Isolation of Diradical Products of Twisted Double Bonds

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Molecules containing multiple bonds between atoms – most often in the form of olefins – are ubiquitous in nature, commerce and science, and as such have a huge impact on everyday life. Given their prominence, over the last few decades frequent attempts have been made to perturb the structure and reactivity of multiply-bound species through bending and twisting[1,2]. However, only modest success has been achieved in the quest to completely twist double bonds in order to homolytically cleave the associated π bond. In this report, we present the isolation of double-bond-containing species based on boron, as well as their fully-twisted diradical congeners, by the incorporation of attached groups with different electronic properties. The compounds mark the first structurally-authenticated set of diamagnetic multiply-bound and diradical singly-bound congeners of the same class of compound.

Olefins are ubiquitous in biological systems, crude oil, medicine and industry, and have been detected in interstellar media, comets, and carbonaceous meteorites[3-5]. Having one degree of electronic unsaturation more than relatively inert alkanes, olefins are the simplest and most earth-abundant hydrocarbons that show reactivity under ambient conditions, leading to their universal industrial use as well as their implication in questions related to the origins of life[6]. Olefins are molecules that contain a double bond between two carbon atoms consisting of one bond of σ symmetry and one of π symmetry (Fig. 1a, left). This π bond is the root of the countless synthetic uses of olefins, as it contains a concentration of electron density that can interact with a wide range of reagents.

The π orbital of olefins requires the parallel alignment of two carbon p orbitals, and thus also the coplanarity of the two carbon atoms, as depicted in Fig. 1a, left. Since at least the 1960s, a major

goal of organic chemistry has been to push the limits of the olefin model through the construction of strained, bent and twisted alkenes[1,2]. Twisting a (symmetrical) olefin by 90º would completely break its π bond, presumably leading to a triplet diradical (Fig. 1a, right) and making it susceptible to otherwise unfavored cycloaddition reactions[7,8] and further decomposition pathways[9]. This destabilizing response of alkenes to twisting is also the basis of the widely applicable Bredt's rule[10-12], which states that double bonds at the bridgehead positions of small bicyclic systems are disfavored (and reactive) due to their necessarily twisted geometry.

It is thus unsurprising that efforts to isolate "twisted olefin" compounds have resulted in only partial success: isolation of diamagnetic, incompletely twisted structures (up to 66º in the structurally-authenticated compound perchloro-9,9′-bifluorenylidene)[13-18]. Beyond carbon-carbon double bonds, sterically-hindered heavier olefin analogs such as disilenes (of the form $R_2Si=SiR_2$) also withstand significant twisting of the double bond (up to 55º)[19-23]. In a key 2015 study, Sekiguchi and coworkers reported that one of these disilenes ($Si_2(SiMetBu_2)_4$) was able to thermally populate a triplet state by twisting of the (already highly twisted) Si=Si bond above 77 ºC. This diradical compound was characterized by EPR spectroscopy and calculated to have an average SiSiSiSi dihedral angle of 75.2º, however, its structure could not be authenticated experimentally. This work remains the forefront of chemists' efforts to isolate the diradical products of twisting element-element double bonds.
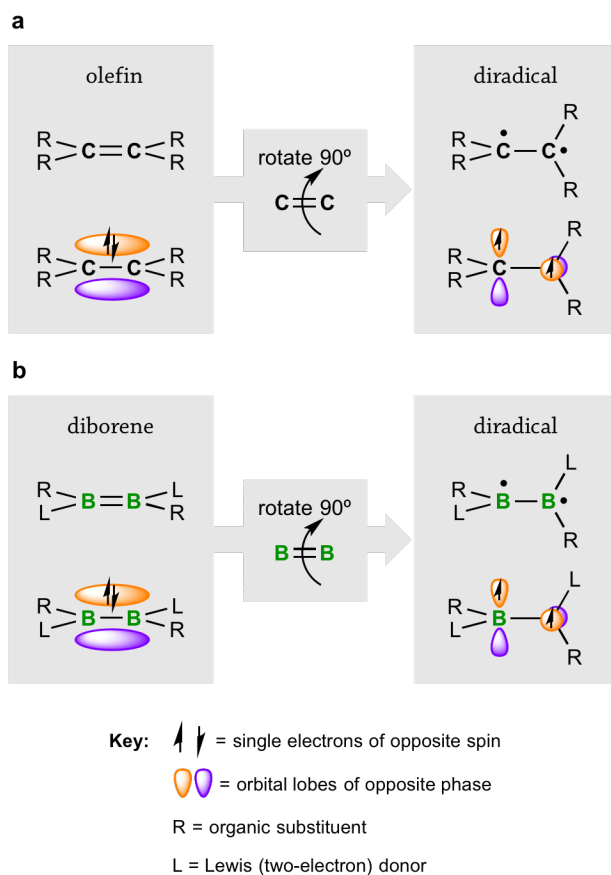
Figure 1 | Twisting double bonds. Orbital changes accompanying the twisting of element-element double bonds in alkenes (**a**) and diborenes (**b**) to form diradical species.

In this work we present the isolation of planar, doubly-base-stabilised diborenes (Fig. 1b, left)[24-27], as well as their 90º-twisted diradical congeners (Fig. 1b, right), through the use of different Lewis basic units. The former contain conventional B=B double bonds, while the latter show no B-B multiple bonding and host unpaired electrons in each of two independent, delocalized π systems. The isolation of the stable ground-state diradical species is facilitated by the outstanding ability of cyclic (alkyl)(amino)carbene (CAAC)[28,29] units to captodatively stabilize[30] adjacent radicals[31-34]. This work marks the first isolation and structural confirmation of the diradical products of complete homolysis and 90º twisting of double bonds.
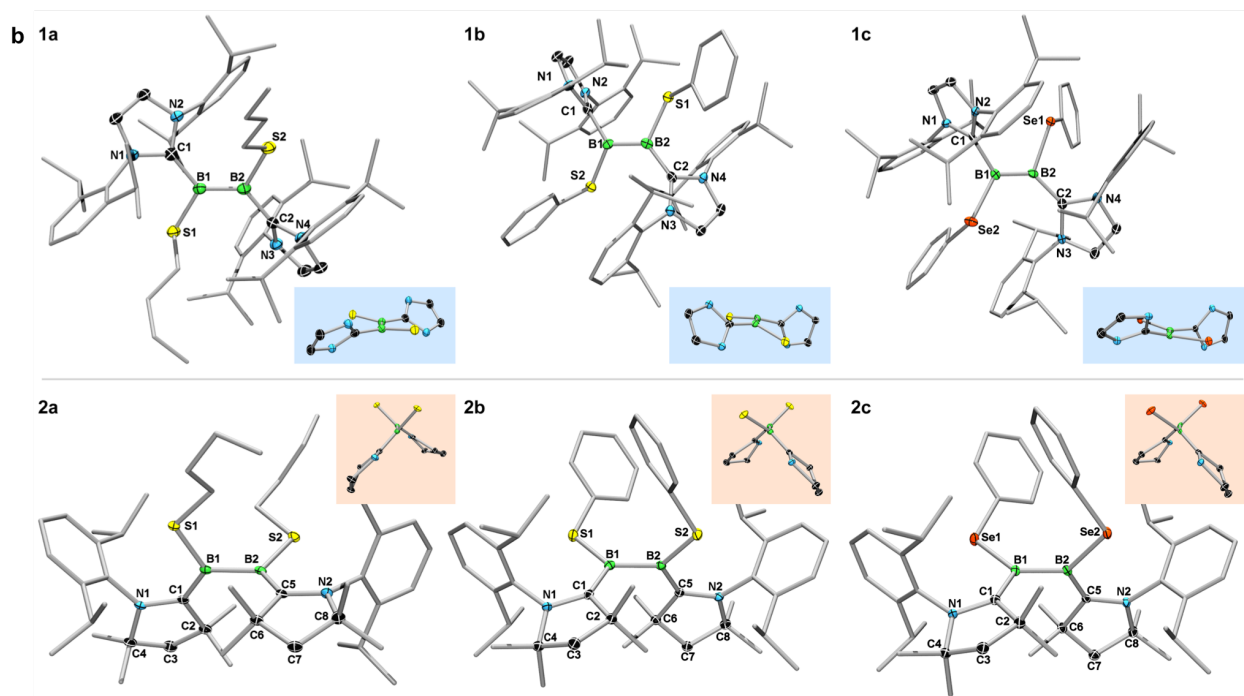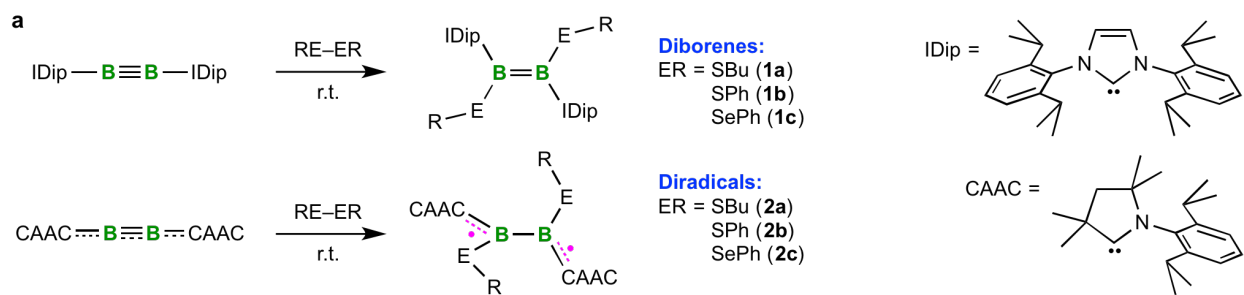
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Figure 2 | Synthesis (a) and crystallographically-determined structures (b) of planar diborenes 1a-c and perpendicular diradicals 2a-c. Blue insets: views along the roughly planar B=B units of **1a-c**. Orange insets: views along the B-B axis showing the near-perpendicular boron planes.

Simple room-temperature addition of either equal amounts or slight excesses of dibutyldisulfide, diphenyldisulfide or diphenyldiselenide to solutions of the triple-bond-containing diboryne species $B_2(IDip)_2$ (IDip = 1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene) led to new ^{11}B NMR signals

to higher field of that of the triply-bound precursor (δ_B 39)[24], signifying the formation of three new products, **1a-c** (Fig. 2a, top). After short purification steps, **1a-c** were obtained as pure green (**1a**) or purple (**1b,c**) solids with ^{11}B NMR signals (**1a**: δ_B 30; **1b**: δ_B 25; **1c**: δ_B 22) in a similar range to those of known doubly NHC-stabilized diborenes (δ_B 18-28)[24-27], but significantly more downfield than those of two previously-observed diboratellurirenium cations (*cyclo*-[Te(R)B(NHC)B(NHC)][+]) prepared by the analogous reactions of $B_2(IDip)_2$ with diphenylditelluride (δ_B 0)[35]. Single-crystal X-ray diffraction confirmed the *trans*-diborene nature of **1a-c**, all three molecules displaying effectively planar LRB=BRL double bond units (Fig. 2b, top), and short B=B double bonds (**1a**: 1.585(4) Å; **1b**: avg. 1.568(6) Å; **1c**: avg. 1.565(5) Å).

We also attempted the analogous addition of dibutyldisulfide, diphenyldisulfide or diphenyldiselenide to solutions of a more cumulenic CAAC analogue of $B_2(IDip)_2$ ($B_2(CAAC)_2$; CAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)[36]. However, to our surprise, all three reaction mixtures became very dark, and all attempts to obtain NMR spectra from the mixtures gave either silent spectra or exceptionally broad signals well outside the normal diamagnetic chemical shift ranges. Solvent extraction and recrystallization provided the black solids **2a-c** (Fig. 2a, bottom) with elemental analyses corresponding to 1:1 addition of the reagents in moderate yields. Single-crystal X-ray diffraction allowed us to elucidate the structures of **2a-c** (Fig. 2b, bottom). In marked contrast to the structures of diborenes **1a-c**, the structures of **2a-c** showed orthogonal C-B-S/Se planes, with S/Se-B-B-S/Se torsion angles near 90º (**2a**: 85.5(1)º; **2b**: 100.9(1)º; **2c**: 99.7(2)º), and long, single B-B bonds (**2a**: 1.728(2) Å; **2b**: 1.713(2) Å; **2c**: 1.700(4) Å). On either side of the midpoint of the molecules, the N-C-B-S/Se units are near-planar, with relatively small N-C-B-E torsion angles (**2a**: 1.7(2)º, 14.6(2)º; **2b:** 17.4(2)º, 1.5(2)º; **2c:**

18.7(3)°, 0.1(4)°) suggesting significant π-electron delocalization over this portion of the molecule. The B-S/Se distances of **2a-c** (d(B-S): 1.84-1.86 Å; d(B-Se): 1.99-2.00 Å) were found to be slightly shorter than those of **1a-c** (d(B-S): 1.88-1.92 Å; d(B-Se): 2.01-2.06 Å), and the B-C distances of **2a-c** (1.53-1.55 Å) are likewise shorter than those of **1a-c** (1.57-1.62 Å).

The significantly greater delocalization in the C-B-S/Se portion of **2a-c**, the apparent absence of B-B multiple bonding, and the inability to procure NMR data of the compounds, suggested that they may be captodatively-stabilized[30] triplet diradicals, each with two push-pull systems involving the π-donating S/Se atom and the π-accepting CAAC carbene carbon atom (i.e. LRB(●)– B(●)RL; Fig. 2a, bottom). Furthermore, the coplanar B and C atoms and short B-C bonds of **2a-c** are reminiscent of our related captodatively-stabilized neutral monoradical species DurB(●)(Cl)(CAAC) reported in 2014[31]. In order to confirm the diradical nature of **2a-c**, we performed electron paramagnetic resonance spectroscopy (EPR) on **2a-c** in frozen 2-methyltetrahydrofuran glass. While we observed an intense half-field transition for **2a** and **2b** (Figs. 3a, S12-S16), only a weak signal was observed for compound **2c** (Fig. S17). The obtained spectra of **2a** and **2b** are dominated by rhombic zero-field splitting (ZFS) due to dipole interaction, indicating that the spin system in question is a triplet state. Analysis of the spectra yields estimates of the ZFS parameters (**2a**: D = 0.036 cm^{-1}, E = 0.0054 cm^{-1}; **2b**: D = 0.042 cm^{-1}, E = 0.0077 cm^{-1}), the axial parts of which correspond to interspin distances of 4.5 and 4.4 Å (assuming point dipole approximation), respectively. These distances are significantly longer than the ca. 1.70-1.73 Å boron-boron distances found by X-ray crystallography, and match better the distance between the two CAAC carbene carbon atoms (**2a**: ca. 4.0 Å; **2b**: ca. 3.9 Å). Thus the two unpaired electrons must be significantly delocalized into the substituents, most likely towards the carbene carbon

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atoms, which is in line with that expected by the captodative effect of the π-donor nitrogen and π-acceptor boron atoms.

To probe the exchange interaction between spin carriers in diradical **2a**, temperature-dependent magnetic measurements were performed on a solid sample (Fig. 3b). The effective magnetic moment increases from 2.50 μ_B at RT to 2.81 μ_B at 10 K, clearly indicating the presence of ferromagnetic interaction inside the molecule. Quantitative analysis based on the $\hat{H} = -2J\hat{S}_1\hat{S}_2$ spin Hamiltonian allowed determination of the exchange coupling parameter to be $J = +15$ cm^{-1}, *i.e.* the ground state of the molecule is a triplet and lies $2J = 30$ cm^{-1} (0.086 kcal mol^{-1}) lower than the singlet state. The exchange coupling determined from solid-state SQUID measurements is also reflected to some degree in the temperature-dependence of the signal intensities observed in the solution-state EPR spectra of **2a** Fig. S14).
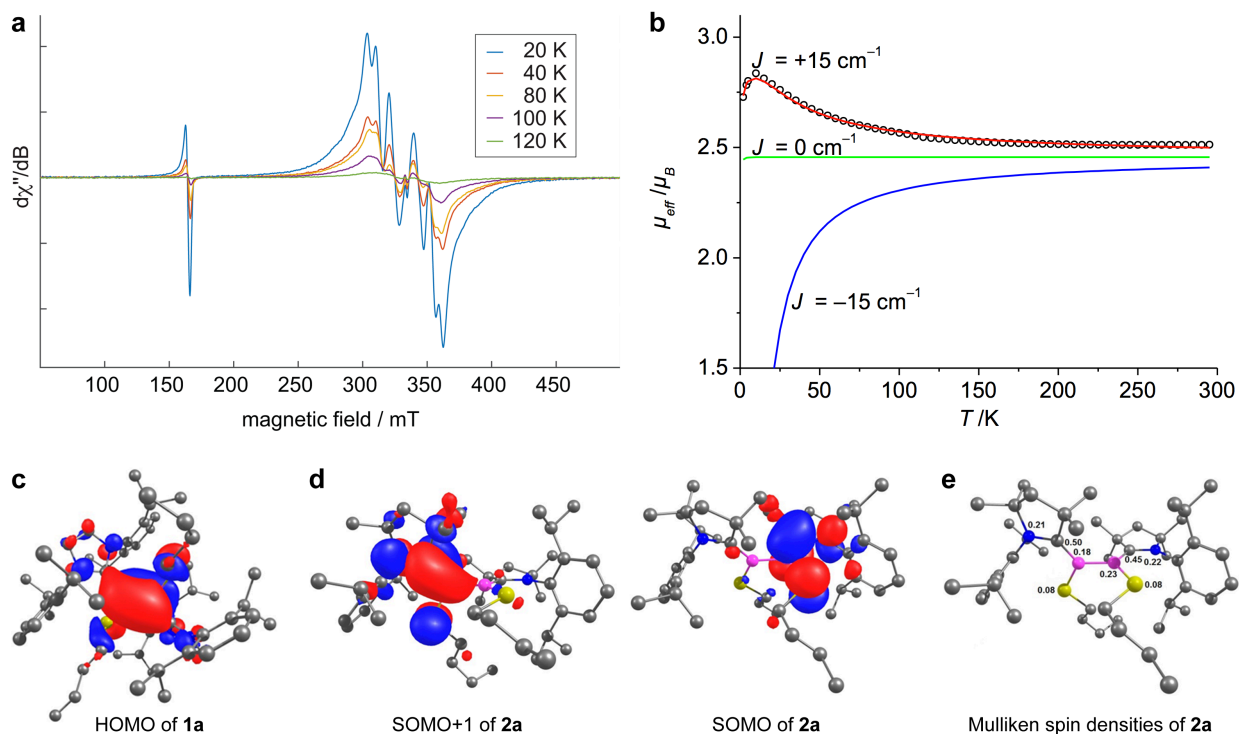

a

b

c   HOMO of **1a**

d   SOMO+1 of **2a**

            SOMO of **2a**

e   Mulliken spin densities of **2a**

Figure 3 | Spectroscopic, magnetic and computational studies of compounds 1a and 2a. a, Temperature-dependent EPR spectra of 1 mM **2a** in 2-Me-THF. Experimental parameters: temperature = 20−120 K; microwave frequency = 9.38 GHz; microwave power = 0.1 mW; modulation amplitude = 2 G; conversion time = 60 ms; modulation frequency = 100 kHz. **b,** Temperature dependence of the magnetic moment of **2a**. Black cycles: experimental data. Red line: best fit data for the ferromagnetically coupled case with $J = +15$ cm^{-1} and $g = 2.01$. For comparison, the theoretical data for the non-coupled ($J = 0$ cm^{-1}, green line) and antiferromagnetically coupled ($J = -15$ cm^{-1}, blue line) cases are also depicted. **c,** HOMO plot of **1a** at the M05-2X/def2-SVP level. **d,** SOMO plots of **2a** at the M05-2X/def2-SVP level. **e,** Mulliken spin densities of relevant atoms of **2a** at the M05-2X/def2-SVP level.

Density functional theory (DFT) calculations for diamagnetic diborenes **1a-c** and the diradicals **2a-c** (Figs. S22-S39) agree with the experimental findings that the singlet states of **1a-c** are always more stable than the triplet states whereas the triplet states of **2a-c** are always more stable than the singlet states. The calculated bond lengths (Figs. S22-S39) and Wiberg bond indices (WBIs) support the proposed bonding arrangements depicted in Fig. 2a, with B=B double bond character (**1a**: 1.55, **1b**: 1.58, **1c**: 1.60) in **1a-c** and single B-B bond character (**2a**: 0.97, **2b**: 0.98, **2c**: 0.99) in **2a-c**. Figs. 3c and 3d (and Figs. S40-S45) illustrate the stark contrasts between the highest-energy occupied orbitals of diborenes **1a-c** and diradicals **2a-c**. The former, as exemplified by **1a**, possess highest occupied molecular orbitals (HOMOs; Fig. 3c) consisting of bonding B-B π interactions that extend slightly towards the p$_\pi$ orbital of the carbene carbon atoms. The latter, as exemplified by **2a**, have two near-degenerate singly-occupied molecular orbitals (SOMOs; Fig. 3d), each of which is delocalized over one N-C-B-S/Se moiety, with a bonding interaction between

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B and C, weak antibonding between C and N and weaker antibonding between B and S/Se. These singly-occupied orbitals clearly illustrate the presence of two captodatively-stabilized radicals in each of **2a-c**, and that each unpaired electron resides in one respective N-C-B-S/Se π system. The calculated Mulliken spin densities of **2a** (Fig. 3e) show that the unpaired electrons reside predominantly in the CAAC carbon p_π orbitals (0.50 and 0.45 e), with lower but roughly equivalent spin density on the B (0.18 and 0.23 e) and N (0.21 and 0.22 e) atoms.

While DFT computations and experiment agree in terms of geometry and the energetic order of the singlet and triplet states, the DFT computations considerably overestimate the size of the singlet-triplet gap of compound **2a**. The overestimation may result from the need for multi-reference approaches[37,38] to describe the singlet and triplet states on equal footing. Because **2a** is too large for such costly approaches, we investigated the error of the DFT approaches for a smaller model system **2a** that reflects all of the essential binding effects of **2a** but is sufficiently small for multireference calculations. The results (Table S3) show that all functionals indeed overestimate the stability of the triplet state considerably. While the very accurate NEVPT2[39,40]/def2-TZVP approach predicts a S-T gap of only –0.4 kcal mol^{-1} (triplet lower than singlet), the values obtained with DFT range from –4 to –28 kcal mol^{-1}. The MN12-L/6-311G(d,p) approach used to estimate the S-T gap of the full system **2a** overestimates the stability of the triplet state by about 6-7 kcal mol^{-1}. Transferring this error to the predictions of the MN12L[41]/6-311G(d,p)[42,43] approach for the full system **2a** (–6.4 kcal mol^{-1}), a near-zero S-T gap results, which is in line with the measured value.

The electrochemical behavior of **2a-c** also distinguishes these diradicals from diborenes **1a-c** (Figs. S20 and S21). Diborenes **1a-c** show facile oxidation events in their cyclic voltammograms (with

no apparent reduction processes), as previously observed for related diborenes[44]. In contrast, diradicals **2a-c** show less-facile oxidation events, with additional reduction waves, in line with the presence of the more π-accepting CAAC ligands. It should also be noted that variable-temperature NMR experiments suggest that the diamagnetic diborenes **1** and the diradical species **2** do not convert to their alternative conformations upon heating to 80 ℃.

The synthesis of diborenes **1a-c** and their twisted congeners **2a-c** marks the first isolation and structural authentication of diamagnetic, multiply-bound molecules and their diradical, single-bond congeners, products of formal homolysis of the central multiple bond. Crystallographic, EPR spectroscopic, magnetic and theoretical studies confirm that **2a-c** are diradical species. Spectroscopic and computational studies also confirm the substantial energy differences between the singlet and triplet states of the molecules, with the singlet states being favored in **1a-c** and the triplet states in **2a-c**.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Data Availability The data that support the findings of this study are available from the corresponding author on reasonable request.

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Supplementary Information is available in the online version of the paper.

Author Contributions

H.B. conceived the study. J.B., T.D., W.C.E., K.H., and M.H. performed the synthetic experiments. M.A.C., E.W., M.R., R.M., and B.E. performed the computational studies. I.K. and E.B. acquired and analyzed the EPR data. S.D. and F.M. performed the magnetic measurements. M.A.C., R.D. and W.C.E. prepared the manuscript. All authors read and commented on the manuscript.

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