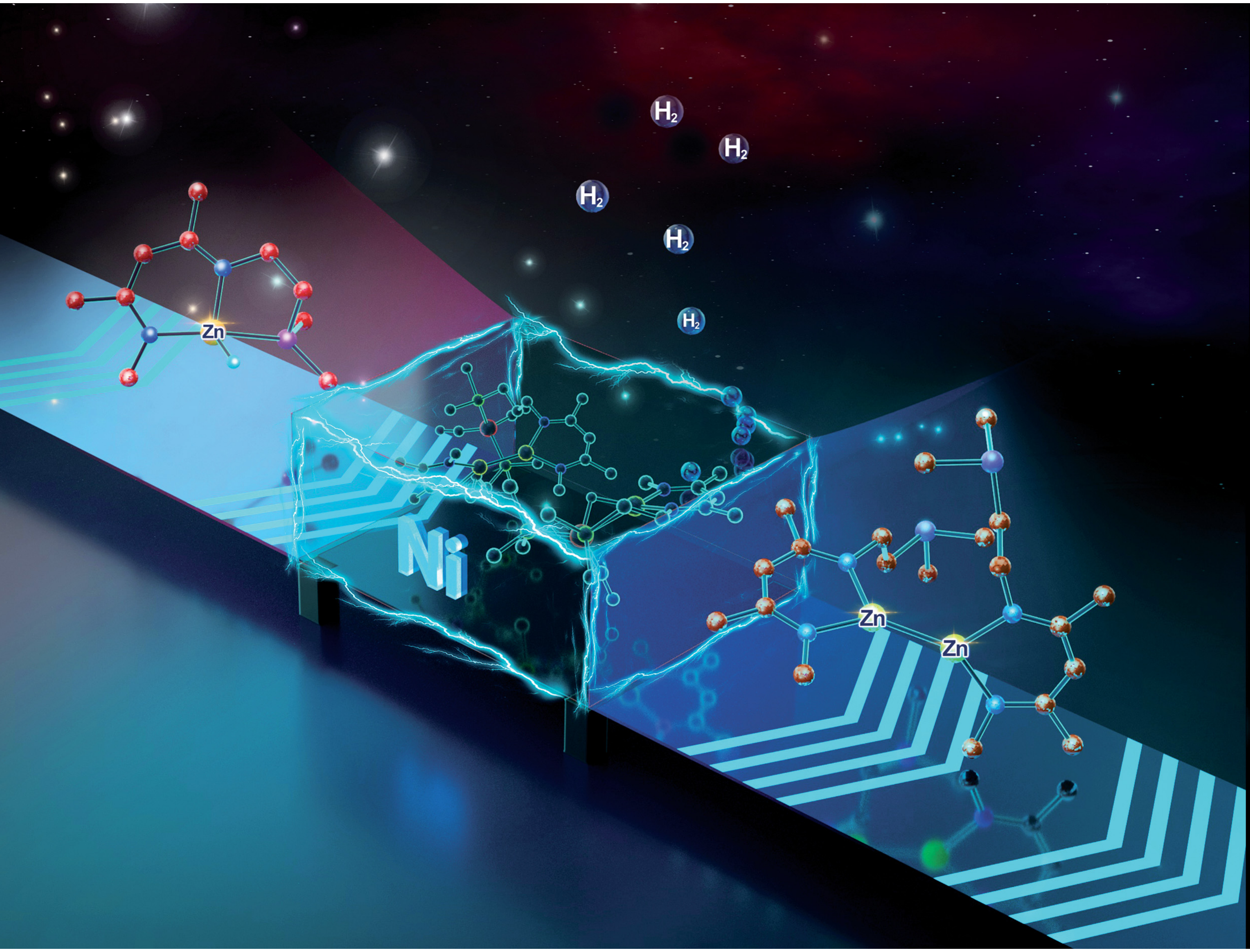

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Nickel-catalyzed synthesis of Zn(I)–Zn(I) bonded compounds†

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Laurent Maron *[b] and Xin Xu *[a]

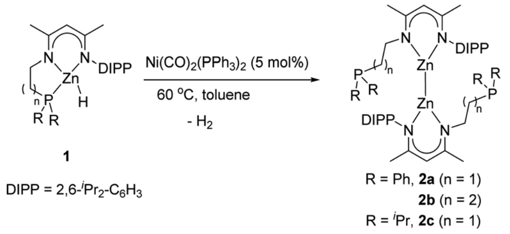
This work reports the first catalyzed synthesis of d-block metal–metal bonded complexes. The treatment of terminal zinc hydrides [LZnH] [L = $CH_3C(2,6\text{-}^iPr_2C_6H_3N)CHC(CH_3)(N(CH_2)_nCH_2PR_2)$; *n* = 1, 2; R = Ph, ^{i}Pr] in the presence of 5 mol% $Ni(CO)_2(PPh_3)_2$ afforded Zn(I)–Zn(I) bonded compounds $[L_2Zn_2]$ in high isolated yields with concomitant elimination of dihydrogen. Stoichiometric reactions, kinetic studies and DFT calculations were conducted to elucidate the reaction mechanism.

Catalytic reactions that enable bond formation play a pivotal role in synthetic chemistry.[1] In this respect, transition metal-catalyzed C–C bond-forming reactions are pervasive in the synthesis of organic molecules and macromolecules.[2–5] Bond formation between other p-block elements through catalytic processes has also been well-established;[6] the generation of homonuclear B–B,[7] Si–Si,[8] and P–P[9] bonds by metal-catalyzed dehydrocoupling reactions are representative examples. In contrast, catalyzed synthesis of d- and s-block metal–metal bonds is unknown.

The study of metal–metal bonding is of fundamental importance for furthering our understanding of chemical bonds, catalysis, and bioinorganic chemistry as well as metal surface chemistry.[10,11] To date, all reported d- or s-block metal–metal bonded complexes have been prepared *via* stoichiometric reactions, such as reduction, ligand redistribution, alkane/salt elimination, *etc.* Among these methods, reducing reactions with alkali metal-based reductants provide major access to low-valent metal–metal bonded compounds.[12] However, this method is disfavored because of potential safety hazards and the formation of stoichiometric metal halide by-products.

We herein found that a commercially available nickel(0) reagent, $Ni(CO)_2(PPh_3)_2$, was an efficient catalyst for the synthesis of Zn(I)–Zn(I) bonded compounds from Zn(II) hydrides, with concomitant elimination of H_2 as the only by-product. This is the first example of the catalyzed synthesis of d-block metal–metal bonded compounds. To shed light on the catalysis mechanism, we isolated and characterized a series of Zn/Ni heterometallic intermediates and conducted NMR kinetic studies.

In our prior work, we found that a palladium(0) reagent $Pd(PPh_3)_4$ could induce stoichiometric dehydrocoupling of NNP ligand-based zinc hydrides to form the corresponding trimetallic products;[13] however, this reagent is not applicable to a catalytic reaction. Encouraged by this result, some other widely used Pd and Ni reagents, such as $Pd(OAc)_2$, $Pd(dba)_2$ (dba = dibenzylideneacetone), $Pd_2(dba)_3$, $(C_3H_5)PdCl$, $Ni(COD)_2$, and $NiCl_2(PPh_3)_2$, were also screened under catalytic conditions (5 mol% catalyst loading, 60 °C, and 24 h), but none were effective. Gratifyingly, when a commercially available Ni(0) catalyst, $Ni(CO)_2(PPh_3)_2$, was applied under the given conditions, Zn(II) hydride **1a** was completely transformed into Zn(I)–Zn(I) bonded compound **2a** (an 85% isolated yield) with the release of H_2, as evidenced by the corresponding NMR reaction (Scheme 1). Moreover, such a Ni-catalyzed dehydrocoupling reaction could also tolerate other tridentate NNP ligand-based zinc hydrides, affording the corresponding dizinc complexes



Scheme 1 Catalytic dehydrocoupling of zinc hydrides with $Ni(CO)_2(PPh_3)_2$.

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(Scheme 1). However, different reaction times were required for **2b** (13 h, 83%) and **2c** (24 h, 64%) to achieve a satisfactory yield, indicating that the length of the pendant arm significantly affects the rate of the catalytic reaction. When using (Dipp-nacnac)ZnH[14] (Dipp-nacnac = [{(2,6-^{i}Pr$_2$C$_6$H$_3$)N(Me)C}$_2$CH]) as a substrate, however, no dehydrocoupling product was obtained, even under harsher conditions (10 mol% [Ni] catalyst, 80 °C, and 36 h). Hence, it is inferred that the pendant phosphine arm on the β-diketiminato ligand framework plays a crucial role for this catalytic dehydrogenation reaction.

Thermal dehydrogenation of metal hydrides to form the corresponding metal–metal bonded complexes has been reported for group 12 elements.[15] Thus, a control experiment in which zinc hydrides **1** were treated under typical reaction conditions (60 °C, 24 h) in the absence of a nickel catalyst was also examined, which did not give any dehydrocoupling product and complex **1** remained unreacted. This was further confirmed by DFT calculations, which showed an inaccessible energy barrier up to 35.1 kcal mol^{-1} (for details, see Fig. S50 in the ESI†).

Complex **2a** was comprehensively characterized by elemental analysis, multinuclear NMR spectroscopy, and single crystal X-ray diffraction. The molecular structure of **2a** (Fig. 1) showed a homonuclear bimetallic framework with a direct Zn–Zn bond. The bond length of Zn1–Zn2 was found to be 2.371(1) Å, comparable with those in other reported Zn–Zn bonded compounds supported by β-diketiminato ligands, *i.e.*, (Dipp-nacnac)$_2$Zn$_2$ (2.3586(7) Å)[16] and (Mes-nacnac)$_2$Zn$_2$ (2.3813(8) Å) (Mes-nacnac = [{(2,4,6-Me$_3$C$_6$H$_2$)N(Me)C}$_2$CH]).[17] The coordination geometry of each zinc atom (ΣZn1^{ZnNN} = 359.7(2)° and ΣZn2^{ZnNN} = 359.9(2)°) is planar tricoordinate with a pendant phosphine arm becoming dissociated from zinc during the course of the reaction. Each zinc atom is located on the plane of the delocalized monoanionic *β*-diketiminato ligand and two ligands are arranged in a nearly orthogonal orientation with a N1–Zn1–Zn2–N3 torsion angle of 81.9(2)°. Both complexes **2b** and **2c** showed similar spectroscopic properties and structural data to those of **2a**, with selected data shown in Table 1 for comparison (for details including molecular structures, see the ESI†).

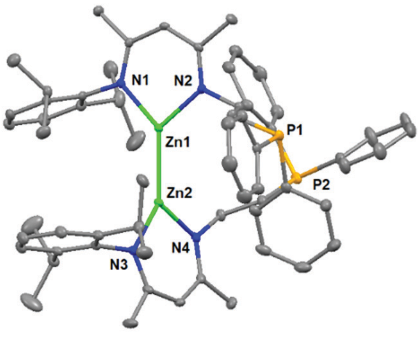


Fig. 1 Molecular structure of complex **2a**. Hydrogen atoms are omitted for clarity, and displacement ellipsoids are drawn at the 30% probability level.

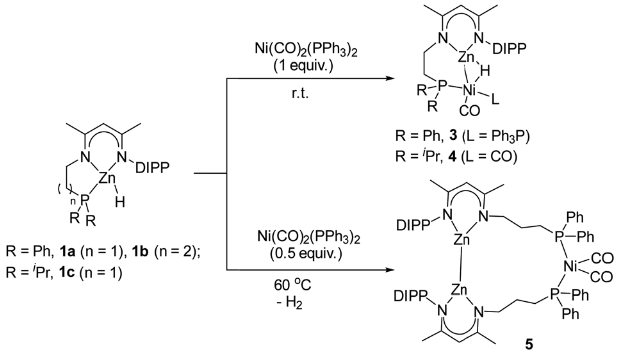
Table 1 Selected structural data and ^{31}P{^{1}H} NMR of Zn–Zn bonded compounds **2**[a]

Compounds	**2a**	**2b**	**2c**
Zn1–Zn2	2.371(1)	2.334(1)	2.342(2)
Zn1–N1	1.987(2)	1.985(2)	1.979(2)
Zn1–N2	2.007(2)	1.968(2)	1.987(2)
Zn2–N3	1.986(2)	1.984(2)	1.972(2)
Zn2–N4	2.000(2)	1.977(2)	1.991(2)
ΣZn1^{ZnNN}	359.7(2)	358.1(2)	359.4(3)
ΣZn2^{ZnNN}	359.9(2)	359.0(3)	359.3(4)
N1–Zn1–Zn2–N3	81.9(2)	133.5(2)	83.4(1)
^{31}P{^{1}H}	−20.5	−16.9	0.6
^{31}P{^{1}H} of the ligand	−21.5	−16.6	−1.5

[a] Bond lengths in Å, angles in deg, and NMR in ppm (C$_6$D$_6$).

The bonding properties of Zn(I)–Zn(I) bonded compound **2a** were further studied by DFT calculations. Natural bonding orbital (NBO) analysis found a Zn–Zn bond that was fully covalent and, as expected, not polarized (50–50%). This bond involved *sp* hybrid orbitals on each Zn (78%s + 22%p), which has a lower s character compared with the reported Zn–Zn bonds,[16,17] and appeared to be the HOMO−2 molecular orbitals (see Fig. S51 in the ESI†). The Wiberg bond index (WBI) was 0.97 in line with a highly covalent Zn–Zn bond.

To gain more insights into this Ni-catalyzed dehydrocoupling reaction, stoichiometric reactions of zinc hydrides **1** with the Ni(0) reagent Ni(CO)$_2$(PPh$_3$)$_2$ were performed (Scheme 2). Initially, the reaction of **1a** with the Ni reagent in a 1 : 1 molar ratio gave the hydride-bridged heterobimetallic [Zn–H–Ni] complex **3** in 61% isolated yield, which was unambiguously characterized by elemental analysis, multinuclear NMR spectroscopy, and single crystal X-ray diffraction. The solid-state structure of complex **3** (Fig. 2) showed that Zn–H was bound to the Ni center [Zn1–Ni1 2.348(1) Å, Zn1–H1 1.68(3) Å, Ni1–H1 1.58(4) Å, and Zn1–H1–Ni1 92.0(2)°] in an η^2-fashion, indicating a stretched σ–Zn–H complex.[18] The coordination sphere of the nickel center was completed by one pendant PPh$_2$ group [Ni1–P1 2.183(1) Å], one PPh$_3$ ligand [Ni1–P2 2.180(1) Å] and one CO ligand [Ni1–C32 1.727(4) Å]. In the solution-state ^{1}H NMR spectrum, the bridged hydride signal was clearly observed at a high field at δ -3.47 ppm.[19] The reaction of zinc hydride **1c** with Ni(CO)$_2$(PPh$_3$)$_2$ (1 equiv.) produced the



Scheme 2 Stoichiometric reactions of zinc hydrides **1** with Ni(CO)$_2$(PPh$_3$)$_2$.

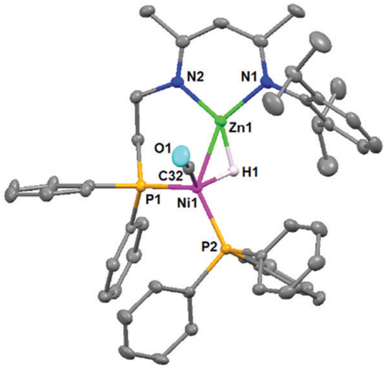


Fig. 2 Molecular structure of complex **3**. Hydrogen atoms (except Zn–H) are omitted for clarity, and displacement ellipsoids are drawn at the 30% probability level.

analogous [Zn–H–Ni] complex **4** in 73% yield (Scheme 2). Complex **4** features similar spectroscopic properties and structural data to those of **3**, with the molecular structure shown in Fig. S33 in the ESI.† In contrast, the reaction of zinc hydride **1b** with one equivalent of $Ni(CO)_2(PPh_3)_2$ under the same conditions afforded several undefined species.

Subsequently, the treatment of zinc hydride **1b** with a 0.5 molar equivalent Ni reagent was also investigated (Scheme 2), yielding complex **5** as a colorless solid in 67% isolated yield with the concomitant release of the H_2 and PPh_3 ligands. However, the analogous product could not be obtained for zinc hydride **1a** or **1c** under the same conditions, highlighting that the length of the pendant phosphine arm plays a crucial role in the stability of reaction intermediates. Single crystals of complex **5** were obtained from a layered toluene/hexane solution at room temperature. The solid-state structure of complex **5** (Fig. 3) showed a thirteen-membered metallacycle containing a Zn–Zn bond with a bond length of 2.378(1) Å, comparable with other unsupported Zn(I)–Zn(I) bonds.[20] The excessively long Ni···Zn distances (>6.9 Å) also rule out the Ni···Zn interaction. The four-coordinate nickel center was found to be completed by pairs of phosphine ligands [Ni1–P1 2.217(1) Å and Ni1–P2 2.213(2) Å] and CO ligands [Ni1–C65 1.777(3) Å and Ni1–C66 1.770(3) Å]. During the course of this reaction, dehydrocoupling of the Zn–H to the Zn–Zn bond occurred. Notably, all three isolated heterometallic complexes **3**, **4**, and **5** enabled the formation of the final Zn–Zn bonded complex **2** under the above catalytic conditions (for more details, see the ESI†), suggesting their possible involvement in the catalytic cycle.

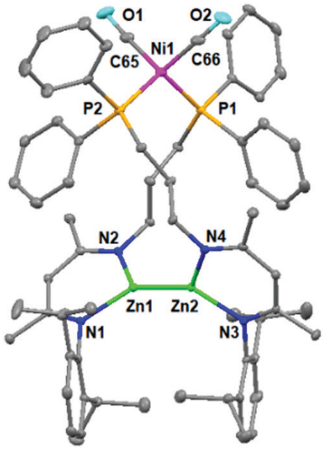
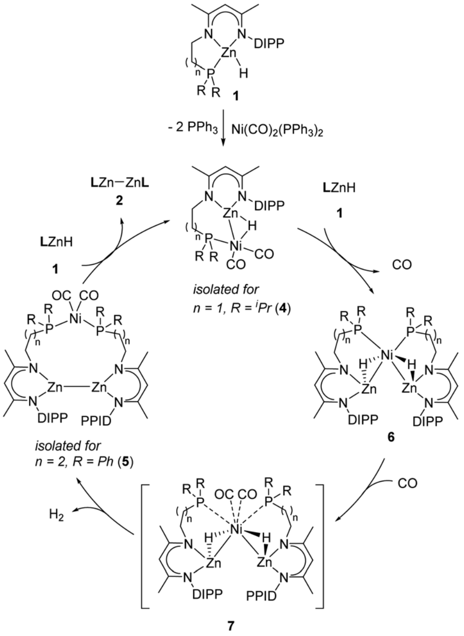


Fig. 3 Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity, and displacement ellipsoids are drawn at the 30% probability level.

Kinetic studies of the catalytic dehydrocoupling reactions were also performed by varying the catalyst loading in the range of 5–15 mol% and monitoring by ^1H NMR spectra (for details, see the ESI†). In all cases, zero-order kinetic behaviors were observed on zinc hydride **1a**. As a result, a first-order dependence on $[Ni(CO)_2(PPh_3)_2]$ was obtained (Fig. S44 in the ESI†). The replacement of substrate **1a** (Zn–H) with the deuterium-labeled complexes **1a–d** (Zn–D) resulted in a kinetic isotope effect (KIE) of 1.04(5) (Fig. S39 in the ESI†), suggesting that Zn–H bond cleavage is unlikely to be involved in the rate-determining step of catalysis. The activation parameters for the current reaction were accessed through Eyring analyses at five different temperatures from 50 °C to 70 °C ($\Delta H^{\ddagger}$ = 14.4(4) kcal mol^{-1}, $\Delta S^{\ddagger} = -37.8(13)$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger}$ = 25.7(8) kcal mol^{-1} at 298.2 K) (Fig. S49 in the ESI†). The large negative value of $\Delta S^{\ddagger}$ is indicative of an associative mechanism.

Based on the above investigation, we proposed a plausible mechanistic framework for the Ni-catalyzed Zn–Zn bond formation as shown in Scheme 3. The reaction is initiated by the coordination of the Zn–H bond to the Ni center to give a σ–Zn–H complex, similar to the transition metal-catalyzed dehydrocoupling of p-block compounds.[6,21] The resultant complex then reacts with another molecule of zinc hydride, possibly to produce the hydride-bridged [Zn–Ni–Zn] species **6**



Scheme 3 Plausible mechanistic framework for Ni-catalyzed synthesis of Zn–Zn bonded compounds.

with the release of CO ligands, which can also be obtained from the reaction of zinc hydride with $Ni(COD)_2$.[13] In addition, complex **6** can also be used as a catalyst for the current transformation when placed under a CO atmosphere (see the ESI,† for details). Complex **6** is unstable in the presence of CO and undergoes H_2 elimination[19] to form the heterotrimetallic [Zn–Zn][Ni] complex *via* the inferred intermediate **7**. The direct conversion of complex **4** to **7** is unlikely to occur due to a zero-order kinetic behavior observed for **LZnH** (**1**). Further reaction of the [Zn–Zn][Ni] complex with zinc hydride produces the Zn–Zn bonded product **2**, with the regeneration of the σ-Zn–H complex to complete the catalytic cycle.

In summary, the nickel-catalyzed dehydrocoupling of zinc hydrides to Zn–Zn bonded compounds was successfully achieved. Mechanistic studies revealed that the catalytic reaction is initiated by the formation of a σ-Zn–H complex, similar to the transition metal-catalyzed synthesis of p-block element–element bonds. We propose that the NNP ligand employed in this study plays a crucial role for the reaction, because such a bifunctional ligand brings together the zinc hydride substrate and the transition metal catalytic center, thus facilitating the formation of a Ni···H–Zn σ-complex and the following dehydrocoupling reaction. This work realizes the first example of d-block metal–metal bond formation in a catalytic fashion and may offer a new pathway to construct a broader range of metal–metal bonds.

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Conflicts of interest

There are no conflicts to declare.

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