Metallaborane reaction chemistry. A predicted and found tailored facile and reversible capture of SO_2 by a B-frame-supported bimetallic: structures of $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$ and $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$†

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The formally *closo* twelve-vertex {*ortho*-M_2B_{10}} dimetallaborane system has been predictively tailored for reversible uptake of SO_2 across the metal–metal bond, as exemplified by the formation of $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ from $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$.

We previously demonstrated that the *closo*-structured twelve-vertex cluster compound $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ shows a remarkable haem mimicry, in that it exhibits a readily reversible sequestration of molecular dioxygen across the intact metal–metal linkage to give $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$.[1–3] The other small unsaturated molecules SO_2 and CO are, by contrast, irreversibly sequestered to give $[(PMe_2Ph)_4(SO_2)Pt_2B_{10}H_{10}]$ and $[(PMe_2Ph)_4(CO)Pt_2B_{10}H_{10}]$, respectively.[2,3] By alteration of the metal atoms, and/or their exopolyhedral ligands and/or the boron-cluster substituents, this $\{M_2B_{10}\}$ system is in principle uniquely tailorable for a variety of small-molecule sequestration, delivery, exchange and activation.[2–4] We now confirm this tailorability, with this preliminary report, of the engineering of the system by variation of two of these factors—the metallic elements used and the exopolyhedral metal ligands—to engender, now, reversibility of SO_2 sequestration. The direction of synthetic investigation to efficiently achieve this goal was determined by predictive DFT calculations.[4] Although reversible addition of SO_2, for example to a single platinum atom, has long been known, and also the instance of non-dissociable SO_2 bound across a Pt–Pt vector similarly long recognised,[5] the *reversibility* of the latter type of binding is novel. The directed engineering of such reversibility, either to a single metal atom or to a metal–metal vector, is as far as we are aware previously unprecedented.

DFT calculations were carried out on the formally *closo* $\{M_2B_{10}H_{10}\}$ system, based initially on $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$, by variation of metal centre between platinum and palladium, and by variation of the ligands on the metal centres. The species O_2, CO and SO_2 were used as model small molecules. Structures were initially energy-minimised at the STO-3G*/LANL2DZ level and subsequently refined at the B3LYP/LANL2DZ level using the Gaussian 03 package.[6] Criteria of binding strength were the shortness of metal–oxygen, metal–carbon, and metal–sulfur distances, respectively, as well as lengthening of the respective O–O, C–O and S–O distances. Generally it was found that change in ligand from PMe_2Ph to PMe_3 increased the binding strength, and from PMe_2Ph to PPh_3 decreased it. A change from Pt_2 *via* PtPd to Pd_2 weakened the small-molecule coordination, and a change from a phosphine to a nitrogen ligand strengthened it. However, these general effects are not linearly additive, but can act either synergically or antagonistically, as we have also found that although a particular combination of ligands and metals may sequester one type of molecule, say O_2, more strongly than another combination, it may well sequester another type of molecule, say SO_2, more weakly. A complex matrix of behaviour needs to be established in order to delineate thoroughly the factors. Meanwhile, however, the indications were that a mixed amine phosphine ligand system, with a combination of Pd and Pt centres, would bind SO_2 much more weakly than $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$, suggesting that a reversibility of SO_2 addition could thereby be engineered. Thus, the B3LYP/LANL2DZ-calculated Pt–S and S–O distances of 2.5314 Å and 1.5005 Å, respectively, in $[(PMe_2Ph)_4(SO_2)Pt_2B_{10}H_{10}]$ change to 2.654 Å and 1.485 Å in $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ (where phen = phenanthroline, $N_2C_{12}H_8$). We have thence confirmed this prediction experimentally by investigation of the behaviour of SO_2 with $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$.

A sample of $[(phen)PdB_{10}H_{12}]$ was made from $B_{10}H_{14}$ *via* $[(PPh_3)_2PdB_{10}H_{12}]$ essentially according to the procedure of Siedle and Todd.[7] Subsequently, a solution of $K[HBEt_3]$ (1.0 M in thf; 0.56 ml, corresponding to 560 μmol) was added to a stirred toluene suspension of $[(phen)PdB_{10}H_{12}]$ (113 mg, 280 μmol) at −70 °C. The mixture was then allowed to warm to *ca.* −50 °C, whereupon $[PtCl_2(PMe_2Ph)_2]$ (151 mg, 280 μmol) was added *via* tipper tube. The mixture was allowed to warm to room temperature, with stirring, overnight. Filtration gave a dark brown-purple microcrystalline solid, $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$ **1** (130 mg, containing a small amount of KCl: *ca.* 150 μmol; *ca.* 54% of compound **1**). Pure **1** was thence recrystallisable from a solution in 1,2-$Cl_2C_2H_4$ by overlayering with C_6H_{14}, to give crystals suitable for a single-crystal X-ray diffraction analysis (Fig. 1, upper).‡§ Compound **1** is robust compared to $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$;[2] for example, a solution in acetone in air overnight showed no sign of decomposition.

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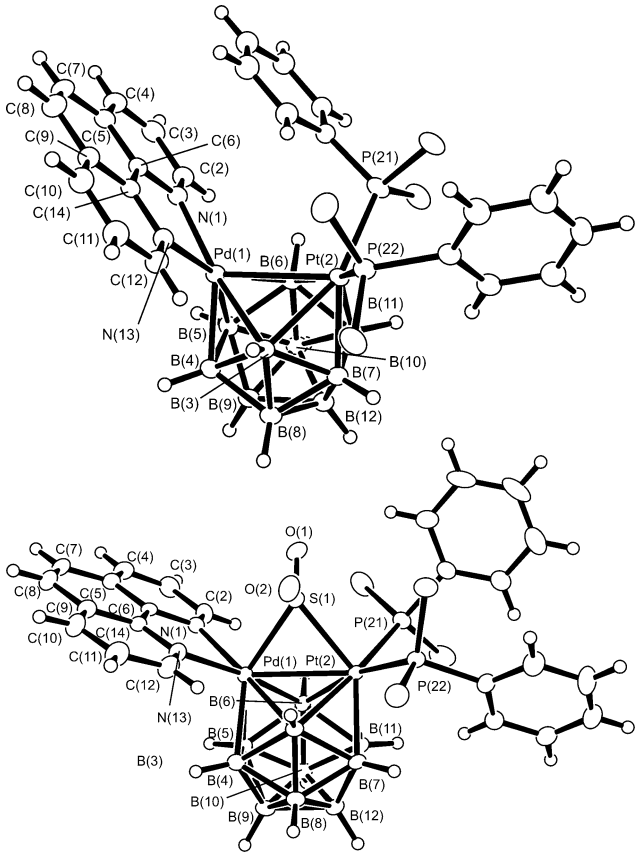

Fig. 1 ORTEP-type[8] representations of the crystallographically determined‡ molecular structures of (top) purple $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$ **1** and (bottom) orange-yellow $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ **2**, drawn with 50%-probability ellipsoids for the non-hydrogen atoms. Methyl hydrogen atoms are omitted for clarity. Selected interatomic distances for **1** are: from Pt(2) to Pd(1) 2.8744(3), to P(1) 2.3343(7), to P(2) 2.3399(7), to B(3) 2.336(3), B(6) 2.335(3), to B(7) 2.245(2), to B(11) 2.240(3) Å; from Pd(1) to B(3) 2.261(3), B(6) 2.278(3), B(4) 2.195(3), B(5) 2.197(3), N(1) 2.176(2), and to N(13) 2.199(2) Å; the PPtP angle is 97.63(2)°. For **2**, selected interatomic distances are: from Pt(2) to Pd(1) 2.7880(5), to P(1) 2.3886(1), to P(2) 2.3664(1), to B(3) 2.343(4), B(6) 2.351(4), to B(7) 2.265(4), to B(11) 2.286(4), and to S(1) 2.4369(1) Å; from Pd(1) to B(3) 2.245(4), B(6) 2.275(4), B(4) 2.236(4), B(5) 2.257(4), N(1) 2.222(3), N(13) 2.180(3) and to S(1) 2.4161(1) Å; S(1)–O(1) is 1.474(3) and S(1)–O(2) is 1.474(3) Å; the PPtP angle is 97.03(3)°, the PdSPt angle is 70.13(3) and the OSO angle is 113.7(2)°. The dihedral angles between the Pt(2)P(1)P(2) and Pd(1)N(1)N(2) planes are approximately 65.1 and 59.0° for compounds **1** and **2**, respectively.

Passage of SO_2 through a solution of **1** in CH_2Cl_2 resulted in a colour change from dark purple to lighter purple-yellow. Reduced pressure, the passing of N_2 gas through the solution, or evaporation, promoted reversal of the process to regenerate compound **1**. NMR investigation§ of the yellow solution showed a compound of the same symmetry as compound **1**, and a single-crystal X-ray diffraction analysis‡, on orange-yellow crystals obtained from the yellow solution by over-layering with C_6H_{14} at room temperature, showed that SO_2 addition had occurred across the metal–metal vector to give orange-yellow $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ **2** (Fig. 1, lower). The measured Pt–S distances of 2.4369(1) Å in **2** and 2.355(2) Å in $[(PMe_2Ph)_4(SO_2)Pt_2B_{10}H_{10}]$[2] compare well to the trend predicted in the DFT calculations, and the considerable increase in the Pt–S distance in **2** marries well with the observed occurrence of *reversible* SO_2 uptake in this system, compared to the *irreversible* formation of $[(PMe_2Ph)_4(SO_2)Pt_2B_{10}H_{10}]$ from $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$.[2] Any changes in the S–O distances are too small to be significant compared to the standard uncertainties in the experimental measurements. Finally, it may be noted that a striking colour change in the SO_2-saturated solution of **1** in CH_2Cl_2, between yellow at *ca.* −35 °C and yellow-purple at ambient temperature, indicates the presence of an equilibrium condition for the addition of SO_2 to **1** to give **2** over this temperature range. As with the reversibility of the addition of O_2 to $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$,[1,2] it is apparent that a significant component of the high entropy factor implicit in the ready reversibility derives from the required extensive repositioning of the ligand sphere about the dimetal site (Fig. 2). In this regard, a referee has suggested that the phenomenon that is often called 'π-stacking', as manifested here in the parallel packing of the aromatic rings of the phosphine ligands (Fig. 2, bottom right), may contribute to the conformation of compound **2**. However, it may be

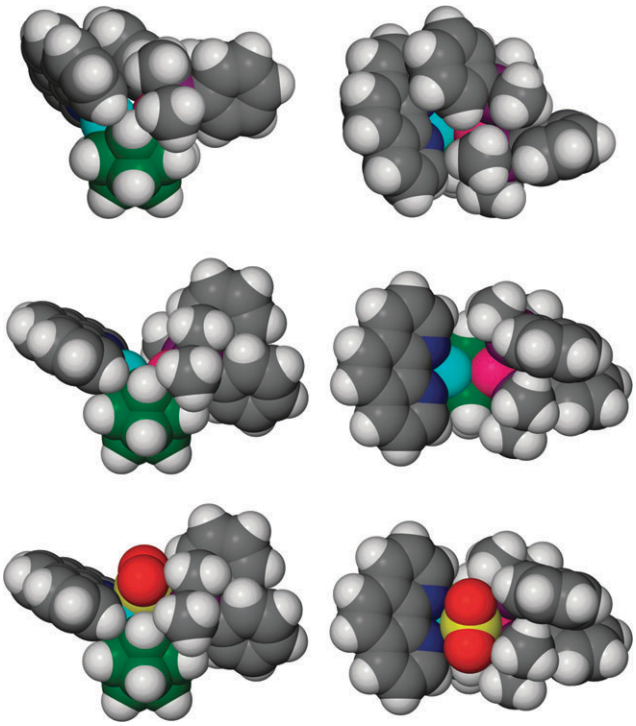

Fig. 2 Space-filling representations of the crystallographically determined molecular structures of (top) $[(PMe_2Ph)_2PtPd(phen)B_{10}H_{10}]$ **1**, (bottom) $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ **2**, and (centre) $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}]$ with the elements of SO_2 omitted to show the underlying dimetal unit. It is seen that the P-organyl groups of the $\{(PMe_2Ph)_2\}$ assembly on the Pt atom of **1** (top) twist out of the way (centre) to accommodate the SO_2 molecule on the {PtPd} unit (bottom). The opening up of access to the metal–metal vector by the relative 'flattening' of the phenanthroline ligand sphere *versus* the twisting phosphine ligand sphere is also noteworthy. The overall substantial twisting and flattening required to accommodate the SO_2 molecule contributes entropically to the relatively high reversibility of addition.

noted that there is also a related alignment of a phenyl ring with one of the rings of the phenanthroline moiety in the starting compound **1** (Fig. 2, top pair). In any event, the thermodynamics of the equilibrium should be eminently adjustable by variations in substituents on the cluster and the ligands and these will also be predictable by DFT calculation.

The DFT-predicted reversibility of SO_2 addition to this type of system is therefore confirmed, and the unique tailorability of this system for general small-molecule reversible sequestration, delivery and potential reactivity activation is therefore demonstrated. A particular advantage presented by the use of the phenanthroline ligand is that it readily opens up the system, using bidentate amine ligands and the well-established synthetic techniques of organic chemistry, to a vast range of property modification, such as tailoring for water solubility, for attachment to polymer backbones, for electro-chemical and chemical disposition on surfaces, for antenna attachment for possible photoactivation, and for chiral and polar control of the approach of molecules to the active dimetal site.

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Notes and references

‡ X-Ray data for compound **1**: crystal data for squeeze: $C_{28}H_{40}B_{10}N_2P_2PdPt$, M = 876.15, 0.48 × 0.15 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (no. 2), a = 12.6626(12), b = 12.9085(12), c = 14.5518(14) Å, α = 71.088(5), β = 74.801(5), γ = 81.734(6)°, V = 2167.0(4) Å^3, Z = 2, D_c = 1.343 g cm^{-3}, F_{000} = 852, Mo-Kα radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 57.7°, 52 168 reflections collected, 11 253 unique (R_{int} = 0.0354). Final GooF = 1.040, $R1$ = 0.0225, w$R2$ = 0.0586, R indices based on 10 237 reflections with $I > 2\sigma(I)$ (refinement on F^2), 419 parameters, 6 restraints. Lp and absorption corrections applied, μ = 3.732 mm^{-1}. Disordered 1,2-$Cl_2C_2H_4$ solvent molecules were incorporated in the model using PLATON SQUEEZE;[9] CCDC 672233.

Crystal data for compound **2**, $[(PMe_2Ph)_2Pt(SO_2)Pd(phen)B_{10}H_{10}](CH_2Cl_2$ trisolvate): $C_{31}H_{46}B_{10}Cl_6N_2O_2P_2PdPtS$, M = 1194.99, 0.23 × 0.14 × 0.05 mm^3, monoclinic, space group $P2_1/n$ (no. 14), a = 14.689(2), b = 17.188(2), c = 18.742(3) Å, β = 98.046(8)°, V = 4685.2(12) Å^3, Z = 4, D_c = 1.694 g cm^{-3}, F_{000} = 2336, Mo-Kα radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 58.9°, 109 904 reflections collected, 12 289 unique (R_{int} = 0.0633). Final GooF = 1.044, $R1$ = 0.0311, w$R2$ = 0.0729, R indices based on 10 072 reflections with $I > 2\sigma(I)$ (refinement on F^2), 509 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.853 mm^{-1}; CCDC 672234.

§ Selected NMR and mass spectrometric data for compounds **1** and **2** (CD_2Cl_2) [δ in ppm, ^{31}P rel. H_3PO_4, ^{11}B rel. $BF_3(OEt_2)$ and ^{1}H rel. $SiMe_4$]. Compound **1**: $\delta(^{31}P)$ (300 K): +2.61 [$^1J(^{195}Pt–^{31}P)$ 2764 Hz]; $\delta(^{11}B)$ [$\delta(^1H)$] (300 K): 2BH +29.4 [+5.50], 2BH +26.7 [+4.21], 2BH +21.2 [+4.27, +3.93, $^1J(^{195}Pt–^1H)$ *ca.* 60 Hz], 2BH +19.7 [+4.15], 1BH −24.3 [+1.30, $^1J(^{195}Pt–^1H)$ *ca.* 42 Hz]; $\delta(^1H)(PMe_2Ph)$ (263 K): +1.54 (6H) [$N(^{31}P–^1H)$ *ca.* 8 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 26 Hz], +1.45(6H) [$N(^{31}P–^1H)$ *ca.* 10 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 23 Hz] and (sharp multiplets) around +6.74 to 7.29 (phenyl) and +7.81 to +9.29 (phenanthroline). HRMS TOF, ES$^+$ obtained on an LCT Micromass instrument: found 877.2274, calc. for $C_{28}H_{40}B_{10}N_2P_2Pd_1Pt_1$ 877.2280. Compound **2**: $\delta(^{31}P)$ (300 K): −8.23 [$^1J(^{195}Pt–^{31}P)$ 2790 Hz]; $\delta(^{11}B)$ [$\delta(^1H)$] (300 K): 1BH +25.1 [+5.09], 1BH +23.8 [+2.28], 2BH +22.2 [+4.37], 2BH +21.7 [+4.37], 2BH +8.7 [+3.81] and 2BH −10.5 [+2.57, $^1J(^{195}Pt–^1H)$ *ca.* 54 Hz]; $\delta(^1H)(PMe_2Ph)$ (300 K) +1.86 (6H) [$N(^{31}P–^1H)$ *ca.* 11 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 25 Hz], +1.54 (6H) [$N(^{31}P–^1H)$ *ca.* 11 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 20 Hz] and (sharp multiplets) around +7.36 to 7.49 (phenyl) and +7.86 to +8.87 (phenanthroline). The compound was not amenable to mass spectrometric characterisation *via* a molecular ion, due to its ready loss of SO_2; the spectra from the crystalline sample of **2** showed only SO_2^+.

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