

Reversible Capture of Small Molecules On Bimetalaborane Clusters: Synthesis, Structural Characterization, and Photophysical Aspects

Jonathan Bould,^{*,†,⊥} Tomáš Baše,[†] Michael G. S. Londesborough,[†] Luis A. Oro,[‡] Ramón Macías,[‡] John D. Kennedy,[⊥] Pavel Kubát,[§] Marcel Fuciman,^{||} Tomáš Polívka,^{||} and Kamil Lang^{*,†}

[†]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, v.v.i., 250 68 Husinec-Řež, Czech Republic

[‡]Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza, 50009-Zaragoza, Spain

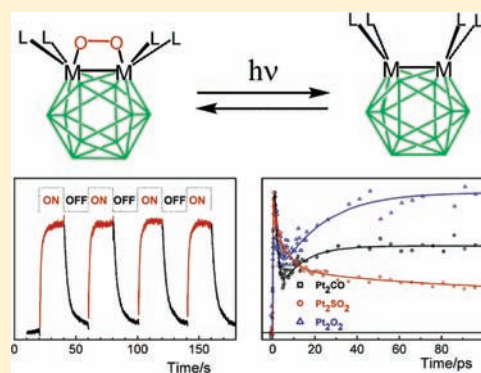
[§]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

^{||}Institute of Physical Biology, University of South Bohemia, Zámek 136, 373 33 Nové Hradky, Czech Republic

[⊥]The School of Chemistry of the University of Leeds, Leeds LS2 9JT, U.K.

S Supporting Information

ABSTRACT: Metallaborane compounds containing two adjacent metal atoms, [(PMe₂Ph)₄MM'B₁₀H₁₀] (where MM' = Pt₂, **1**; PtPd, **7**; Pd₂, **8**), have been synthesized, and their propensity to sequester O₂, CO, and SO₂ and to then release them under pulsed and continuous irradiation are described. Only [(PMe₂Ph)₄Pt₂B₁₀H₁₀], **1**, undergoes reversible binding of O₂ to form [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **3**, but solutions of **1**, **7**, and **8** all quantitatively take up CO across their metal–metal vectors to form [(PMe₂Ph)₄(CO)Pt₂B₁₀H₁₀] **4**, [(PMe₂Ph)₄(CO)PtPdB₁₀H₁₀] **10**, and [(PMe₂Ph)₄(CO)Pd₂B₁₀H₁₀] **11**, respectively. Crystallographically determined interatomic M–M distances and infrared CO stretching frequencies show that the CO molecule is bound progressively more weakly in the sequence {PtPt} > {PtPd} > {PdPd}. Similarly, SO₂ forms [(PMe₂Ph)₄(SO₂)Pt₂B₁₀H₁₀] **5**, [(PMe₂Ph)₄(SO₂)PtPdB₁₀H₁₀] **12**, and [(PMe₂Ph)₄(SO₂)Pd₂B₁₀H₁₀] **13** with progressively weaker binding of the SO₂ molecule. The uptake and release of gas molecules are accompanied by changes in their absorption spectra. Nanosecond transient absorption spectroscopy clearly shows that the O₂ and CO molecules are liberated from the bimetallic binding site with high quantum yields of about 0.6. For **3**, in addition to dioxygen release in the triplet ground state, singlet oxygen O₂(¹Δ_g) was also detected with a quantum yield <0.01. In most cases, the release and rebinding of the gas molecules can be cycled with little photodegradation of the compounds. Femtosecond transient absorption spectroscopy further reveals that the photorelease of the O₂ and CO molecules, from **3** and **4** respectively, is an ultrafast process taking place on a time scale of tens of picoseconds. For SO₂, the release is even faster (<1 ps), but only in the case of mixed metal PtPd adducts, most probably because of the metal–metal bonding asymmetry in the mixed metal clusters; for the corresponding symmetric Pt₂ and Pd₂ adducts, **5** and **13**, the release of SO₂ is significantly slower (>1 ns). All these compounds may have potential to serve as light-triggered local and instantaneous sources of the studied gases.



INTRODUCTION

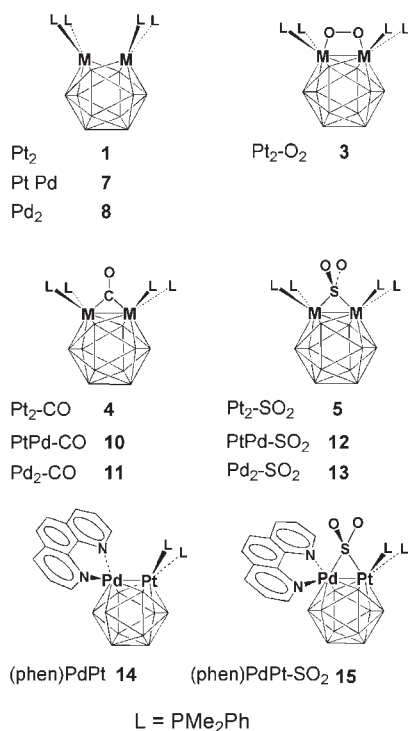
The reversible binding of small molecules on metal atoms, metal–metal vectors, and metal surfaces is often used, both in Nature and in industry, to overcome otherwise insurmountable thermodynamic barriers in chemistry. Examples of uses found for this type of interaction are numerous and perhaps the most important one is the reversible uptake of dioxygen on the iron center in hemoglobin. In this context, we have previously reported the quantitative and reversible uptake of O₂ by the metal–metal linkage in the intensely dark purple icosahedral twelve-vertex bimetalaborane cluster compound [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** made from the reaction of [PtCl₂(PMe₂Ph)₂] with [(PMe₂Ph)₂PtB₁₀H₁₂] **2** to give the yellow-

orange dioxygen bimetalaborane complex [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **3** (Scheme 1).¹ The reversibility is readily induced by pressure reduction or by mild warming. Also, by analogy with the competitive binding of gases other than oxygen to hemoglobin, compound **1** interacts with CO and SO₂ to give tan-colored [(PMe₂Ph)₄(CO)Pt₂B₁₀H₁₀] **4** and orange [(PMe₂Ph)₄(SO₂)Pt₂B₁₀H₁₀] **5** (Scheme 1).^{1b} In a similar manner to O₂, the uptake of CO and SO₂ by **1** occurs very readily and quantitatively, but in these cases the additions are not reversible under normal conditions of pressure reduction or mild heating. Reversible SO₂

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Scheme 1. Schematic Structures of Investigated Compounds Showing Compound Numbering and Acronyms Used in the Text



and/or CO uptake on monometallic² or bimetallic species^{3–6} has been reported previously, but rarely in conjunction with oxygen uptake⁷ as occurs in the system we describe here. The reversibility of O_2 addition to **1** to give **3** contrasts with the irreversible formation of the only other known analogous O_2 complex to a metal–metal-bonded system, that is, the formation of dark purple $[Ir_2I_2(CO)_2(O_2)(Ph_2PCH_2PPh_2)_2]$ **6** from $[Ir_2I_2(CO)_2(Ph_2PCH_2PPh_2)_2]$, first reported 20 years ago.⁸

In this paper, we investigate whether the sequestration of SO_2 and CO by our bimetallic system can be made to be reversible by changing one or both of the metal atoms from platinum to palladium. Additionally, we demonstrate that sequestered molecules of O_2 , CO, and SO_2 can be reversibly ejected by pulsed UV–vis irradiation: here, time-resolved spectroscopic studies spanning the time-range from femtoseconds to microseconds provide a quantitative refinement of the qualitative observations obtained from steady-state UV–vis spectroscopy.

As an easy reference, and as an aid to the reader, Scheme 1 shows a schematic listing of the structures described in this paper and their compound numbers. For example, $[(PMe_2Ph)_4(O_2)-Pt_2B_{10}H_{10}]$ **3**, is referred to below as Pt_2-O_2 **3**.

RESULTS AND DISCUSSION

Compound Syntheses. The bimetallic compounds $[(PMe_2Ph)_4-MM'B_{10}H_{10}]$ are synthesized by the addition of 2 equivalents of $KHBET_3$ to suspensions of $[(PMe_2Ph)_2MB_{10}H_{12}]$ ($M = Pt$ or Pd) in toluene at low temperature, followed by the addition of $[M'Cl_2(PMe_2Ph)_2]$ ($MM' = PtPt$ for **1**, $PtPd$ for **7**, and $PdPd$ for **8**) and slow warming to room temperature. The air-stable Pt_2 **1** and Pd_2 **8** compounds are then obtained essentially pure

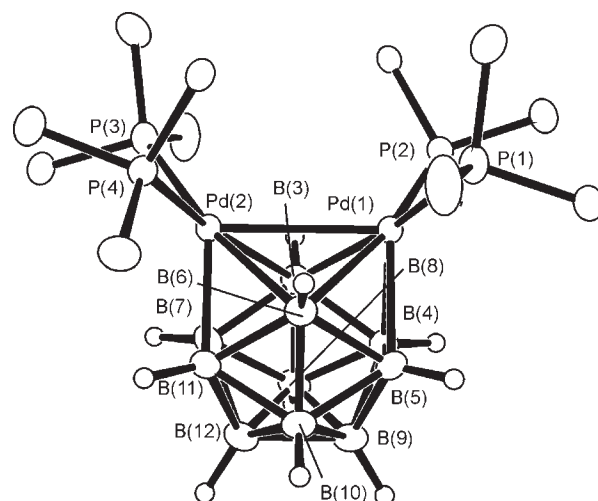


Figure 1. Representation of the crystallographically obtained molecular structure of $[(PMe_2Ph)_4Pd_2B_{10}H_{10}]$, Pd_2 **8**, showing the cluster numbering system employed, with 50% thermal ellipsoids for non-hydrogen atoms. The phenyl rings (except for the *ipso* carbon atoms) and methyl group hydrogen atoms are omitted to aid clarity. The molecule possesses a C_2 axis such that equivalent cluster positions are $Pd(1) \equiv Pd(2)$, $B(3) \equiv B(6)$, $B(4) \equiv B(11)$, $B(5) \equiv B(7)$, $B(8) \equiv B(10)$, and $B(9) \equiv B(12)$. Selected measured geometric parameters for Pd_2 **8** are listed in Table 1.

by filtration in yields of up to 76% and 57%, respectively, with the latter, new compound, affording a satisfactory elemental analysis. The yield for **1** is an improvement on the 23% previously reported from preparations using tetrahydrofuran (THF) as solvent.^{1b} Interestingly, it may also be noted that a crystalline precipitate of the Pt_2 **1** compound may also be obtained in about 50% yield from a toluene solution of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ at reflux containing added PMe_2Ph ⁹ (see Experimental Section). Single-crystal X-ray diffraction data were obtained for the dipalladium compound **8** (Figure 1), together with the cluster numbering scheme. The molecular structure of Pt_2 **1** is previously reported.¹ The isolation of the mixed palladium–platinum analogue $PtPd$ **7** from the reaction mixture using $KHBET_3$ is less straightforward. Crystallization of the purple-brown solid afforded in the reaction is difficult and results in some decomposition of the compound. Nevertheless, sufficient quantities for a satisfactory elemental analysis and for further reaction chemistry have been obtained (31% yield). Its identity is also readily inferred from the results of multinuclear NMR spectroscopy in comparison with those for the Pt_2 **1** and Pd_2 **8**, (Supporting Information) and from its well-characterized adducts with SO_2 and CO, which were made in situ as described below.

The diplatinum compound **1** was first isolated in 1985,⁹ though its propensity to take up O_2 was not recognized until some 20 years later.^{1a} The dark-purple crystalline solid exhibits excellent air stability; a small sample of the compound, stored in a sample tube with plastic cap, was found to be unchanged after 20 years. The two new species $PtPd$ **7** and Pd_2 **8** are also air-stable in the solid state, but samples of Pd_2 **8** have been observed to degrade over a period of a few months. They are, however, stable in chlorinated solvents in the absence of air. In the presence of air, solutions of Pd_2 **8** in $CHCl_3$ are not stable, perhaps suggesting activation of atmospheric oxygen via a transient weak dioxygen

Table 1. Selected Measured Interatomic Dimensions from Single-Crystal X-ray Diffraction Studies with Selected Equivalent DFT Calculated Dimensions in [Square Brackets]

	Pt ₂	Pd ₂	Pt ₂ -CO	PtPd-CO	Pd ₂ -CO	Pt ₂ -SO ₂	PtPd-SO ₂	Pd ₂ -SO ₂
	1 ^{a,c}	8 ^c	4 ^a	10 ^b	11	5 ^a	12 ^b	13
M(1)–M(2)	2.9552(4) [2.9545]	2.9163(3) [2.9095]	2.7487(3) [2.8246]	2.749(3) [2.7961]	2.7491(6) [2.785]	2.8194(4) [2.8728]	2.810(7) [2.8545]	2.8041(6) [2.8375]
M(1)–P(1)	2.3344(4)	2.3860(6)	2.3402(16)	2.3416(18)	2.4007(11)	2.383(3)	2.384(4)	2.4172(13)
M(1)–P(2)	2.3382(4)	2.3806(6)	2.3516(17)	2.3656(17)	2.4013(9)	2.353(3)	2.351(4)	2.3798(13)
M(2)–P(3)			2.3331(17)	2.378(3)	2.4090(12)	2.345(2)	2.421(6)	2.4276(15)
M(2)–P(4)			2.3440(17)	2.419(4)	2.4006(8)	2.376(2)	2.379(7)	2.3915(13)
M(1)–C/S			2.098(6) [2.219]	2.112(4) [2.260]	2.148(3) [2.249]	2.388(2) [2.5942]	2.367(4) [2.6465]	2.3689(13) [2.5909]
M(2)–C/S			2.106(6) [2.219]	2.167(5) [2.203]	2.175(3) [2.249]	2.355(2) [2.5942]	2.405(7) [2.5592]	2.4139(13) [2.5909]
M(1)–B(3)	2.3626(17)	2.346(3)	2.332(7)	2.314(4)	2.329(3)	2.339(10)	2.284(10)	2.304(5)
M(1)–B(4)	2.2035(18)	2.212(3)	2.264(7)	2.268(4)	2.293(3)	2.258(10)	2.232(9)	2.260(5)
M(1)–B(5)	2.2225(18)	2.233(3)	2.255(7)	2.265(4)	2.280(3)	2.219(12)	2.239(9)	2.253(5)
M(1)–B(6)			2.305(6)	2.333(4)	2.305(3)	2.322(10)	2.328(10)	2.313(5)
M(2)–B(3)			2.298(7)	2.325(5)	2.306(3)	2.301(9)	2.330(11)	2.304(5)
M(2)–B(6)			2.348(7)	2.291(5)	2.344(3)	2.348(6)	2.329(11)	2.324(5)
M(2)–B(7)			2.280(6)	2.261(5)	2.269(3)	2.258(10)	2.223(11)	2.237(5)
M(2)–B(11)			2.266(6)	2.268(5)	2.284(3)	2.219(12)	2.229(12)	2.262(6)
S(1)\C(1)–O(1)			1.174(7) [1.1676]	1.153(4) [1.1623]	1.158(3) [1.1581]	1.454(7) [1.490]	1.458(6) [1.486]	1.455(4) [1.485]
S(1)–O(2)						1.461(7)	1.456(6)	1.460(4)
O(1)–S(1)–O(2)						113.7(4) [115.7]	112.7(4) [115.8]	113.5(2) [116.1]
M(1)–C(1)\S(1)–M(2)			81.36(19) [79.1]	79.94(15) [77.6]	78.97(10) [76.5]	72.94(6) [67.2]	72.14(18) [66.5]	71.78(4) [66.4]

^aData from reference 1b. ^bM(1) = Pt. ^cThere is crystallographically imposed 2-fold symmetry for compounds 1 and 8, such that M(1), P(1), P(2), B(3), B(4), and B(5) are equivalent to M(2), P(3), P(4), B(6), B(11), and B(7), respectively.

adduct, although monitoring by ¹¹B NMR spectroscopy shows no sign of such an intermediate. We have not yet conducted a detailed investigation of the products from these air-induced reactivities, but we have established by a single-crystal X-ray diffractions analysis that one product is a yellow-colored compound [(Cl)(PMe₂Ph)₃Pd₂B₁₀H₉(PMe₂Ph)] 9 (Figure S1, Supporting Information). Here, a PMe₂Ph ligand has been displaced from a palladium center by a chlorine substituent, and the PMe₂Ph has moved onto a boron atom. This results in a more open crevice for access to the dipalladium center, which augurs for some synthetic usefulness for this type of process, as fine tailoring of these dimetal species for small-molecule sequestration and activation will involve both entropic adjustment of the cavity size about the dimetal center and also electronic adjustment by substituents on the boron atoms of the cluster. The diplatinum analogue of 9 was isolated in the original work that resulted in the Pt₂ 1 compound.⁹

Structural Studies of the CO and SO₂ Complexes. We initially assessed the system by DFT calculation of molecular geometry at the B3LYP/6-31G*/LANL2DZ level¹⁰ to build up a matrix of information as to how modification of the metal would be expected to weaken or strengthen the binding of the small molecules, to validate our experimental observations thus enabling us to identify future synthetic targets. Details on these preliminary predictive calculations may be seen in the Supporting

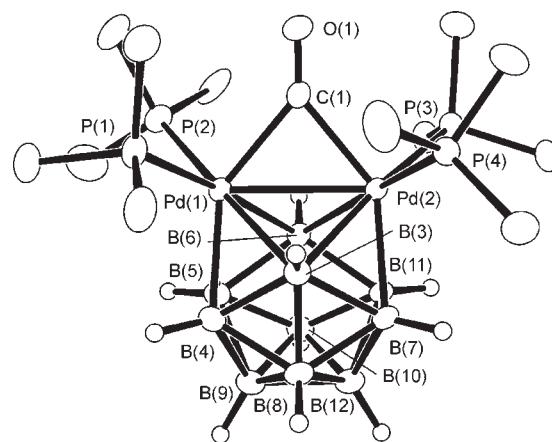


Figure 2. Representation of the crystallographically determined molecular structure of [(PMe₂Ph)₄(CO)Pd₂B₁₀H₁₀], Pd₂-CO 11, displayed with 50% thermal ellipsoids for non-hydrogen atoms. Phenyl group atoms (with the exception of the *ipso* carbon atoms) and the methyl group hydrogen atoms are omitted to aid clarity. Selected measured geometric parameters are listed in Table 1.

Information but, for comparison purposes, selected calculated geometric dimensions for the molecules reported here are listed

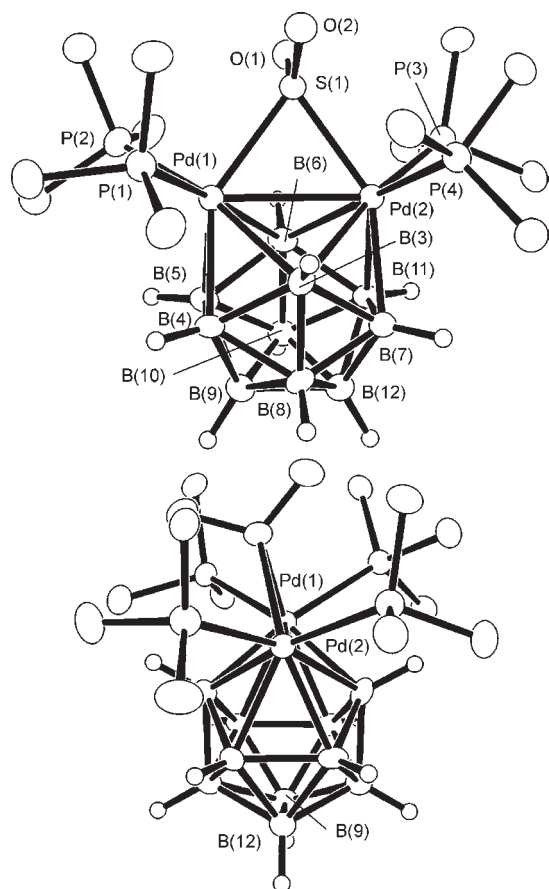


Figure 3. Representation of the crystallographically determined molecular structure of $[(\text{PMe}_2\text{Ph})_4(\text{SO}_2)\text{Pd}_2\text{B}_{10}\text{H}_{10}]$, $\text{Pd}_2\text{-SO}_2$ **13**, displayed with 50% thermal ellipsoids for non-hydrogen atoms. Phenyl group atoms, with the exception of the *ipso* carbon atoms and the methyl group hydrogen atoms are omitted to aid clarity. The lower diagram shows a side view illustrating the tilting of the SO_2 group with respect to the $\text{Pd}(1)\text{Pd}(2)\text{B}(9)\text{B}(12)$ plane. The corresponding representation of the molecular structure of the PtPd-SO_2 **12** analogue is visually isostructural and is therefore not shown. Selected measured geometric parameters for **12** and **13** are listed in Table 1.

in Table 1 and pertinent values shown in the Supporting Information are referred to in the text as required.

In contrast to Pt_2 **1**, no color changes are observed when dichloromethane solutions of PtPd **7** or Pd_2 **8** are saturated with dioxygen, and NMR spectroscopy shows no change. This reflects the trend in the calculated O–O interatomic distances that feature a shortening from 1.367 Å for $\text{Pt}_2\text{-O}_2$ to 1.351 Å for PtPd-O_2 to 1.336 Å for $\text{Pd}_2\text{-O}_2$ (Scheme S4, Supporting Information), synonymous with a weakening the interaction between dioxygen and the metal–metal cluster vector.

Under one atmosphere pressure of CO at room temperature, solutions of PtPd **7** and Pd_2 **8** exhibit immediate color changes from brown and dark purple-red respectively, to a pale tan-yellow in both cases. IR spectroscopy indicates the formation a CO adduct [$\nu(\text{CO})$ 1847 cm^{-1} for PtPd-CO **10**, 1882 cm^{-1} for $\text{Pd}_2\text{-CO}$ **11** ($\text{Pt}_2\text{-CO}$ **4** is 1810 cm^{-1})^{1b}]. This was confirmed by a single-crystal X-ray diffraction studies on **10** and **11** (Figure 2) and by ^1H , ^{11}B , and ^{31}P NMR spectroscopy which show that the addition is quantitative. Selected calculated and experimental geometric parameters together with those of the $\text{Pt}_2\text{-CO}$ **4**

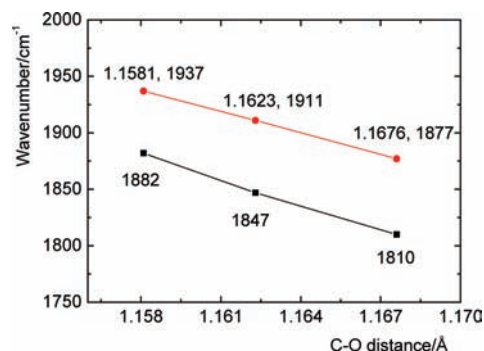


Figure 4. Measured (lower line) and DFT-calculated (upper line) infrared stretching frequencies of the CO group in $\text{Pt}_2\text{-CO}$ **4** (right) PtPd-CO **10** (center) and $\text{Pd}_2\text{-CO}$ **11** (left), plotted against the B3LYP/6-31G*/LANL2DZ calculated C–O distance.

analogue are listed in Table 1. The overall structure of PtPd-CO **10** is very similar to that for $\text{Pd}_2\text{-CO}$ **11**, but the disordered positions for the Pt and Pd atoms and for two of the PMe_2Ph groups means that the measured interatomic dimensions are less precise than those for the $\text{Pt}_2\text{-CO}$ **4** and $\text{Pd}_2\text{-CO}$ **11**, thus precluding a detailed comparison.

Sulfur dioxide reacts with PtPd **7** and Pd_2 **8** by addition to the metal–metal vector to give the two yellow-orange colored species PtPd-SO_2 **12** and $\text{Pd}_2\text{-SO}_2$ **13**, respectively. The reaction is also immediate and quantitative, as with Pt_2 **1**, which gives light orange $\text{Pt}_2\text{-SO}_2$ **5**.^{1b} The compounds PtPd-SO_2 **12** and $\text{Pd}_2\text{-SO}_2$ **13** are characterized by single-crystal X-ray diffraction analyses (Figure 3, Table 1) and by NMR spectroscopy (Experimental Section; a detailed analysis of the ^{11}B NMR spectra of the new compounds described in this paper may be also found in the Supporting Information).

All three SO_2 adducts, $\text{Pt}_2\text{-SO}_2$ **5**, PtPd-SO_2 **12**, and $\text{Pd}_2\text{-SO}_2$ **13**, exhibit qualitatively very similar SO_2 binding modes to the metal–metal unit. The sulfur atoms bridge the metal–metal linkage, which is not cleaved, and the sulfur atom exhibits approximately tetrahedral coordination to the two metal atoms and to the two oxygen atoms. In quantitative terms, with allowance for the disorder in the crystallographic structure of PtPd-SO_2 **12**, the density functional theory (DFT) predictions are nicely supported (Table 1), showing progressive lengthening of the metal-to-sulfur distances and progressively decreasing differences for the intermetal separations, from 2.8194(4) [2.8728 calc.] for **5**, to 2.8041(6) [2.8375 calc.] Å for **13**. Some minor differences are evident between the experimentally determined structure and the calculated structure, such as a tilting of the SO_2 group with respect to the plane defined by $\text{Pd}(1)\text{Pd}(2)\text{B}(9)\text{B}(12)$, which is not evident in the calculated structure. This may reasonably be ascribed to the effect of the packing of the SO_2 molecule within the PMe_2Ph ligand sphere, which is itself constrained by crystal packing forces. The organyl groups were replaced by H atoms to reduce computation time and thus the effect due to the constraints of the organyl groups would not be seen.

The calculated intermetal distances are longer than the measured ones by up to about 0.05 Å but this is not unexpected for third-row transition elements,¹¹ and other distances match more closely. The trends are well reproduced, and in particular there is a prediction of progressive weakening to the level of reversibility: the duly observed reversibilities of the additions of

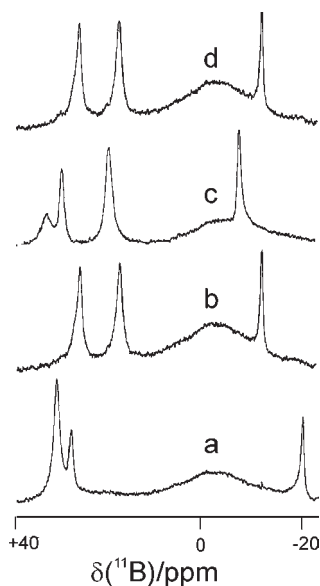


Figure 5. $^{11}\text{B}\{-^1\text{H}(\text{broadband})\}$ NMR spectra of aliquots of a single solution of Pd_2 **8** in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ before (trace a) and after (trace b) addition of CO to give $\text{Pd}_2\text{-CO}$ **11**. Addition of SO_2 to (b) quantitatively affords $\text{Pd}_2\text{-SO}_2$ **13** (trace c), but bubbling CO through the warmed solution of **13** displaces the SO_2 to reform $\text{Pd}_2\text{-CO}$ **11**, (trace d). The large “hump” in the spectra centered at $\delta(^{11}\text{B})$ about -5 ppm is due to boron in the Pyrex NMR sample tube.

CO and SO_2 to the PtPd **7** and Pd_2 **8** compounds are described and discussed below.

Thus, for the CO adducts, the calculated and measured C–O distances are equal within experimental uncertainties, namely, 1.174(7) [1.168] in $\text{Pt}_2\text{-CO}$ **4**, 1.153(4) [1.162] in PtPd-CO **10** (NB: a considerable disorder in the single-crystal used in the X-ray study renders this measured value less reliable), and 1.158(3) [1.158] in $\text{Pd}_2\text{-CO}$ **11**. Plots of the calculated metal separations versus the measured and calculated infrared stretching frequencies show a linear progression (Figure 4). Although there is a systematic overestimation of the stretching frequency of about 60 cm^{-1} , this mirrors the systematic errors in the distances to the metals, and is consistent along the series.

In contrast to the diplatinum system, the addition of CO to Pd_2 **8** is readily reversible, and removal of the solvent from solutions of $\text{Pd}_2\text{-CO}$ **11** on a rotary evaporator results in the loss of the CO to reform Pd_2 **8**. CO may also be displaced by addition of SO_2 to form $\text{Pd}_2\text{-SO}_2$ **13**, but the SO_2 is also not strongly bound, and it may in turn be replaced by bubbling CO through solutions of $\text{Pd}_2\text{-SO}_2$ **13** in warm dichloromethane, as illustrated in Figure 5. The sulfur dioxide unit may be similarly displaced by CO from the mixed-metal adduct PtPd-SO_2 **12**, although it requires an extended time at the reflux temperature of CH_2Cl_2 to accomplish this. This reluctance is in line with the slightly stronger binding to the PtPd vector suggested by the calculated and measured intramolecular dimensions. In solution these compounds probably form an equilibrium mixture involving the complexed and uncomplexed metallaborane which is driven fully to product by the presence of excess CO or SO_2 . A more direct example showing presence of such an equilibrium is in the SO_2 adduct of [(phenanthroline) $\text{Pd}(\text{PMe}_2\text{Ph})_2\text{PtB}_{10}\text{H}_{10}$], (phen) PdPt **14**, namely, [(phenanthroline) $\text{Pd}(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{SO}_2)\text{B}_{10}\text{H}_{10}$], (phen) PdPt-SO_2 **15**. Here, the ^{11}B spectrum of

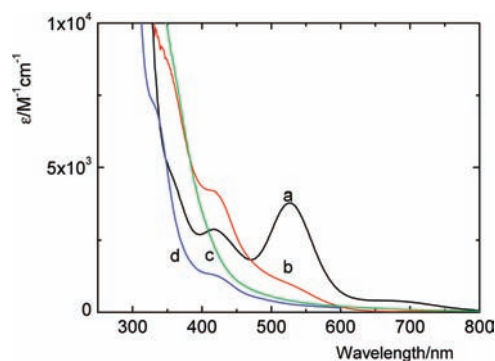


Figure 6. Absorption spectra in CH_2Cl_2 of Pt_2 **1** (a) and corresponding adducts $\text{Pt}_2\text{-O}_2$ **3** (b), $\text{Pt}_2\text{-SO}_2$ **5** (c), and $\text{Pt}_2\text{-CO}$ **4** (d).

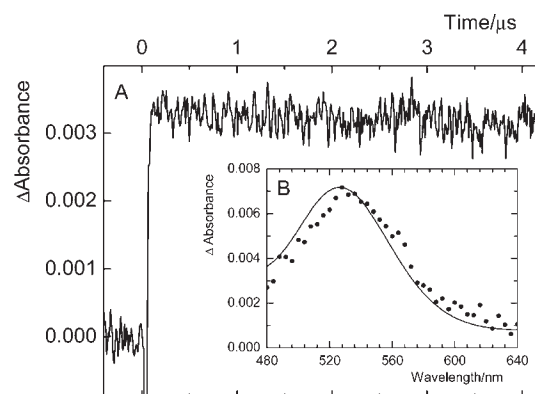


Figure 7. (A) Photorelease of CO after excitation of $\text{Pt}_2\text{-CO}$ **4** (ca. $100\text{ }\mu\text{M}$ in CH_2Cl_2) by a 425 nm laser pulse (ca. 2 mJ/pulse), measured at 524 nm. (B) Inset: transient absorption spectrum recorded 1 μs after excitation by a 308 nm laser pulse (ca. 15 mJ/pulse) compared with the normalized absorption spectrum of Pt_2 **1** (solid line) in CH_2Cl_2 .

crystalline samples of (phen) PdPt-SO_2 **15** dissolved in CD_2Cl_2 shows that it forms an equilibrium mixture of **14** and **15** which requires the addition of excess SO_2 to push it to pure solutions of **15**.¹²

That O_2 , CO, and SO_2 are released by the displacement or by warming solutions differently according to the identity of the metals, indicates that the reversibility of the binding is a tunable feature which might be of interest for, inter alia, the design of sensor materials and as handy sources of gas fluxes in a defined environment. For many possible applications, an external trigger to engender the instant release of the bound molecule would be required. This led us to examine the photophysical properties of the adducts, as photolysis by laser pulses using specific wavelengths could be a suitable and well-defined trigger for such a process.

Absorption Spectra. Figure 6 shows absorption spectra of Pt_2 **1** and its O_2 , CO, and SO_2 adducts. Compound Pt_2 **1** exhibits a quite distinctive absorption band at 527 nm, which is well separated from other electronic transitions. Reaction of Pt_2 **1** with O_2 , CO, or SO_2 is instantaneous, and the adduct formation is accompanied by the disappearance of this absorption band. In the case of $\text{Pt}_2\text{-SO}_2$ **5**, absorption below 350 nm is obscured by that of free SO_2 (Figure S2c, Supporting Information). We have included (phen) PdPt **14** and (phen) PdPt-SO_2 **15**¹² to provide extra examples of the mixed metal species. The absorption

changes observed for PtPd **7** and (phen)PdPt **14** are comparable to those in Pt₂ **1**, with the respective absorption bands at 495 and 528 nm disappearing after the addition of SO₂ (Figures S3, Supporting Information). Large absorption changes are also observed after the formation of Pd₂-SO₂ **13** from Pd₂ **8** (Figure S2, Supporting Information). In all cases, the adducts have sufficiently different absorption spectra when compared with the original cluster compounds to allow the spectroscopic monitoring of the reactions occurring in solution.

Nanosecond Laser Flash Photolysis. Nanosecond transient absorption spectroscopy of the Pt₂-CO **4** adduct shows the absorption changes (Figure 7) that arise from the liberation of CO from the bimetallic binding site. The changes occur within an excitation pulse width (ca. 28 ns) (Figure 7A), and the transient absorption spectrum nicely matches the absorption spectrum of Pt₂ **1** (Figure 7B), confirming that the photoproduct is indeed Pt₂ **1**. Furthermore, it is apparent that CO molecules are liberated from the bimetallic binding site very quickly. The diffusion-controlled back-reaction proceeds on a millisecond time scale (Figure S4, Supporting Information) that depends on the concentration of dissolved CO.

The quantum yield of the CO release, measured to be 0.60 ± 0.03 upon 308 nm irradiation, shows a high efficiency of scission of the Pt₂-CO linkage. To the best of our knowledge, the thermodynamics and the mechanism of CO photorelease and rebinding have mostly been studied with heme model compounds to understand processes through which heme proteins perform their physiological function.¹³ However, these processes are complex because of a heme center spin transition and, in some cases, because of the formation of a four-coordinate heme center or other factors, such as the flexing shape of the protein crevice, and cannot therefore be compared to the behavior of the Pt₂-CO **4** adduct.

The results further show that Pt₂-SO₂ **5** behaves similarly to Pt₂-CO **4** even though the absorption changes are smaller (data not shown). Because of the absorption of dissolved SO₂ below 350 nm, the quantum yield of the SO₂ photorelease from Pt₂-SO₂ **5** could not be measured. The adducts Pd₂-SO₂ **13**, PtPd-SO₂ **12**, and (phen)PdPt-SO₂ **15** also instantly release SO₂ (Figure S5, Supporting Information), and the liberated SO₂ recombines with the corresponding cluster to give the original adducts. There is little information in the literature on the reversible binding of SO₂ to metal complexes. For example, although it has previously been shown that some four-coordinate iridium species such as Vaska's compound [IrCl(CO)(PPh₃)₂],^{2b} and platinum compounds containing the terdentate-coordinating monoanionic [2,6-(CH₂NMe₂)₂-C₆H₃]⁻ ligand,^{3b,14} can reversibly bind SO₂, there are no reports, to our knowledge, on the release of SO₂ upon UV-vis irradiation.

Of the bimetallic boron clusters reported here, only Pt₂ **1** binds dioxygen.^{1b} Like Pt₂-CO **4**, the photorelease of O₂ from Pt₂-O₂ **3** occurs with a high quantum yield of 0.58 ± 0.03 after excitation by a 308 nm pulse. In addition to dioxygen in the ground triplet state [i.e., O₂(³Σ_g⁻)], a contribution of singlet oxygen O₂(¹Δ_g), was detected. This is surprising, as O₂(¹Δ_g) is most often produced by energy transfer to the dioxygen ground state from an electronically excited triplet state of a photosensitizer molecule.¹⁵ Under our conditions, we can exclude the photosensitized formation of O₂(¹Δ_g) as no long-lived excited states were detected (see below). Thus, the O₂(¹Δ_g) formation is clearly a result of the relaxation of excited states of the dioxygen adduct. To assess the efficiency of the O₂(¹Δ_g) generation we

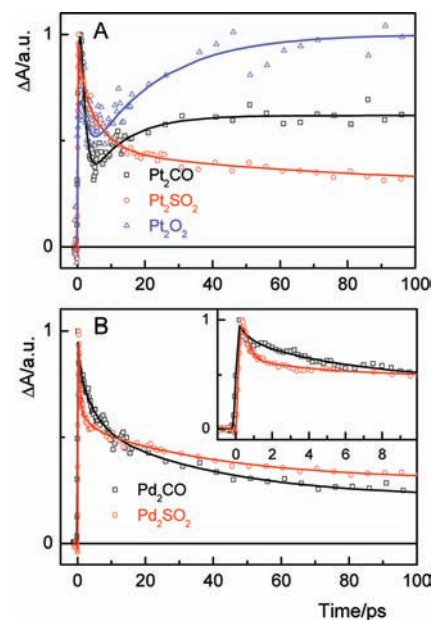


Figure 8. Kinetics following about 130 fs UV-excitation of the O₂, CO, and SO₂ adducts of (A) Pt₂ **1** and (B) Pd₂ **8** saturated with the added respective gases. Excitation is at 395 nm, with a probing wavelength of 535 nm for Pt₂-O₂ **3**, Pt-CO **4**, and Pt₂-SO₂ **5**, and of 540 nm for Pd₂-CO **11** and Pd₂-SO₂ **13**. All kinetics are normalized to maxima, with the solid lines corresponding to fits obtained from global fitting.

have measured its photoluminescence at 1270 nm (Figure S6, Supporting Information), as emission at this wavelength arises from relaxation of O₂(¹Δ_g) back to the triplet ground state O₂(³Σ_g⁻). The quantum yield of O₂(¹Δ_g) formation, Φ_Δ, estimated using a porphyrin standard,¹⁶ is below 0.01, thus indicating that the splitting channel leading to O₂(¹Δ_g) is of minor importance, although the option of modifying the system specifically to generate ¹Δ_g dioxygen is a future possibility that we are currently pursuing. Following photorelease, the bare diplatinum unit Pt₂ **1** rebinds O₂, albeit with some minor photodegradation being evident. Indeed, the lifetime of O₂(¹Δ_g), which is a measure of its reactivity with dissolved molecules, is dictated by the quenching efficiency of the metallaborane unit (Figure S6, Supporting Information). As a result, the measured lifetime for O₂(¹Δ_g) of 45 to 55 μs is much less than the reported value of 100 μs in pure CH₂Cl₂ in the absence of any singlet oxygen quenching activity.¹⁶

For comparison purposes, it may be noted that some binuclear μ-superoxo- and μ-peroxo cobalt complexes similarly produce ground-state dioxygen upon irradiation.¹⁷ Some mono-nuclear complexes also eliminate triplet-state dioxygen. For example, [IrCl(O₂)(CO)(PPh₃)₂] does so with a quantum yield of up to 0.43 and, as with Pt₂-O₂ **3**, the quantum yield Φ_Δ is low at 0.03.¹⁸ Conversely, the photolysis of the oxodiperoxomolybdenum(VI) complex, [MoO(O₂)₂], produces O₂(¹Δ_g) with Φ_Δ up to 0.42 depending on the excitation wavelength.¹⁹ The complex producing O₂(¹Δ_g) upon photolysis, with a behavior most similar to Pt₂-O₂ **3**, is the bis(triphenylphosphine)dioxygenplatinum peroxo complex [(Ph₃P)₂Pt(O₂)]; for this compound, this behavior is attributed to a ligand (i.e., O₂) transition with a ligand-to-metal (O₂ → Pt) charge transfer contribution.²⁰ Unfortunately, no Φ_Δ values were given. To the best of our knowledge, Pt₂-O₂ **3**, is the *only* example of a

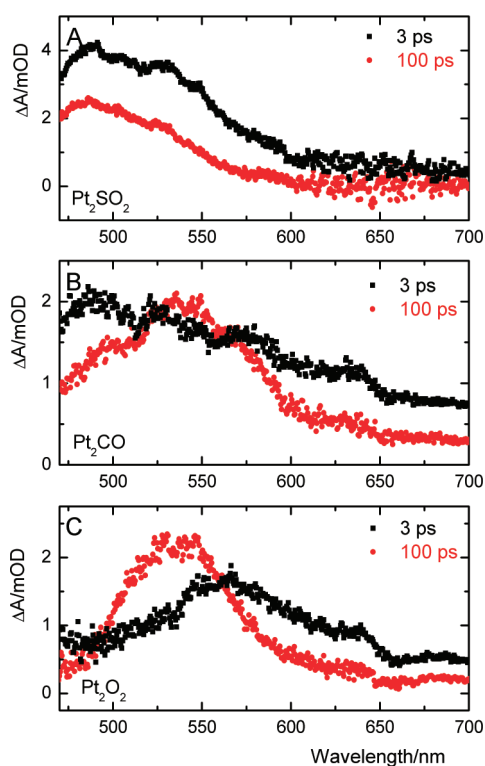


Figure 9. Transient absorption spectra of (A) $\text{Pt}_2\text{-SO}_2$ 5, (B) $\text{Pt}_2\text{-CO}$ 4, and (C) $\text{Pt}_2\text{-O}_2$ 3 measured after two different delay intervals, 3 ps (black) and 100 ps (red), after excitation at 395 nm.

bimetallic complex that reversibly binds dioxygen and releases it upon irradiation.

Femtosecond Transient Absorption. To obtain further insight into the photorelease mechanism of CO, SO_2 , and O_2 molecules from the adducts following UV–vis irradiation, we studied the ultrafast dynamics upon excitation with pulses of about 130 fs duration centered at 395 nm. The resulting kinetics for the Pt_2 - and Pd_2 -based homometal adducts measured at 535 and 540 nm (the wavelengths where the photoproducted ground-state Pt_2 1 and Pd_2 8 compounds absorb) are shown in Figure 8. The kinetics of both of the compounds $\text{Pt}_2\text{-CO}$ 4 and $\text{Pt}_2\text{-O}_2$ 3 reveal an initial fast decay followed by a rise component, whereas no corresponding rise component is observed for $\text{Pt}_2\text{-SO}_2$ 5. To identify the origin of this qualitatively different behavior, we have compared the transient absorption spectra recorded after different delay intervals. While the transient absorption spectra of $\text{Pt}_2\text{-SO}_2$ 5 do not significantly differ in shape when recorded after delays of 3 and 100 ps, the broad and featureless spectra of $\text{Pt}_2\text{-O}_2$ 3 and $\text{Pt}_2\text{-CO}$ 4 after 3 ps are replaced by a well-defined band centered at about 535 nm after a 100 ps delay (Figure 9). Further, a comparison of the transient absorption spectra at 200 ps with the difference absorption spectra (Figure 10) shows that, whereas the 200 ps spectra for $\text{Pt}_2\text{-O}_2$ 3 and $\text{Pt}_2\text{-CO}$ 4 match well the absorption spectrum of Pt_2 1 in the ground state, the transient absorption spectrum of $\text{Pt}_2\text{-SO}_2$ 5 peaks at 490 nm, and is thus significantly different from the 535 nm maximum.

The initial signals generated from $\text{Pt}_2\text{-CO}$ 4 and $\text{Pt}_2\text{-O}_2$ 3 decay with a about 1.5 ps time constant. Since the transient absorption spectra at 3 ps do not contain bands attributable to the compound Pt_2 1, this decay can be assigned to a fast relaxation of the excited states of the corresponding adducts

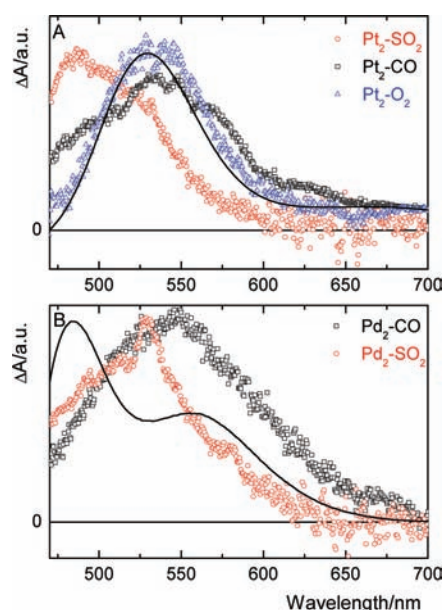


Figure 10. Transient absorption spectra of (A) $\text{Pt}_2\text{-SO}_2$ 5, $\text{Pt}_2\text{-CO}$ 4, $\text{Pt}_2\text{-O}_2$ 3, and (B) $\text{Pd}_2\text{-SO}_2$ 13, $\text{Pd}_2\text{-CO}$ 11 adducts recorded at 200 ps after excitation at 395 nm. Difference absorption spectra given as a difference between absorption spectra of the Pt_2 1 and Pd_2 8 clusters and the corresponding adducts are shown as solid lines for comparison.

(Figure 9). The following rise, occurring with an 11 ps time constant in $\text{Pt}_2\text{-CO}$ 4 and 20 ps in $\text{Pt}_2\text{-O}_2$ 3, describes the formation of Pt_2 1 in the ground state after the gas photorelease (Figures 9 and 10). In contrast, the excited-state relaxation of $\text{Pt}_2\text{-SO}_2$ 5 can be satisfactorily described by at least three decay components of 1, 6, and 80 ps. The photoproduct generated within the time window of the experiment is not ground-state Pt_2 1 (Figure 10). Instead, an intermediate complex, which may be, for example, an excited $\text{Pt}_2\text{-SO}_2$ with one S–Pt bond broken, is formed within the first 200 ps, and the complete release of SO_2 from the $\text{Pt}_2\text{-SO}_2$ adduct probably takes place on a longer time scale inaccessible in our femtosecond experiments (>1 ns). This indicates that the binding affinity of SO_2 toward the Pt_2 1 cluster is markedly greater than that of O_2 or CO, consistent with the conclusions from the results of DFT calculations (Supporting Information) and of experimental displacement reactions discussed in the section above.

For the dipalladium species, the kinetics recorded after the excitation of the Pd_2 -based adducts shown in Figure 8 demonstrate a different binding to the Pd_2 8 and Pt_2 1 compounds for SO_2 compared to CO. Thus, the adduct $\text{Pd}_2\text{-SO}_2$ 13 behaves comparably to $\text{Pt}_2\text{-SO}_2$ 5 and the excited states decay multiexponentially with time constants of 0.3, 2.5, and 40 ps. This behavior demonstrates that the nature of the metal binding sites quantitatively affects the relaxation of the whole complex and that it is faster in $\text{Pt}_2\text{-SO}_2$ 5. In contrast, however, the behavior of $\text{Pd}_2\text{-CO}$ 11 qualitatively differs from that of $\text{Pt}_2\text{-CO}$ 4, as shown by the features of the transient spectra at 200 ps, which differ significantly from the difference absorption spectrum of $\text{Pd}_2/\text{Pd}_2\text{-CO}$ (Figure 10). While excitation of $\text{Pt}_2\text{-CO}$ 4 leads to the photorelease of CO with an 11 ps time constant, $\text{Pd}_2\text{-CO}$ 11 undergoes excited-state relaxation with no formation of ground state Pd_2 8 within the measured time window. For comparison here, it may be noted that the ultrafast kinetics of CO photorelease have been studied in

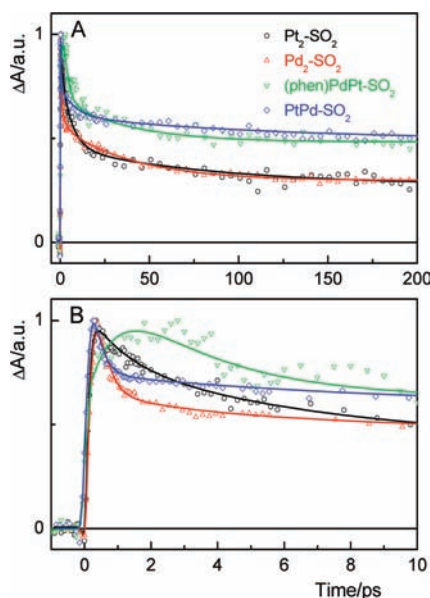


Figure 11. (A) Kinetics of the SO₂ complexes after excitation at 395 nm. Probing wavelengths were 530 nm for Pt₂-SO₂ **5**, 540 nm for Pd₂-SO₂ **13**, 520 nm for (phen)PdPt-SO₂ **15**, and 505 nm for PtPd-SO₂ **12**. The bottom panel (B) shows an expansion of the first 10 ps of the traces in the upper panel.

detail in some heme compounds.^{21,22} In these, the CO ligands are photodissociated instantaneously, and vibrational cooling of the ferrous ground state takes place in a few ps. Geminate recombination occurs from the nanosecond to millisecond time scales, and the CO molecules are stored within the protein matrix in docking sites.

Since both homometal SO₂ adducts Pt₂-SO₂ **5** and Pd₂-SO₂ **13** adducts have a comparable behavior, we also studied ultrafast dynamics of two SO₂-based adducts with mixed-metal binding sites, namely, PtPd-SO₂ **12** and (phen)PdPt-SO₂ **15** (Figure 11). The results clearly show that the nature of the metal atoms alters the amplitude and time constant of the initial fast component. In addition, the ultrafast dynamics are more complicated in (phen)PdPt-SO₂ **15**, showing a 0.8 ps rise that may be assigned to the formation of (phen)PdPt **14** because of the subpicosecond release of SO₂. This conclusion is also supported by a reasonable match between the transient absorption spectrum of (phen)-PdPt-SO₂ **15** taken at 200 ps and the corresponding difference absorption spectrum (Figure S7, Supporting Information). Thus, (phen)PdPt-SO₂ **15** may actually release the SO₂ molecule on a subpicosecond time scale, and the further dynamics, which are comparable to other SO₂-bound adducts, may then reflect a relaxation of (phen)PdPt **14** that is generated in a "hot" state. The time constants of this relaxation, as obtained from global fitting, are 2.5 and 35 ps. A similar situation occurs for PtPd-SO₂ **12**, for which the transient absorption spectrum recorded at 200 ps matches the PtPd/PtPd-SO₂ difference absorption spectrum (Figure S7, Supporting Information). However, no rise is detected; suggesting that for this compound the SO₂ release is ultrafast and takes place within the excitation pulse. In accord with the hypothesis of ultrafast SO₂ release in PtPd-SO₂ **12**, comparison of the transient absorption spectra measured at 0.25 and 200 ps (Figure S8, Supporting Information) shows that already at 250 fs the transient absorption spectrum matches the difference absorption spectrum. Thus, we conclude that in

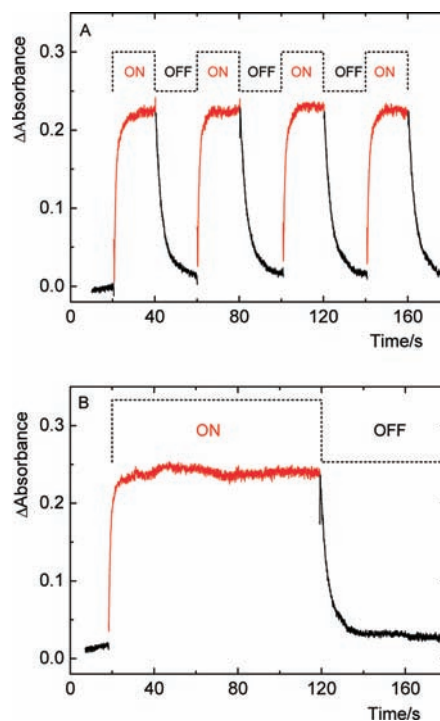


Figure 12. (A) Release and rebinding of O₂ under cyclic irradiation of Pt₂-O₂ **3** in CH₂Cl₂ (140 μM solution). The absorbance changes recorded at 524 nm during irradiation (light ON, red line) and dark periods (light OFF, black line), respectively, indicate the release of, and reverse binding of, O₂. The oxygen-saturated solution was irradiated by a Xe lamp (>370 nm). (B) Continuous irradiation for about 100 s under the same conditions as above.

clusters with mixed metal sites the photoinduced release of SO₂ is significantly faster than for the SO₂ adducts **5** and **13** of the homometal compounds Pt₂ **1** and Pd₂ **8**, most likely because of the metal–metal bonding asymmetry that is present in the mixed metal clusters, and which would reinforce the sequential asymmetric scission of the M-SO₂ bonds suggested above for the homometal compounds.

Continuous Irradiation. The reversible uptake of the studied gas molecules under UV–vis irradiation described above also may be observed on the macroscopic scale, and we also probed the reversibility of the adduct formation, as well as compound photostability, under the condition of continuous irradiation ($\lambda > 370$ nm). With Pt₂-O₂ **3**, the cycling of a sequence of irradiation periods of 20 s, alternating with dark intervals, shows that nearly 60% conversion to the dioxygen-free compound Pt₂ **1** is reached in about 10 s of irradiation (Figure 12A). The rebinding of O₂ occurs within 20 s in the dark interval. The photostability of the Pt₂ **1** compound under the irradiation conditions used is demonstrated by longer irradiation periods which lead to a constant stationary concentration, also about 60% (Figure 12B). It therefore appears that the release and rebinding of O₂ can be cycled with high efficiency without considerable photodegradation of the Pt₂ cluster. Pt₂-CO **4** behaves similarly (Figures S9, S10, Supporting Information), but, in agreement with the higher affinity of CO toward Pt₂ **1** compared to O₂, the maximum stationary concentration of photoproduct **1** is about 10%, rather than the 60% observed for Pt₂-O₂ **3**. The Pt₂-SO₂ **5** complex, in which the SO₂ molecule is the most strongly bound of the series reported here, does not show release under these

Table 2. Crystallographic Data for Pd₂ 8, PtPd-CO 10, Pd₂-CO 11, PtPd-SO₂ 12, and Pd₂-SO₂ 13

^a	8	10	11	12	13
formula	C ₃₂ H ₅₄ B ₁₀ P ₄ Pd ₂	C ₃₃ H ₅₄ B ₁₀ OP ₄ PdPt	C ₃₃ H ₅₄ B ₁₀ OP ₄ Pd ₂ ·CHCl ₃	C ₃₂ H ₅₄ B ₁₀ O ₂ P ₄ PtPdS·CH ₂ Cl ₂	C ₃₂ H ₅₄ B ₁₀ O ₂ P ₄ Pd ₂ S·C ₆ H ₆
diffractometer	Nonius KappaCCD	Brüker X8 Apex	Brüker X8 Apex	Nonius KappaCCD	Nonius KappaCCD
size	0.16 × 0.15 × 0.12	0.35 × 0.28 × 0.03	0.19 × 0.12 × 0.02	0.07 × 0.06 × 0.01	0.31 × 0.18 × 0.13
formula wt.	883.53	1000.23	1030.97	1064.76	1025.70
color, shape	orange prism	orange plate	red prism	yellow plate	red fragment
crystal sys.	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	<i>C2/c</i>	<i>Pna2₁</i>	<i>P2₁/c</i>	<i>Pna2₁</i>	<i>Pc2₁n</i>
<i>a</i> /Å	23.4332(3)	23.566(5)	12.4922(11)	23.901(5)	23.964(5)
<i>b</i> /Å	11.4378(2)	10.827(2)	24.4954(22)	10.743(2)	10.788(2)
<i>c</i> /Å	17.2521(3)	17.533(4)	15.7457(13)	17.573(4)	17.682(4)
β /deg	122.771(1)	90	97.903(4)	90	90
<i>V</i> /Å ³	3888.03(11)	4473.6(16)	4772.4(7)	4512.2(16)	4571.4(16)
<i>D</i> _{calc} /g·cm ⁻³	1.509	1.485	1.435	1.65	1.49
<i>F</i> ₀₀₀	1792	1976	2080	2216	2088
data/restr/par	4457/0/221	11046/1/548	11803/0/507	9819/1/502	8929/10/498
extinction parameter				0.00114(10)	
μ mm ⁻¹	1.114	3.694	1.083	3.833	1.006
GOF	1.055	1.032	1.023	1.025	1.034
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0323	0.0243	0.0361	0.0469	0.0433
<i>wR</i> 2 (all data)	0.0761	0.0631	0.0879	0.0961	0.1038
$\rho_{\text{max and min}}$ /e ⁻ Å ⁻³	0.83 and -1.42	0.66 and -1.46	1.246 and -1.162	1.11 and -1.05	1.25 and -0.97
Flack		0.022(5)		0.026(8)	

^a Common factors. All measured at 150(2) K, *Z* = 4.

conditions whereas PtPd-SO₂ 12, which binds SO₂ less strongly, exhibits well-measurable changes because of the release of SO₂ (Figure S11, Supporting Information). Pd₂-SO₂ 13 also releases SO₂ under these conditions, but now the release and rebinding sequence is accompanied by significant compound photodegradation.

CONCLUSIONS

Predictive DFT work suggested that PtPd 7 and Pd₂ 8 would be synthetically viable targets, and that CO and SO₂ would bind to them in an analogous manner to that established for Pt₂ 1. In addition, DFT calculations suggested that the Pd₂ 8 would bind SO₂ and CO more weakly than the corresponding diplatinum compound Pt₂ 1, thus allowing for reversibility observed earlier for the uptake of SO₂ and CO addition in a similar manner to that observed previously for the reversible uptake of O₂ by Pt₂ 1. Experiments then successfully showed that the binding of the molecules is indeed progressively weaker in the sequence {PtPt} → {PtPd} → {PdPd}. The binding of CO is shown to be weakened sufficiently that ready reversibility of CO and SO₂ uptake was observed for the Pd₂ 8 bimetallic site and to a lesser extent for the PtPd 7 compound.

We found that the sequestered molecules could be ejected by UV-vis irradiation. Very interesting consequences follow from the discovery of the light-activated control of the gas molecule release. Fast and spatiotemporal control of active molecule delivery are fundamental criteria for any potential application of these gas-releasing systems,²³ and the on/off triggering by light described here satisfies both of these requirements. Other additional important features imposed on such delivery systems are photostability, the ability to reversibly bind the active molecules, the possibility to follow the course of the binding/release processes, and the accurate prediction of system improvements; these

are all addressed in this work. In this context it is noteworthy that the dioxygen adduct Pt₂-O₂ 3 releases dioxygen upon UV-vis irradiation with high quantum yields, and, moreover, a fraction of the dioxygen is released in singlet configuration.

The results show that the tailoring of this system by variation of metal is highly viable and useful, and that DFT predictions are a very useful aid to predicting viable targets and therefore optimizing the use of valuable synthetic bench time. The results augur well for future tailoring and fine-tuning of this system by variation of metal and metal ligand, by variation of boron cluster substituent, or by cluster constituents, such as replacing B by C, S, and so forth (as a fourth way of modification), and also for extension to other small molecules, not only in terms of sequestration, but also in terms of activation. In this latter regard there is potential here for these B-frame bimetallics to rival the very extensively investigated area of so-called "A-frame" bimetallics in versatility and consequent utility, and we hope to explore all these possibilities.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under standard vacuum or inert-atmosphere techniques, although subsequent operations were generally carried out in air, except for a number of those involving solutions of the oxygen-sensitive [(PMe₂Ph)₄PtPd-B₁₀H₁₀] 7 and [(PMe₂Ph)₄Pd₂B₁₀H₁₀] 8. B₁₀H₁₄ was obtained commercially (Katchem, Prague). Dichloromethane, hexane, and pentane (Fluka) were dried over appropriate desiccants and stored in 500 mL RB flasks fitted with Teflon vacuum taps and transferred by vacuum distillation into vessels cooled by liquid N₂. KHBET₃ (Aldrich, 1.0 M THF solution) was used as received. Other starting materials were of reagent or analytical grade and were used as purchased. Reactions were generally carried out in a 5 mm o.d. NMR tube with a vacuum tight

Teflon screw cap. [*cis*-PtCl₂(PMe₂Ph)₂] was made by the literature route²⁴ from stirred water mixtures of K₂[PtCl₄] and PMe₂Ph. [(PMe₂Ph)₂PtB₁₀H₁₂] was made essentially according to the method reported earlier²⁵ in yields of about 90%. [PdCl₂(PMe₂Ph)₂] was prepared using ethanol solutions of K₂[PdCl₄] and PMe₂Ph from which the [PdCl₂(PMe₂Ph)₂] precipitates. The resultant yellow suspension was filtered and washed with a small amount of alcohol to obtain the [PdCl₂(PMe₂Ph)₂] and was used without further purification. [(PMe₂Ph)₂Pd₂B₁₀H₁₂] was made by addition of [PdCl₂(PMe₂Ph)₂] to a stirred solution of B₁₀H₁₄ in CH₂Cl₂ that also contained 2 equiv of 1,8-bis-(dimethylamino)naphthalene ("Proton Sponge"), followed by flash chromatography down a silica-gel column (70/30 CH₂Cl₂/*n*-hexane). To achieve a maximum yield of [(PMe₂Ph)₂Pd₂B₁₀H₁₂] the ethanol filtrate from the preparation of [PdCl₂(PMe₂Ph)₂] was reduced to dryness on a rotary evaporator, redissolved in CH₂Cl₂ and added to a CH₂Cl₂ solution containing excess B₁₀H₁₄ and Proton Sponge; the mixture was then stirred overnight and then also subjected to flash column chromatography. This procedure allows an almost quantitative overall yield of [(PMe₂Ph)₂Pd₂B₁₀H₁₂].

Criteria of purity consisted of clean ¹¹B, ¹H, and ³¹P NMR spectra consistent together with molecular and crystal structures obtained by single-crystal X-ray diffraction analyses. A range of mass spectrometry techniques were attempted on all the compounds reported here but none gave identifiable fragments.

NMR spectroscopy was performed at about 5.9 and 11.75 T (fields corresponding to nominal 250 and 500 MHz ¹H frequencies respectively) using commercially available instrumentation and using techniques and procedures as adequately described and enunciated elsewhere.²⁶ Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1\text{H})$ (± 0.05 ppm) (nominally tetramethylsilane, Si(CH₃)₄), $\Xi = 32.083972$ MHz for $\delta(^{11}\text{B})$ (± 0.5 ppm) (nominally Et₂OBF₃ in CDCl₃) and $\Xi = 40.480730$ MHz for $\delta(^{31}\text{P})$ (± 0.5 ppm) (nominally 85% aqueous H₃PO₄), calibrations being effected by use of solvent deuterium or residual proton signals as internal secondary standards. Ξ is as defined by McFarlane.²⁷ Cluster ¹¹B and ¹H NMR data are presented as assignment $\delta(^{11}\text{B})$ [$\delta(^1\text{H})$ for directly bound H(exo) in brackets]. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using a diamond cell or on a KBr plate in a Nicolet Nexus 670 FT-IR spectrometer.

Calculations were carried out using the Gaussian 03 package.^{10a} Structures were initially optimized using standard ab initio methods with the STO-3G* basis-sets for B, C, P, S, N, and H, with the LANL2DZ basis-set for the metal atoms. The final optimizations, including frequency analyses to confirm the true minima, were performed using B3LYP methodology with 6-31G* and LANL2DZ basis-sets.^{10b-e} In all cases the compounds were modeled using hydrogen atoms rather than organyl groups on the phosphine ligands to reduce computation time. Computed carbonyl frequencies were scaled with a 0.9613 scaling factor.²⁸

Syntheses. *Improved Preparation of [(PMe₂Ph)₄Pt₂B₁₀H₁₀] (Pt₂ 1).* (Case A) Toluene (20 mL) was injected through a septum into a two-neck round-bottomed flask containing [(PMe₂Ph)₂PtB₁₀H₁₂] (0.202 g, 0.341 mmol) and a stir bar. The mixture was cooled in a dry ice bath to -71 °C and KHBET₃ (0.68 mL, 0.68 mmol) then injected, after which the mixture was allowed to warm slowly to -30 °C, giving a colorless solution. The temperature was lowered to -50 °C, [PtCl₂(PMe₂Ph)₂] (0.155 g, 0.34 mmol) added against a flow of nitrogen, the stirring continued, and the mixture allowed to warm slowly to room temperature. A clear orange solution quickly formed which gradually darkened with a dark solid appearing on the bottom of the flask. The next day the mixture was filtered giving 0.178 g of dark purple microcrystalline solid which was quickly washed with benzene, then pentane. A further 0.096 g was scraped from the wall of the reaction vessel affording 0.274 g, 0.258 mmol, 76% of Pt₂ 1.^{1b}

(Case B) PMe₂Ph (0.2 mL, 1.4 mmol) was injected into a suspension of [(PMe₂Ph)₂PtB₁₀H₁₂] (0.342 g, 0.557 mmol) in degassed toluene

(100 mL), and the solution heated at reflux under nitrogen overnight. The color slowly changed from yellow to brown/dark purple. After cooling and rapid filtration in air, washing with benzene gave microcrystalline Pt₂ 1 (0.157 g, 0.148 mmol; 53% yield based on Pt).

In both cases A and B, purification of Pt₂ 1 is better done by filtration of CH₂Cl₂ solutions in air and crystallization from aerated CH₂Cl₂/hexane solution stored at < -20 °C. This procedure gives the orange-colored Pt₂-O₂ 3, from which compound Pt₂ 1 may be easily regenerated in situ for further experimentation by purging solutions of the compound with an inert gas.

Preparation of [(PMe₂Ph)₄PtPd₂B₁₀H₁₀] (PtPd 7). The above procedure for 1 was followed with [(PMe₂Ph)₂PtB₁₀H₁₂] (0.099 g, 0.167 mmol) in toluene (23 mL) and KHBET₃ (0.34 mL, 0.34 mmol) added. After allowing to warm to -30 °C the temperature was reduced to -50 °C and [PdCl₂(PMe₂Ph)₂] (0.076 g, 0.168 mmol) added against a flow of nitrogen, and the reaction mixture allowed to warm slowly to room temperature with stirring. Subsequently, a purple-brown solid was obtained by filtration after washing with benzene and pentane. The solid was dissolved in CH₂Cl₂, passed through a sintered glass filter, crystallized from CH₂Cl₂/*n*-pentane at about -20 °C, and identified it as [(PMe₂Ph)₄PtPd₂B₁₀H₁₀] by multielement NMR spectroscopy (51 mg, 0.052 mmol, 31%). Elem. anal. for [(PMe₂Ph)₄PtPd₂B₁₀H₁₀]. CH₂Cl₂, found(calc.): C 37.57(37.49) H 5.14(5.34). Attempts to obtain single-crystals suitable for X-ray analysis from dichloromethane hexane or chloroform hexane solutions were unsuccessful. NMR data (298 K, CD₂Cl₂), $\delta(^{11}\text{B})$ [¹H]/ppm: BH(7,11), +31.9 [+5.23]; BH-(9,3,6,4,5,12) +25.3 [+4.67, +4.51(2), +4.35(2), +3.91]; BH(8,10), -23.0 [+1.14]. $\delta(^1\text{H})$ PMe₂(Pt)_A: +1.71 {N(³¹P-¹H) 9.8 Hz, ³J-(¹⁹⁵Pt-¹H) 24.6 Hz}, PMe₂(Pt)_B: +1.62 {N(³¹P-¹H) 9.2 Hz, ³J-(¹⁹⁵Pt-¹H) 21.4 Hz}, N(³¹P-¹H) ca. 10 Hz; PMe₂(Pd)_A: +1.47 {N(³¹P-¹H) 8.2 Hz}, +1.45, N(³¹P-¹H) 7.7 Hz}, and for PPh +7.17 to +7.41 {multiplets}. $\delta(^{31}\text{P})$ /ppm, CD₂Cl₂, -50 °C: on Pt +3.5 [³J(³¹P-³¹P) 10, ¹J(¹⁹⁵Pt-³¹P) 2640 Hz], on Pd -21.1 [³J(³¹P-³¹P) 10 Hz, possible ²J(¹⁹⁵Pt-³¹P) ca. 40 Hz].

Preparation of [(PMe₂Ph)₄Pd₂B₁₀H₁₀] (Pd₂ 8). The above procedure as described for Pt₂ 1 was followed using toluene (100 mL) and [(PMe₂Ph)₂Pd₂B₁₀H₁₂] (0.203 g, 0.403 mmol), with 0.81 mL, 0.81 mmol, of KHBET₃ solution injected at -70 °C. The mixture was allowed to warm slowly with stirring to -50 °C and held at that temperature for 30 min during which time the mixture turned brown. [PdCl₂(PMe₂Ph)₂] (0.443 g, 0.403 mmol) was added against a flow of nitrogen, and the reaction mixture left to warm slowly to room temperature with stirring overnight. Next morning the mixture was quickly filtered and washed with benzene giving 0.14 g of a purple-brown solid. A further 0.065 g of solid was scraped from the walls of the reaction vessel. Both solids were identified as [(PMe₂Ph)₄Pd₂B₁₀H₁₀] (compound 8, combined yield 0.234 g, 0.23 mmol; 57%). Dark red single-crystals were obtained from saturated CDCl₃ solutions of the compound under anaerobic conditions stored at -20 °C. Elem. anal. C₃₂H₅₄B₁₀P₄Pd₂, found(calc.): C 43.55(43.48), H 6.17(5.97). NMR data (298 K, CDCl₃): BH(9,12) +29.7 [+4.41], BH(3,6) ca. +32.6 [+4.85] and (near-coincident resonances) BH(4,5,7,11) ca. +32.6 [+5.48], and BH(8,10) -20.1 [+0.99]; with $\delta(^1\text{H})$ for PMe₂ +1.49 and +1.72 {both with N(³¹P-¹H) ca. 8 Hz}, and for PPh +7.22, +7.34 and +7.40 4H {multiplets}; also $\delta(^{31}\text{P})$ -15.3 ppm.

Reaction of Pd₂ 8 with CO to Give Pd₂-CO 11. CD₂Cl₂ (ca. 0.5 mL) was condensed into an NMR tube containing a sample of Pd₂ 8 (ca. 3 mg); the tube was then sealed, removed from the Schlenk line, and shaken to dissolve the sample. The tube was reattached to the Schlenk line and opened to an atmosphere of pure CO. A pale tan color was observed to diffuse down slowly from the top of the dark purple-red solution. Agitation of the tube eventually resulted in the disappearance of the purple-red color to form a tan-colored solution, and ¹¹B, ³¹P, and ¹H-¹¹B NMR spectroscopy then indicated a complete conversion to Pd₂-CO 11. Removal of the solvent from CH₂Cl₂ solutions of the

compound on a rotary film evaporator (water bath, ca. 30 °C) resulted in regeneration of Pd₂ **8**, pure by NMR spectroscopy. Crystals suitable for single-crystal X-ray work were obtained by diffusion of *n*-pentane through a layer of benzene into a CHCl₃ solution of the compound. Because of the easy loss of CO from the compound, the sample was agitated slightly to accelerate mixing and to initiate crystallization, but this caused the formation only of small crystals, which necessitated the use of a rotating-anode X-ray source to obtain a suitable data set for the diffraction analysis. Infrared, diamond cell: $\nu(\text{BH})$ 2511br, $\nu(\text{CO})$ 1882 cm⁻¹. NMR data (298 K, CDCl₃): BH(9,12) ca. +28.5 [+4.64] and (coincident boron resonances) BH(3,6) ca. +28.5 [+2.16], BH-(4,5,7,11) +19.6 [+4.33] and BH(8,10) -11.3 [+1.98]; with $\delta(^1\text{H})$ for PMe₂ +1.26 and +1.53 {both with $N(^{31}\text{P}-^1\text{H})$ ca. 10 Hz}, and for PPh +7.05 to +7.40 {multiplets}; also $\delta(^{31}\text{P})$ -14.1 ppm.

Reaction of Pd₂ **8 with SO₂ to Give Pd₂-SO₂ **13**.** The procedure followed that described above for Pd₂-CO **11**. A golden coloration, rather than the tan of the CO reaction, diffused down the column of solution in the tube. Quantitative conversion was confirmed by NMR spectroscopy. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by diffusion of *n*-pentane through a thin layer of benzene into a CH₂Cl₂ solution of the compound. NMR data (298 K, CD₂Cl₂): BH(9,12) +31.4 [+4.58], BH(3,6) +34.7 [+2.65], BH-(4,5,7,11) +21.3 [+4.23] and BH(8,10) -6.2 [+2.09]; with $\delta(^1\text{H})$ for PMe₂ +1.25 and +1.44 {both with $N(^{31}\text{P}-^1\text{H})$ ca. 10 Hz}, and for PPh +7.25 to +7.50 {multiplets}; also $\delta(^{31}\text{P})$ -8.35 ppm.

Reaction of PtPd **7 with CO to Give PtPd-CO **10**.** The procedure carried out for compound **11** was repeated. Very dark red crystals suitable for single-crystal X-ray diffraction analysis were obtained by diffusion of *n*-pentane into CH₂Cl₂ solutions of the compound. NMR data (298 K, CD₂Cl₂): BH(9) ca. +23.9 [+5.29], BH(12) ca. +20.7 [+4.18]; BH(3,6) +16.6 [+1.35], BH(4,5) +14.6 [+4.08], BH(7,11) +7.3 [+3.80] { $J(^{195}\text{Pt}-^1\text{H})$ ca. 55 Hz} and BH(8,10) -13.9 [+2.09]; with $\delta(^1\text{H})$ for PMe₂(Pt)_A +1.47 { $N(^{31}\text{P}-^1\text{H})$ 10.0 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ 17.5 Hz}, PMe₂(Pt)_B +1.41 { $N(^{31}\text{P}-^1\text{H})$ 10.4 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ 22.5 Hz}, PMe₂(Pd)_A +1.35 { $N(^{31}\text{P}-^1\text{H})$ 9.6 Hz}, PMe₂(Pd)_B +1.28 { $N(^{31}\text{P}-^1\text{H})$ 9.8 Hz} and for PPh +7.28 to +7.47 {multiplets}; also $\delta(^{31}\text{P})$ -24.6 [$^1J(^{195}\text{Pt}-^{31}\text{P})$ 2644 Hz] and -18.1 [$^3J(^{195}\text{Pt}-^{31}\text{P})$ 63 Hz]. Infrared, evaporated CH₂Cl₂ solution on to a KBr plate: $\nu(\text{BH})$ 2511br, $\nu(\text{CO})$ 1847 cm⁻¹.

Reaction of PtPd **7 with SO₂ to Give PtPd-SO₂ **12**.** The addition of SO₂ induced a ginger coloration. Green-yellow microcrystals were obtained from *n*-pentane/CH₂Cl₂ solution, and yellow-plate single-crystals for X-ray diffraction analysis were obtained by diffusion of *n*-pentane into a CH₂Cl₂ solution of the compound. Anal. [(PMe₂Ph)₄(SO₂)PtPd₁₀H₁₀].CH₂Cl₂, found(calc.): C 35.61(35.35), H 5.07-(5.03). NMR data (298 K, CDCl₃): BH(12) ca. +27.4 [+5.76] {antipodal coupling $^4J(^{195}\text{Pt}-^1\text{H})$ ca. 30 Hz} (see text in Supporting Information, page S2), BH(9) ca. +27.4 [+4.73]; BH(3,6) +24.3 [+2.15], BH(4,5) +18.0 [+4.36], BH(7,11) +9.8 [+4.08] and BH(8,10) -7.6 [+2.96] { $J(^{195}\text{Pt}-^1\text{H})$ ca. 55 Hz}; with $\delta(^1\text{H})$ for PMe₂(Pt)_A +1.49 { $N(^{31}\text{P}-^1\text{H})$ 10.0 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ 17.5 Hz}, PMe₂(Pt)_B +1.72 { $N(^{31}\text{P}-^1\text{H})$ 10.4 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ 22.5 Hz}, PMe₂(Pd)_A +1.37 { $N(^{31}\text{P}-^1\text{H})$ 9.6 Hz}, PMe₂(Pd)_B +1.57 { $N(^{31}\text{P}-^1\text{H})$ 9.8 Hz} and for PPh +7.30 to +7.55 {multiplets}; also $\delta(^{31}\text{P})$ -10.7 [$^1J(^{195}\text{Pt}-^{31}\text{P})$ 2605 Hz] and -13.3 [no $^3J(^{195}\text{Pt}-^{31}\text{P})$ resolved]. [¹H-¹H]-COSY interactions between ¹H(4,5) at +4.36 and ¹H-(PMe₂)(Pd) at +1.37 and +1.57, and similarly between ¹H(7,11) at +4.08 and ¹H(PMe₂)(Pt) at +1.49 and +1.72, were observed, implying small but finite longer-range couplings $^5J(^1\text{H}-\text{B}-\text{Pd}-\text{P}-\text{C}-^1\text{H})$ -(*cisoid*) and $^5J(^1\text{H}-\text{B}-\text{Pt}-\text{P}-\text{C}-^1\text{H})$ (*cisoid*), but no correspondingly observable *transoid* interactions. Additionally, in ¹H-¹H spectra, fine doublet splittings on ¹H(4,5) and ¹H(7,11) of about 10 Hz were observable. These were more apparent in the [¹H-¹H]-COSY-¹H plots, which also showed a doublet splitting on ¹H(8,10) of about 3 Hz.

The [¹H-¹H] correlation behavior of the individual doublet components suggest that this fine structure probably arises from phosphorus-to-proton couplings.

Single-Crystal X-ray Diffraction Analyses. Diffraction data were collected either on a Nonius KappaCCD diffractometer with a conventional sealed-tube X-ray source ($\lambda = 0.71073 \text{ \AA}$), or, for very small crystals, on a Bruker X8 Kappa APEX II CCD area-detector diffractometer with an FRS91 rotating anode generator. In each case crystals were cooled with a dinitrogen gas stream. Absorption corrections were made by semiempirical methods. The structures were solved by automatic direct methods and refined by least-squares methods on all measured F^2 values, with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (F_o^2 + 2F_c^2)/3$. Residuals were defined by $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \sqrt{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2}$. Methods and programs were standard.²⁹ Crystallographic data are summarized in Table 2. The programs X-Seed³⁰ and Ortep-3 were³¹ used as an interface to the SHELX programs, and to prepare the figures. Compounds [(PMe₂Ph)₄(CO)PtPd₁₀H₁₀], PtPd-CO **10**, showed a disorder involving the positions of the platinum and palladium atoms. A model of the disorder was established assuming exchange in their positions and was refined with a free variable. Further disorder involved two positions for one phosphine group plus a slight twist in one phenyl group on a second phosphine and these were also refined with a common occupancy and refined with a free variable. Disordered dichloromethane molecules were also apparent and were incorporated in the model using Platon/Squeeze.³² [(PMe₂Ph)₄(SO₂)PtPd₁₀H₁₀] **12** also showed a similar disorder but only involving an exchange in the positions of the platinum and palladium atoms.

Photophysical and Photochemical Methods. *Nanosecond Transient Absorption.* Laser flash photolysis experiments were performed with a Lambda Physik COMPLEX 102 excimer (308 nm, pulse width 28 ns, incident energy up to 15 mJ/pulse) or a Lambda Physik FL 3002 dye laser (425 nm, incident energy ~1 mJ/pulse). Transient absorption spectra were measured within 450–600 nm on a laser kinetic spectrometer (Applied Photophysics, U.K.). The time profiles were recorded using a 250 W Xe lamp equipped with a pulse unit and a R928 photomultiplier (Hamamatsu). The quantum yields for the gas release were determined by the comparative technique using benzophenone as a standard ($\lambda_{\text{ex}} = 308 \text{ nm}$, $\Phi_{\text{T}} = 1.0$, $\Delta\epsilon = 7220 \text{ M}^{-1} \text{ cm}^{-1}$ at 530 nm).³³

Time-Resolved Luminescence of Singlet Oxygen. The near-infrared luminescence of O₂(¹ Δ_g) at 1270 nm was monitored using a Ge detector (1270 nm interference filter, Judson Ge diode) upon laser excitation by a Lambda Physik COMPLEX 102 excimer ($\lambda_{\text{exc}} = 308 \text{ nm}$, fwhm 28 ns, incident energy up to 200 mJ/pulse). Emitted luminescence was detected at the right angle to excitation light. The signal from the detector was collected in a 600 MHz oscilloscope (Agilent Infiniium) and transferred to a computer for further analysis. The signal-to-noise ratio of the signals was improved by the averaging of 100 to 500 individual traces. The short-lived signal produced by the scattering of an excitation laser pulse was eliminated by exciting the argon-saturated sample and by subtracting the obtained signal from the signal recorded in oxygen-saturated solution. The quantum yield of singlet oxygen formation, Φ_{Δ} , was estimated by the comparative method using 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin as a standard ($\Phi_{\Delta} = 0.8$).¹⁶

Femtosecond Transient Absorption. Femtosecond pulses were obtained from a 1 kHz femtosecond laser system (Integra-I, Quantronix). The output pulses had ~130 fs width, an average energy of ~2 mJ/pulse, and a central wavelength of 790 nm. The pulses were divided into two paths serving as excitation and probe pulses. Excitation pulses centered at 395 nm were generated by frequency doubling the primary output in a BBO crystal, while a white-light continuum obtained by focusing a fraction of the 790-nm pulses into a 0.2 cm sapphire plate was used for probing. For signal detection, the probe beam and an identical reference

beam were focused onto the entrance slit of a spectrograph, which then dispersed both beams onto a dual photodiode array detection system (ExciPro, CDP Systems). A 1-mm path length rotating quartz cell spinning at a rate ensuring that each excitation pulse hits a fresh sample was used for measurements. The mutual orientation of the excitation and probe beams was set to the magic angle (54.7°).

Continuous Irradiation. The sample dissolved in CH_2Cl_2 was placed in a sealed 1 cm sample quartz cell. The measurements were performed in a laser kinetic spectrometer LKS 20 (Applied Photophysics, U.K.) where the samples were continuously irradiated by a 250 W Xe lamp. A glass optical filter between the lamp and the irradiated cell was used to cut off the short wavelength components ($\lambda < 370$ nm) to prevent photodegradation of sample by UV light (this alignment is "light ON"). The transmitted light passed through a monochromator and was detected by an R928 photomultiplier (Hamamatsu). Irradiation was switched off by the addition of a 500 nm long pass filter between the lamp and the sample cell (this alignment is "light OFF"). In both cases transmitted light >500 nm served to probe the photochemical release of gases at the band maxima of the boron cluster adduct. The cycles light ON/light OFF were periodically repeated.

■ ASSOCIATED CONTENT

S Supporting Information. Additional information includes details of the DFT calculations mentioned in the text and a listing of DFT calculated atomic coordinates, a detailed analysis of the ^{11}B NMR spectra, Figures S1 to S11, and tables of interatomic distances and angles for compounds **8** to **13** obtained from single-crystal X-ray diffraction data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mails: jbould@gmail.com (J.B.), lang@iic.cas.cz (K.L.).

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