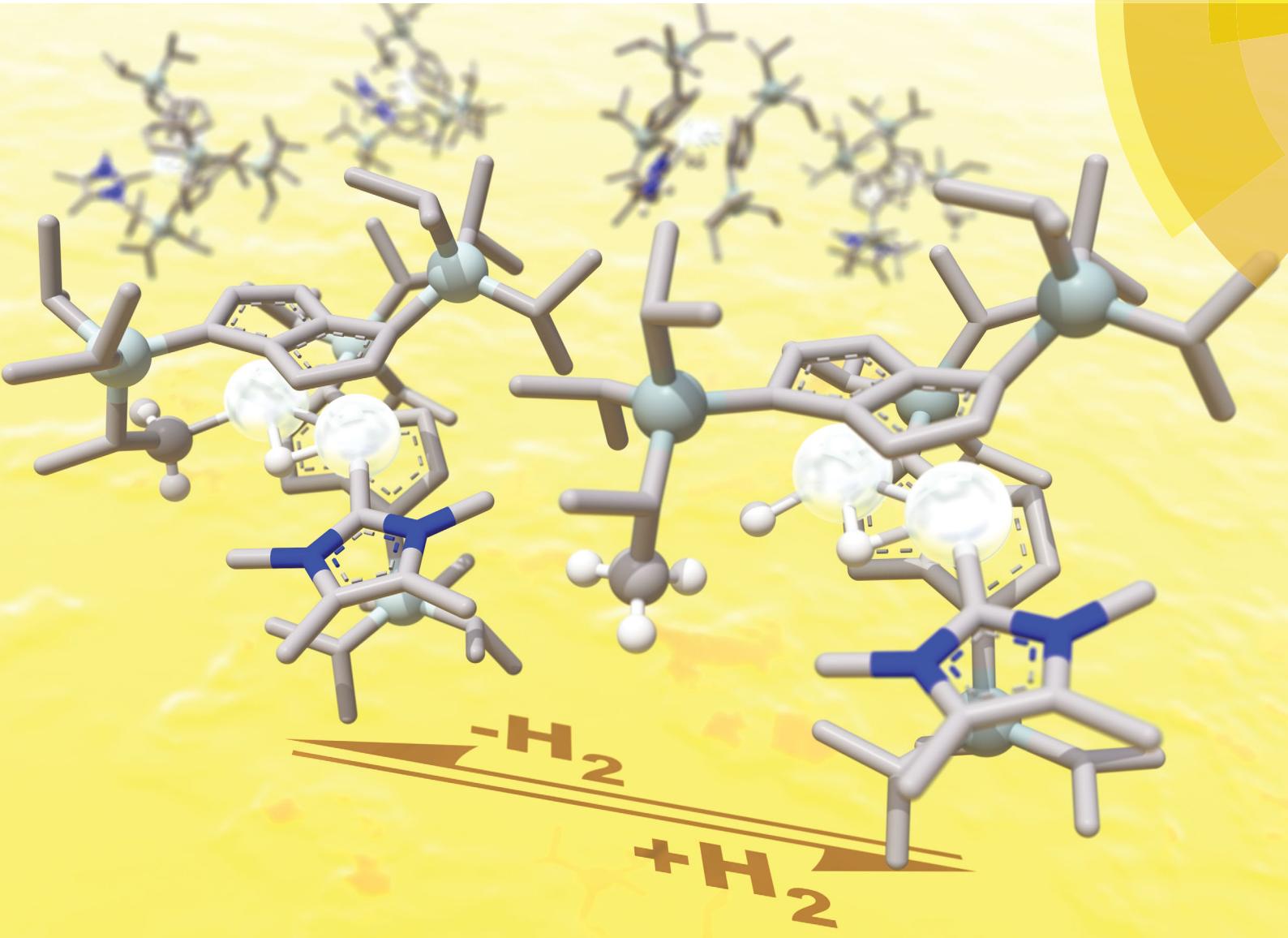


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C–H and H–H activation at a di-titanium centre



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**The reaction of the bis(pentalene)dititanium complex  $\text{Ti}_2(\mu:\eta^5,\eta^5\text{-Pn}^+)_2$  ( $\text{Pn}^+ = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the  $\text{iPr}$  methyl groups of a  $\text{Pn}^+$  ligand and formation of a “tucked-in” bridging hydride complex. The “tuck-in” process is reversed by the addition of hydrogen, which yields a dihydride featuring terminal and bridging hydrides.**

Group IV metallocene chemistry has been instrumental in the development of organometallic chemistry,<sup>1</sup> elucidating fundamental aspects of bonding<sup>2</sup> and reactivity,<sup>3</sup> especially *via* the synthesis, isolation and study of low valent metallocene complexes.<sup>1,4</sup> In this context, the synthesis and isolation of such complexes bearing hydride ligands has been important;<sup>5</sup> for example, such low or mixed valence hydride complexes have been shown to promote or be involved in the fixation of  $\text{N}_2$  to  $\text{NH}_3$ .<sup>6</sup> In this communication, we present the first examples of the synthesis of bridging titanium hydrides under non-reducing conditions, *via* the reaction of bis(pentalene)dititanium complex  $\text{Ti}_2(\mu:\eta^5,\eta^5\text{-Pn}^+)_2$  ( $\text{Pn}^+ = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) with an N-heterocyclic carbene and subsequent hydrogenolysis.

We have previously reported on the reactivity of  $\text{Ti}_2(\mu:\eta^5,\eta^5\text{-Pn}^+)_2$  ( $\text{Pn}^+ = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) (**1**) towards a variety of small molecules and  $\pi$ -acceptor ligands.<sup>7</sup> In order to gain a better insight into the reactivity of (**1**), we decided to study its interaction with strong  $\sigma$ -donor ligands. When (**1**) was treated with an excess of  $\text{PMe}_3$  no reaction was observed. However, addition of 1,3,4,5-tetramethylimidazol-2-ylidene (**2**) to (**1**) in toluene at 0 °C resulted in an immediate colour change from crimson red to a dark pine green (Scheme 1).

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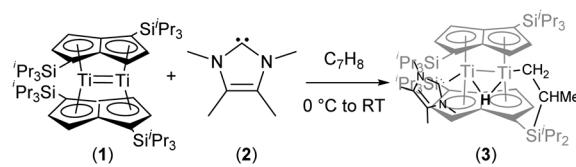
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† Dedicated to Phil on the occasion of his 65th birthday- Lá Breith Sona!

‡ Electronic supplementary information (ESI) available: Full experimental and computational details, and X-ray data. CCDC 1577130–1577132. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc07726b

The formulation of the new complex (**3**) as a “tucked-in” hydride resulting from C–H activation of one of the  $\text{iPr}$  methyl groups of a  $\text{Pn}^+$  induced by addition of the strongly donating NHC (**2**) was initially confirmed by NMR. In particular, the  $^1\text{H}$ -NMR spectrum showed two inequivalent pentalene ring environments, a sharp singlet at –7.91 ppm for the bridging hydride ( $T_1$  479 ms), with one of the diastereotopic protons of the “tucked-in”  $\text{CH}_2$  group appearing as an overlapping dd at –2.91 ppm whilst the other was largely obscured by the complex aliphatic region of the spectrum at *ca* 1.37 ppm; the coordination of the NHC was confirmed by the observation of a peak at 197.78 ppm in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum.

The structure of (**3**) was confirmed by X-ray diffraction and is shown in Fig. 1. The NHC coordinates to one of the Ti centres ( $\text{Ti}_2$  in Fig. 1), while one of the methyl groups on a TIPS substituent has been cyclometallated on the other Ti centre ( $\text{Ti}_1$  in Fig. 1) with concurrent formation of a bridging hydride.<sup>8</sup> The Ti–Ti bond has been retained but lengthened to 2.5610(8) Å (from 2.399(2) Å in (**1**)<sup>7e</sup>) and is typical of a single bond. The Ti–C(carbene) bond (2.300(2) Å;  $\text{Ti}_2\text{-C}1$  in Fig. 1) is within the range of 2.2–2.35 Å reported for other Ti–NHC complexes.<sup>9</sup> The Ti–H bond lengths (*i.e.*  $\text{Ti}_2\text{-H}1$ : 1.72(3) Å,  $\text{Ti}_1\text{-H}1$ : 1.79(3) Å) are identical within esd's and are similar to previously reported monomeric<sup>10</sup> and dimeric<sup>6d,6b,11</sup> titanium hydrides as well as Ti(III) alumino-<sup>12</sup> and borohydrides<sup>13</sup> (1.7–1.9 Å), although it has to be noted that, probably due to the topology of the hydride ligand in (**3**), these Ti–H bond distances fall at the shorter end of the known range. Due to this unique topology, the Ti–H–Ti bond angle (93.4(13)°) approaches a right angle and is the most acute ever observed in dimeric titanium hydrides.<sup>6b,6d,11</sup>



Scheme 1 Synthesis of a new *syn*-bimetallic hydride titanium cluster.



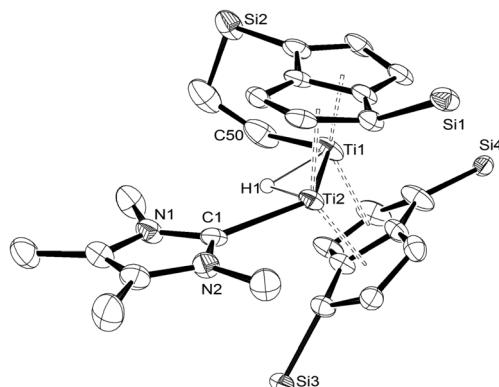


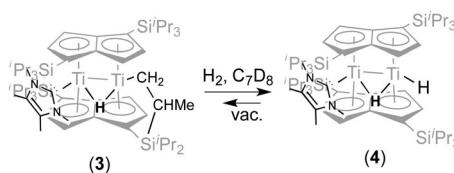
Fig. 1 ORTEP diagram of the molecular structure of (3) displaying 50% probability ellipsoids.  $^1\text{Pr}$  groups omitted for clarity.

It is also worth noting that the addition of (2) to (1) results in the formal oxidation of the two Ti centres (*i.e.* from +2 to +3), and employing the CBC model each Ti has a count of 18 e (16 e in (1)).<sup>14</sup>

With a view to synthesising a new hydride derivative *via*  $\sigma$ -bond metathesis of the Ti-CH<sub>2</sub> bond in (3) with dihydrogen, 2 bar of H<sub>2</sub> was added to a C<sub>7</sub>D<sub>8</sub> solution of (3) in an NMR tube. This indeed resulted in clean conversion of (3) (100% spectroscopic yield) to a new complex (4) (Scheme 2).

Compared to the  $^1\text{H}$  NMR spectrum of (3), (4) displays a new, broader hydride peak ( $\Delta\nu_{1/2} = 29$  Hz) at  $-8.82$  ppm at room temperature, whilst the signal for the “tucked-in” CH<sub>2</sub> group has disappeared completely; the NHC is still coordinated ( $^{13}\text{C}\{^1\text{H}\}$   $\delta$  198.27 ppm). Removal of the H<sub>2</sub> overpressure by freeze-thaw-degassing showed that (4) is persistent in solution, although some regeneration of (3) was observed (Scheme 2). Addition of H<sub>2</sub> to a solution of (3), *via* a Toepler pump, showed that for the conversion of (3) to (4) to occur quickly (minutes) 5 eq of H<sub>2</sub> are required (when 1–2 equivalents of H<sub>2</sub> were added, complete conversion to (4) occurred after *ca.* 1 week). The rate of reaction was also found to be pressure dependent: when (3) was exposed to an atmosphere of 10% H<sub>2</sub> in N<sub>2</sub> at 1.5 bar but in an amount corresponding to only 1 equivalent of H<sub>2</sub> the reaction was again complete in minutes.

Variable temperature  $^1\text{H}$  NMR studies showed that the broad hydride peak at  $-8.82$  ppm in (4) becomes fully resolved into a doublet at  $0\text{ }^\circ\text{C}$  (with no further change below that temperature and down to  $-70\text{ }^\circ\text{C}$ ) with a T<sub>1</sub> of 310 ms, with the concomitant appearance of a second doublet centred at  $2.17$  ppm (T<sub>1</sub> 336 ms), which is too broad to be observable at room temperature (Fig. 2); these two signals are related by a coupling constant of  $J_{\text{HH}} = 11$  Hz. EXSY spectroscopy (in both



Scheme 2 Hydrogenolysis of (3) to afford (4)

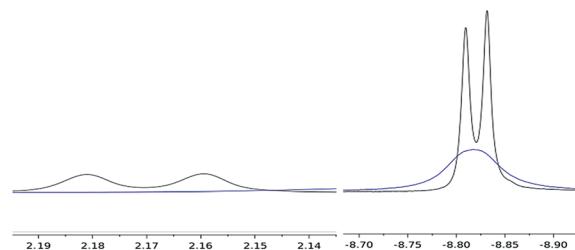


Fig. 2 Hydride peaks in (4) at RT (blue) and at  $0\text{ }^\circ\text{C}$  (black).

the presence and absence of an H<sub>2</sub> overpressure) confirmed that these two protons exchange at  $30\text{ }^\circ\text{C}$  while at  $0\text{ }^\circ\text{C}$  the process is quenched. Thus the peak at  $-8.82$  ppm is assigned to the bridging hydride in (4) and that at  $2.17$  ppm to the terminal one (Scheme 2).

Initial attempts to crystallise (4) by standard methods (*i.e.* removal of volatiles and recrystallisation) were frustrated by the preferential isolation of crystalline (3) (as it is less soluble than (4)) with the mother liquor consisting of a mixture of (3) and (4) (*ca.* 20 : 80 by NMR), due to the partial reversibility of the reaction. However, the solid state molecular structure<sup>8,15</sup> of (4) (Fig. 3) was eventually determined from single crystals grown by cooling slowly a freshly prepared solution of (4) at  $-78\text{ }^\circ\text{C}$  under an overpressure (1.5 atm) of H<sub>2</sub>, and confirms the spectroscopic assignment.

The Ti-C(carbene) bond length in (4) is  $2.291(4)$  Å and is identical to that found in (3). On the other hand, the Ti-Ti bond is slightly shortened in (4) from  $2.5610(8)$  Å in (3) to  $2.5413(8)$  Å possibly due to the negligible steric requirements of the terminal hydride ligand. The Ti-H(bridging) bond distances (Ti1-H1 =  $1.84(5)$  Å; Ti2-H1 =  $1.79(5)$  Å) in (4) are similar within esd's and compare with the ones found in (3); the same applies to the Ti-H(terminal) (*i.e.* Ti2-H2 =  $1.74(4)$  Å in Fig. 2) bond length. The Ti1-H1-Ti2 bond angle in (4) again approaches  $90^\circ$  ( $89(2)^\circ$ ) and is very similar to that found in (3).

When (3) was treated with an excess of D<sub>2</sub> (5 eq.), the formation of (4-D) was observed, but deuterium was found to be only incorporated in the hydridic positions, and not in the new Me group derived from the previously “tucked-in” CH<sub>2</sub> group (confirmed by  $^2\text{H}$ -NMR, DEPT-135 and gHSQC). Hence the reaction of (3) with H<sub>2</sub> to form (4)

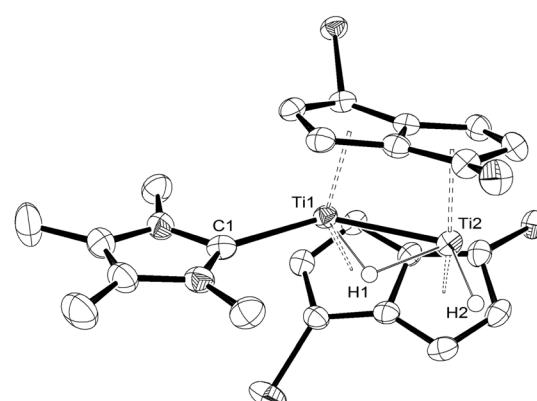


Fig. 3 ORTEP diagram of the molecular structure of (4) displaying 50% probability ellipsoids.  $^1\text{Pr}$  groups omitted for clarity.



**Table 1** Electronic binding energies ( $\Delta E$ ) and Gibbs energy changes ( $\Delta G$ ) for the reaction  $\text{Ti}_2\text{Pn}_2 + \text{NHC} = \text{Ti}_2\text{Pn}_2\text{NHC}$

Ti pentalene dimer	NHC	$\Delta E$ (eV)	$\Delta G^a$ (kJ mol $^{-1}$ )	Ti-Ti-C (°)
$\text{Ti}_2(\text{C}_8\text{H}_6)_2$	$\text{C}_3\text{H}_4\text{N}_2$	-1.31	-66	100
$\text{Ti}_2(\text{C}_8\text{H}_6)_2$	$\text{C}_3\text{Me}_4\text{N}_2$	-1.26	-65	114
$\text{Ti}_2\text{Pn}_2^{\dagger}$	$\text{C}_3\text{Me}_4\text{N}_2$	-0.48	+21	127

<sup>a</sup> Calculations are on gas phase species which leads to an overestimation of the entropy change when there is a change in the number of species.

does not go *via*  $\sigma$ -bond metathesis (which would lead to D incorporation in the Me group in the reaction with  $\text{D}_2$ ). Hence the formation of (4) (and also (3)) was probed computationally (ADF:BP/TZP: details are given in the ESI $\ddagger$ ). Preliminary studies suggested that sterics were important in determining the reaction energies. For example energy of binding an NHC to a  $\text{Ti}_2\text{Pn}_2$  dimer depended critically on the substituents. Introduction of the methyl substituents on the NHC made very little difference to its binding energy but the bulky  $\text{Si}^i\text{Pr}_3$  substituents on the pentalene ligands increased the Ti-Ti-C angle forcing the NHC to a less favourable binding position thus decreasing the binding energy significantly (Table 1).

The degree to which the tuck-in reaction was favoured in the absence of an NHC was also investigated. The formation of  $\text{Ti}_2\text{Pn}_2^{\dagger}(\text{Pn}_2^{\dagger}\text{-H})(\mu\text{-H})$  from  $\text{Ti}_2\text{Pn}_2^{\dagger}$  was calculated to have  $\Delta E = -0.03$  eV and  $\Delta G = 11$  kJ mol $^{-1}$ . However, the energies of the observed tuck-in reaction with the methylated NHC present were calculated to be  $\Delta E = -0.69$  eV and  $\Delta G = 9$  kJ mol $^{-1}$ . Thus the presence of the base improves the energetics of the tuck-in reaction. The significant entropy disadvantage in the gas phase would be lessened in solution.

The HOMO of 3 (Fig. 4) shows a Ti-Ti  $\sigma$ -bond. The calculated Ti-Ti distance is 2.56 Å in excellent agreement with experiment. The Ti-H distances are 1.83 Å and the angle at the bridging hydrogen 89°. Such discrepancies from the experimental values are not unusual when comparing distances to bound hydrogen between theory and X-ray diffraction experiments.

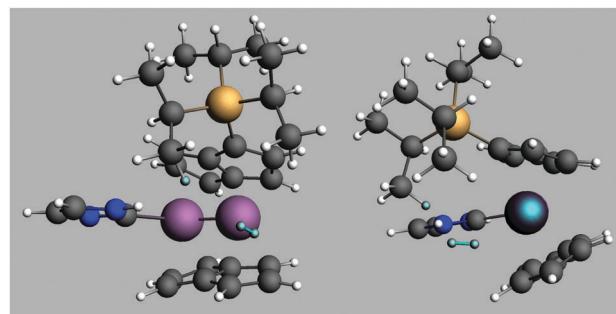


Fig. 5 Structure of the calculated transition state for  $\text{H}_2$  addition. The reacting Hs are highlighted.

Addition of  $\text{H}_2$  to 3 to form 4 is calculated to have reaction energies  $\Delta E = -0.77$  eV and  $\Delta G = -31$  kJ mol $^{-1}$ . The calculated Ti-Ti distance for 4 is 2.54 Å reproducing the shortening from 3 found experimentally. The Ti-H(terminal) distance is 1.74 Å, the Ti-H(bridging) distances 1.81 and 1.82 Å and the Ti-H-Ti angle unchanged at 89°.

A transition state for this reaction was modelled using just one  $\text{Si}^i\text{Pr}_3$  substituent on one of the pentalene ligands and  $\text{C}_3\text{H}_4\text{N}$  as the NHC for computational efficiency. The free energy of activation was estimated as 84 kJ mol $^{-1}$  for such a system. The transition state structure is shown in Fig. 5.

The Ti distance to the previously bridging H is 3.53 Å and the Ti distances to the reacting  $\text{H}_2$  are 2.74 and 3.24 Å, the H-H distance being 0.76 Å. Such a geometry indicates that the tuck-in process is reversed before complete  $\text{H}_2$  addition, consistent with the lack of deuterium incorporation into  $^i\text{Pr}$  groups and the conclusion that  $\sigma$  bond metathesis is not in play. It may be that the steric compression induced by the mere approach of the  $\text{H}_2$  molecule is sufficient to reverse the tuck-in process, an idea given some credence by the pressure dependence of the reaction of (3) with  $\text{H}_2$  (*vide infra*).

In conclusion, we have described the facile preparation of the first example of a *syn*-bimetallic Ti complex (3) featuring a bridging hydride, originating from the C-H activation of a  $^i\text{Pr}$  substituent induced by addition of the strong Lewis base 1,3,4,5-tetramethylimidazol-2-ylidene. Preliminary studies show that this transformation is also effected by other, effectively “planar” Lewis bases, *e.g.* dimethylaminopyridine (DMAP). The resultant C-H activation product (3) readily reacts with an excess of  $\text{H}_2$  to produce very cleanly a unique *syn*-bimetallic di-hydride complex (4) featuring bridging and terminal hydride ligands. Labelling experiments and computational studies strongly suggest that the latter reaction does not proceed *via* a  $\sigma$ -bond metathesis mechanism.

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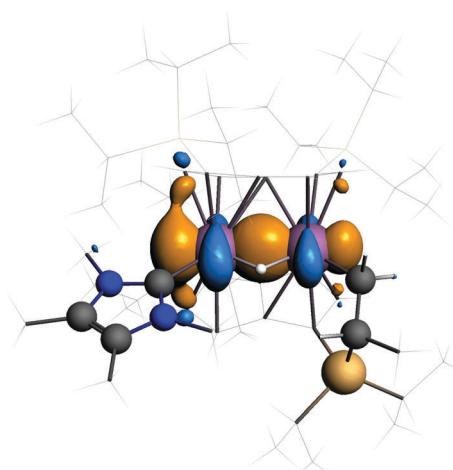


Fig. 4 Isosurface for the HOMO of 3.

## Conflicts of interest

There are no conflicts to declare.



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15 Data were collected up to 0.82 Å resolution using Cu/K $\alpha$  as well up to 0.78 Å using Mo/K $\alpha$  with identical metric parameters.

