

Rhodium Disulfur and Dioxygen Complexes: Examination of Boron Secondary Coordination Sphere Effects

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Abstract:

A series of diphosphine-ligated rhodium(III) η^2 -peroxo and -persulfido compounds are targeted with one subset containing a boron-rich secondary coordination sphere (SCS). A systematic investigation using both experimental and theoretical methods has been performed to assess whether peripheral boranes can be used to engage with rhodium(III)-bound chalcogenides. For the model compound, $[\text{Rh}^{\text{I}}(\text{dnppe})_2]\text{BPh}_4$ ($\text{dnppe} = 1,2\text{-bis}(\text{di-}n\text{-propylphosphino})\text{ethane}$), adducts of the form $[\text{Rh}^{\text{I}}(\text{dnppe})_2(\eta^2\text{-Ch})]\text{BPh}_4$ ($\text{Ch} = \text{O}$ or S) were characterized. For the octaboranyl compound, $[\text{Rh}^{\text{I}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2]\text{BPh}_4$ ($\text{P}_2\text{B}^{\text{Cy}}_4 = 1,2\text{-bis}(\text{di}(3\text{-dicyclohexylboranyl})\text{propylphosphino})\text{ethane}$), however, treatment with O_2 resulted in SCS decomposition *via* B—O bond formation, while reaction with 0.25 equivs. S_8 provided $[\text{Rh}^{\text{I}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\eta^2\text{-S}_2)]\text{BPh}_4$, which based on variable-temperature ^{31}P NMR spectroscopic measurements, does not exhibit a B—S interaction. Using a compound with a single pendant borane as a model, potential energy surface (PES) scans were found to suggest kinetic and thermodynamic feasibility of a B—O interaction with $\Delta G(\text{B—O}) = -2.5 \text{ kcal mol}^{-1}$; a stationary point for the related B—S system was not located.

Keywords:

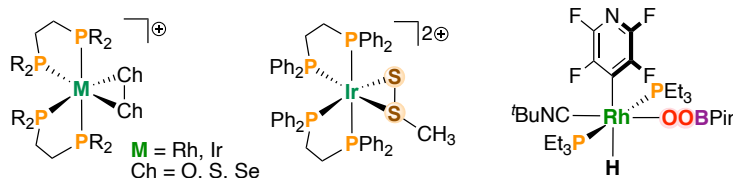
Boron | Secondary Coordination Sphere | Oxygen | Sulfur

1. Introduction:

Diphosphine-ligated rhodium (Rh) and iridium (Ir) complexes have a storied history of chalcogen (Ch) bond activation, providing some of the first examples of $[\text{M}]\text{-}\eta^2\text{-Ch}_2$ ($\text{M} = \text{Rh}, \text{Ir}, \text{Ch} = \text{O}, \text{S}, \text{Se}$) compounds.^{1,2,3,4,5,6,7} For dioxygen, such adducts are particularly noteworthy, representing some of the first fragments showing reversible uptake. Representatives of this class, $[\text{M}(\text{dppe})_2(\eta^2\text{-O}_2)]^+$ ($\text{M} = \text{Rh}, \text{Ir}, \text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$), were also some of the first dioxygen compounds to be characterized in the solid-state by X-ray crystallography.⁵ It is thus unsurprising that the robust synthesis of such phosphine-

ligated Group 9 compounds has led to several studies on chalcogen functionalization, including dioxygen reduction, oxygen- and -sulfur-atom transfer, and reactivity with electrophiles and nucleophiles. As an example, Braun and co-workers showed that the η^2 -peroxo compound, *trans*-[Rh(4-C₅F₄N)(CN^{*i*}Bu)(PEt₃)₂(η^2 -O₂)] underwent {[Rh]–O} bond cleavage on exposure to HBPIn (BPIn = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to provide the boron-protected κ^1 -O-peroxo rhodium(III) complex, *trans*-[Rh(4-C₅F₄N)(CN^{*i*}Bu)(PEt₃)₂(κ^1 -OOBPIn)(H)] (**Figure 1A**).⁸ In a related transformation, the iridium(III) congener, *trans*-[Ir(4-C₅F₄N)(CN^{*i*}Bu)(P^{*i*}Pr₃)₂(η^2 -O₂)] was shown to undergo reaction with ClBCy₂ to give *trans*-[Ir(4-C₅F₄N)(CN^{*i*}Bu)(P^{*i*}Pr₃)₂(Cl)₂] in addition to Cy₂BOBCy₂ and (CyBO)₃, likely through the intermediacy of Cy₂BO-OBCy₂, sourced from a structurally similar κ^1 -OOBCy₂ peroxy compound, *trans*-[Ir(4-C₅F₄N)(CN^{*i*}Bu)(P^{*i*}Pr₃)₂(κ^1 -OOBCy₂)(Cl)] (**Figure 1B**).⁹ In the context of sulfur chemistry, [Ir(dppe)₂(η^2 -S₂)]⁺ was observed to undergo methylation using methyl fluorosulfonate (CH₃SO₃F) to give [Ir(dppe)₂(η^2 -(SCH₃S))] ⁺,¹⁰ whereas [Rh^{III}(κ^2 -dppe)(κ^1 -dppe)(η^2 -S₂)(H)] was found to promote thiirane formation using substituted norbornenes¹¹ (**Figure 1A**).

A. group 9 { η^2 -Ch₂} compounds and reactions with electrophiles



B. reaction of an Ir(III) { η^2 -O₂} complex with BCiCy₂

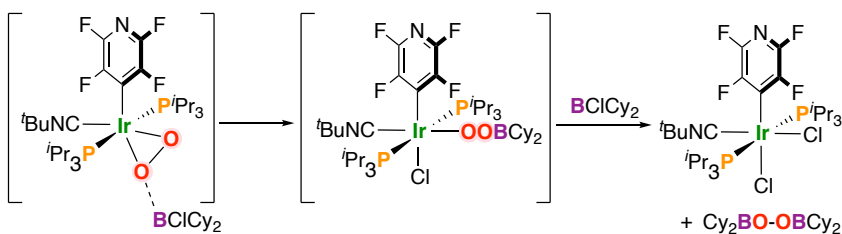


Figure 1. A summary of Group 9 { η^2 -Ch₂} complexes.

In a recent contribution, we reported on the synthesis of a rhodium(I) *bis*(diphosphine) compound, [Rh^I(P₂B^{Cy}₄)₂]BPh₄ (**1**) (P₂B^{Cy}₄ = 1,2-*bis*(di(3-dicyclohexylboraneyl)propylphosphino)ethane) that was found to be reactive toward nucleophiles (hydride and alkyl anions), undergoing functionalization at its boron-rich SCS and not at rhodium.¹² This report was particularly thought-provoking given the similarity in hydride

donor strength (ΔG_{H-}) between the putative (and unobserved) $\{[Rh]-H\}$ “ $[Rh(P_2B^{Cy}_4)_2(H)]$ ” and a trialkyl-substituted borohydride, $[BR_3H]^-$. Continuing our studies on this class of compound, and given the ample precedent for chalcogen activation by $[Rh^I(diphosphine)_2]^+$ compounds, we were interested to test whether a Lewis acidic SCS could be used for chalcogen activation/coordination. As motivations for this study – we asked the following: (1) on the basis of theoretical considerations, would these intramolecular B–Ch interactions be energetically favorable?; (2) given its bulky secondary coordination sphere (SCS), would $[Rh^I(P_2B^{Cy}_4)_2]^+$ react with O_2 or S_8 , and if so, would the boron-rich SCS provide stabilization *via* intramolecular Lewis adduct formation?; or (3) on exposure to O_2 , would the SCS decompose to provide boroxines such as those noted in the examples above? and finally, (4) would the spectral and/or structural characteristics of such putative $[Rh(P_2B^{Cy}_4)_2(\eta^2-Ch_2)]^+$ (Ch = O, S) compounds differ from those of an archetypical model compound, such as $[Rh(dmpe)_2(\eta^2-Ch_2)]^+$ (dmpe = 1,2-bis(di-*n*-propylphosphino)ethane), which lacks boron functionality? Answers to these queries are the focus of ensuing discussion.

2. Results and discussion:

2.1 Theoretical considerations:

We first wished to assess the thermodynamics of intramolecular $[Ch_2]^2$ (Ch = O, S) stabilization by boron using $[Rh^{III}(dmpe)(Me_2BCH_2CH_2CH_2P(Me)CH_2CH_2P(Me)_2)(\eta^2-Ch_2)]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) as a simplified model and calculated potential energy surfaces (PESs) as aids (see, ESI†, **Figures S20 and 21**). For the peroxo Rh^{III} adduct, these scans were performed by varying the B– O_1 bond distance between two extremes, bound and unbound: $d(B-O_1)$ from 3.60 to 1.60 Å. From this scan, a local minimum having $d(B-O_1) = 1.64$ Å was identified, with a pyramidalized boron atom ($\Sigma(\angle X-B-X) = 340^\circ$) (**Figure 2**). The Lewis adduct was found to have similar bonding metrics as compared to the borane-free compound, with minimal changes on boron complexation – distances are provided in **Figure 2**. For comparison, $[Rh(dppe)_2(\eta^2-O_2)]^+$ has bond lengths of $d(O-O) = 1.418(11)$ Å, $d(Rh-O) = 2.026(8)$ Å and 2.025(9) Å.⁵ Taking the interacting and non-interacting isomers, an energy difference (ΔE) of +0.4 kcal mol⁻¹ was calculated with a barrier height (ΔE^\ddagger) taken as the energy difference between the lowest and highest energy isomer) of only +2.4 kcal mol⁻¹. Using these isomers as starting points, accurate DLPNO CCSD(T)

calculations were performed using a THF solvation model, giving $\Delta G(\text{B}-\text{O}) = -2.5 \text{ kcal mol}^{-1}$. Together, these data suggest the feasibility of B—O bond formation at 298 K in THF. For the persulfido Rh^{III} complex, a similar workflow was outlined, however a minimum for a B—S interacting moiety was not obtained. For comparison, at $d(\text{B}-\text{S}) = 1.71, 1.67, 1.64 \text{ \AA}$, the interaction energies were found to steadily increase: 13.4, 17.5, and 22.6 kcal mol⁻¹ (Figure 2).

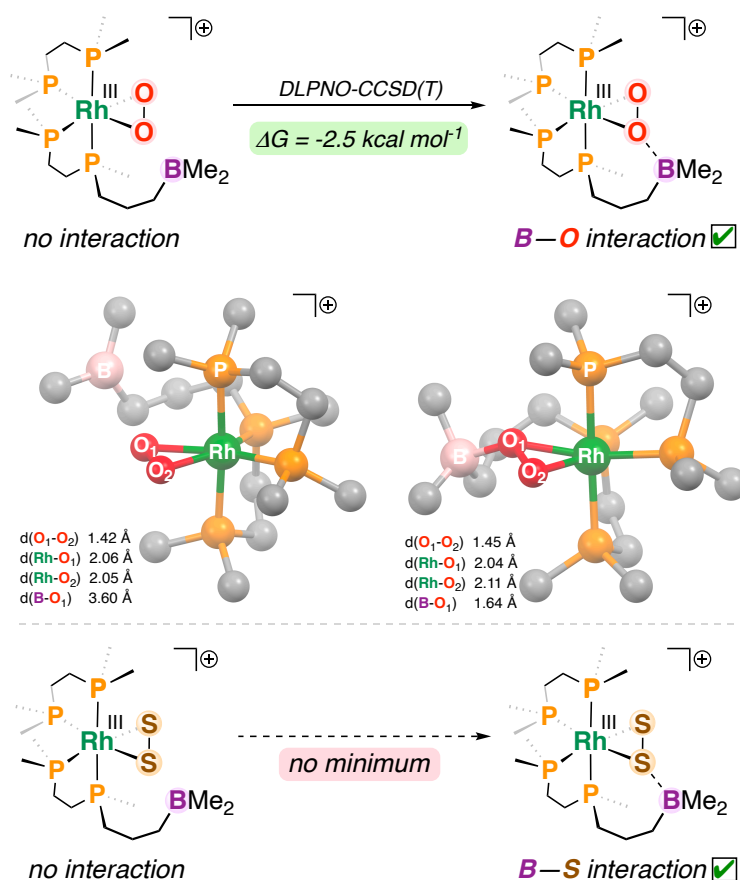


Figure 2. Calculated energies for Rhodium {η²-CH₂} complexes.

As a final query before advancing into our experimental work, we wished to use the [Rh^{III}(dmpe)(Me₂BCH₂CH₂CH₂P(Me)CH₂CH₂P(Me)₂)(η²-O₂)]⁺ blueprint described above to test the effect of metal on B—O interaction energy ($\Delta G(\text{B}-\text{O})$). Although the focus of the current work is on rhodium, we hypothesized that changing the identity of M along the Group 9 series: Co, Rh, Ir would result in more favourable interaction energies, owing to stronger {M(dπ)-to-O₂(π*)} back-bonding. For example, the O—O bond in [Ir(dppe)₂(η²-O₂)]⁺ (1.625(23) Å) is 15% longer than in [Rh(dppe)₂(η²-O₂)]⁺ (1.418(11) Å). It is important to note that compounds of the form, [Co(diphosphine)₂(η²-O₂)]⁺ (like the Rh and Ir analogues

referenced above), are also known.^{13,14} The results from this study are summarized in **Figure 3** and illustrate that $d(\text{O}_1\text{-O}_2)$ increases along the series, causing $\Delta G(\text{B-O})$ to decrease *i.e.*, become more favourable. The magnitude of this change, however, is not large.

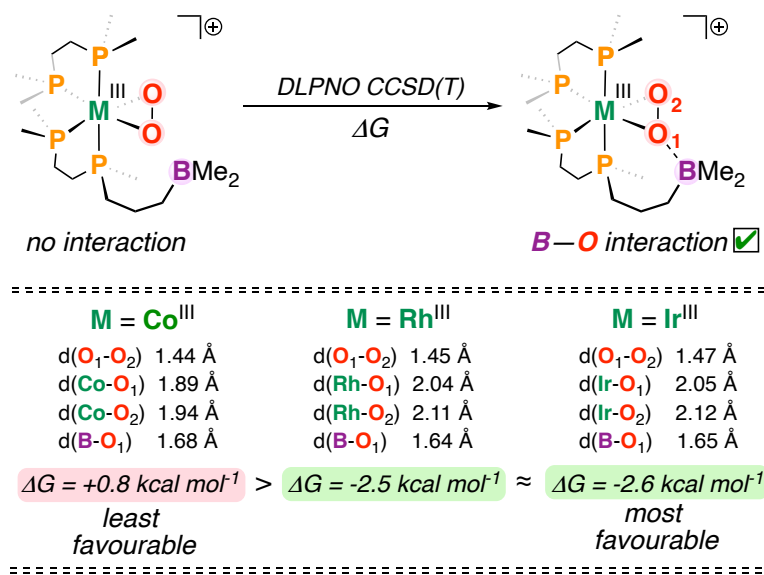


Figure 3. A summary of Group 9 Co, Rh, and Ir $\{\eta^2\text{-O}_2\}$ complexes.

2.2 Experimental work:

Moving towards examining the reactivity of rhodium diphosphine compounds, $[\text{Rh}^{\text{I}}(\text{dnppe})_2]\text{BPh}_4$ (**1**)¹² (*dnppe* = 1,2-*bis*(di-*n*-propylphosphino)ethane) was first screened as a structural isostere devoid of borane functionality (**Figure 4**). Exposure of a degassed THF solution of **1** to 1 atm of dry O_2 resulted in a lightening of its dark orange color. Analysis by ^{31}P NMR spectroscopy provided two resonances: one assigned to unreacted **1** at $\delta_{\text{P}} = 53.7$ ppm (d, $^1J_{\text{Rh,P}} = 126.3$ Hz), and another for $[\text{Rh}^{\text{III}}(\text{dnppe})_2(\eta^2\text{-O}_2)]\text{BPh}_4$ (**1-O**₂), characteristic of an 'A₂B₂X' spin-system, at $\delta_{\text{P}} = 49.6$ ppm (dt, $^1J_{\text{Rh,P}} = 89.0$ Hz, $^2J_{\text{P,P}} = 18.4$ Hz) and 47.3 ppm (dt, $^1J_{\text{Rh,P}} = 125.0$ Hz, $^2J_{\text{P,P}} = 18.4$ Hz) of relative intensity 1:2.74, giving a K_{eq} value of 2.7 atm⁻¹ at 298 K where $K_{\text{eq}} = [\text{1-O}_2]/([\text{1}][\text{O}_2])$ (**Figure 3**). This behavior is consistent with that noted previously for $[\text{Rh}(\text{dppe})_2]^+$, which in methanol at 30 °C, reacts with O_2 to give $[\text{Rh}(\text{dppe})_2(\eta^2\text{-O}_2)]^+$ with a K_{eq} value of 0.6 ± 0.1 atm⁻¹.¹⁵ Compound **1** also reacts with 0.25 equiv. of S₈ to give the persulfido compound, $[\text{Rh}^{\text{III}}(\text{dnppe})_2(\eta^2\text{-S}_2)]\text{BPh}_4$ (**1-S**₂) in >99% conversion, with characteristic resonances at $\delta_{\text{P}} = 47.5$ ppm (dt, $^1J_{\text{Rh,P}} = 123.9$ Hz, $^2J_{\text{P,P}} = 18.8$ Hz) and 41.2 ppm (dt, $^1J_{\text{Rh,P}} = 84.6$ Hz, $^2J_{\text{P,P}} = 18.8$ Hz) (**Figure 4**).

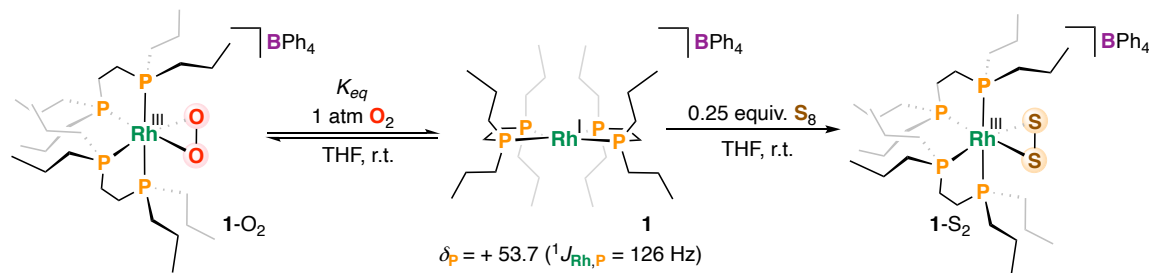


Figure 4. Reactivity of a model compound, $[\text{Rh}(\text{dmppe})_2]\text{BPh}_4$ (**1**) with O_2 and S_8 .

Reactivity of the octaboranyl compound, $[\text{Rh}^{\text{I}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2]\text{BPh}_4$ (**2**)¹² with O_2 and S_8 was next gauged (**Figure 5**). Admission of 1 atm. of O_2 to a degassed THF solution of **2** gave a pale-yellow solution with ^{31}P NMR spectroscopic signatures distinct from **1-O**₂. Two broad resonances were observed at $\delta_{\text{P}} = 53.0$ ppm and 52.0 ppm ($\Delta_{1/2} \approx 80$ Hz), suggesting formation of an unsymmetrical (or fluxional) rhodium complex or a mixture of structurally similar complexes. Notably, unlike in the case of **1**, unreacted **2** was not observed. The noted broadness by ^{31}P NMR spectroscopy prompted a variable temperature study from 298 K to 193 K. As a function of decreased temperature, these resonances baseline-broadened and did not sharpen, suggesting low symmetry of the resultant product(s). By ^{11}B NMR spectroscopy, two signals at $\delta_{\text{B}} \approx 52$ ppm and 31 ppm, assigned to R_2BOR *e.g.*, $\text{Cy}_2\text{BOBCy}_2$ and $\text{RB}(\text{OR})_2$ *e.g.*, $(\text{CyOB})_3$, respectively were observed – these decomposition products are similar to those described by Braun and co-workers for treatment of an $\{[\text{Ir}]-\text{O}_2\}$ complex with BCy_2Cl (*vide supra*).⁹ These data suggest formation of a series of isomeric C_1 -symmetric $[\text{Rh}^{\text{III}}(\text{diphosphine})_2]^+$ compounds, some likely with O_2 bound, that result from decomposition of the projecting pendant boranes. For reference, it is well-accepted that trialkylboranes undergo autooxidation *via* transient $\{[\text{B}]-\text{O}-\text{O}-\text{C}\}$ units, which are prone to structural rearrangement or formation of radical species.¹⁶ As an example, BEt_3 ($\delta_{\text{B}} = 87$ ppm) is oxidized in the presence of O_2 , giving $\text{BEt}_2(\text{OEt})$ ($\delta_{\text{B}} = 56$ ppm) and $\text{BEt}(\text{OEt})_2$ ($\delta_{\text{B}} = 32$ ppm) as well as some amount of Et_2BOBEt .¹⁷ In the case of compound **2-O**₂, two possible $[\text{B}]-\text{C}$ insertion products are possible (either between $[\text{B}]-\text{Cy}$ or $[\text{B}]-^n\text{PrR}$ bonds), further complicating matters and likely contributing to low symmetry of the resultant complexes. Given these results, it would seem difficult to controllably stabilize $\{[\text{M}]-\text{O}_2\}$ fragments using a peripheral boron-based coordination environment and O_2 as a reagent.

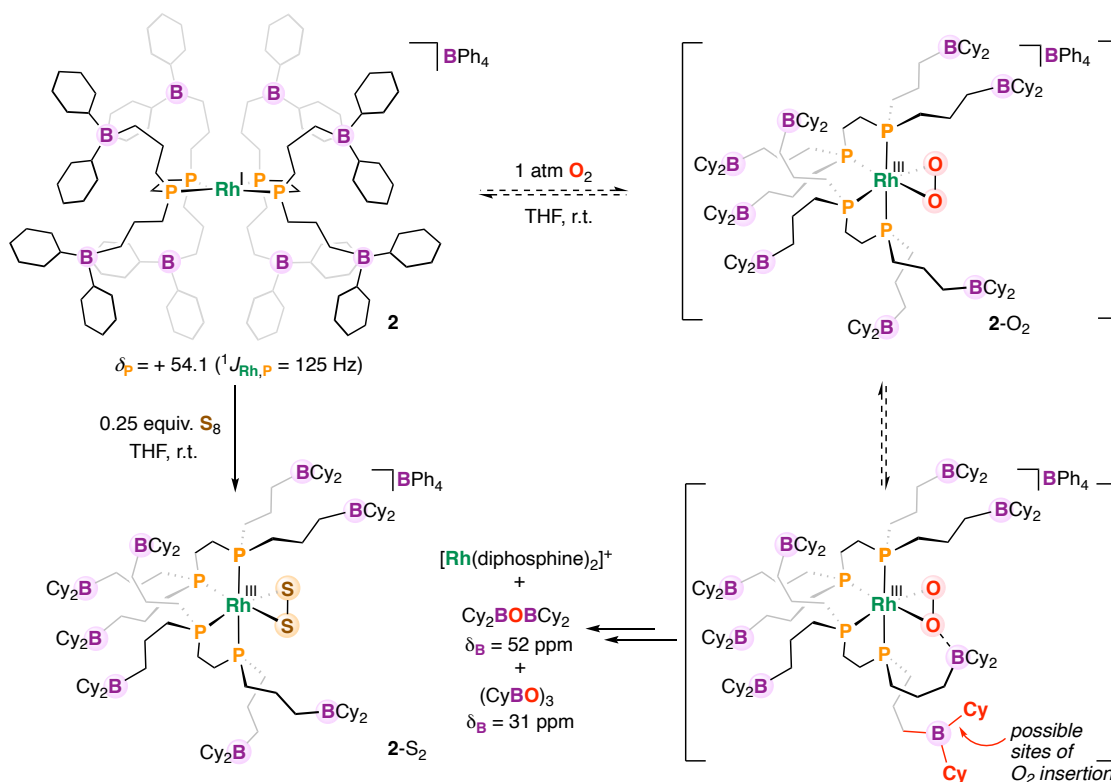


Figure 5. Reactivity of a model compound, $[Rh(P_2BCy_4)_2]BPh_4$ (**2**) with O_2 and S_8 .

Next, compound **2** was reacted with 0.25 equivs. S_8 , resulting in complete consumption of starting material (**Figure 5**). By ^{31}P NMR spectroscopy, two signatures were observed at $\delta_P = 47.2$ ppm (dt, $^1J_{Rh,P} = 123.4$ Hz, $^2J_{P,P} = 18.1$ Hz) and 41.0 ppm (dt, $^1J_{Rh,P} = 84.3$ Hz, $^2J_{P,P} = 18.0$ Hz), consistent with formation of $[Rh^{III}(P_2BCy_4)_2(\eta^2-S_2)]BPh_4$ (**2-S₂**) and are similar to those observed for **1-S₂**. The symmetry observed by NMR spectroscopy suggests a non-interacting B—S unit at 298 K or one where coordination/re-coordination is rapid/dynamic. A variable temperature $^{31}P\{^1H\}$ NMR spectroscopy experiment from 298 K to 193 K showed broadening of the signals for **2-S₂**, however it remains challenging to draw concrete conclusions, given the multiple possible orientations of the $-^nPrBCy_2$ arms, which could be frozen out at low temperature (**Figure 6**). As an example, ^{31}P NMR signal broadening has been observed for a related nickel(II) compound containing the P_2BCy_4 ligand at similar temperatures.¹⁸ Additionally diagnostic of a B—S interaction and thus, sp^3 -boron formation, α -CH signals adjacent to the boron center *e.g.*, $\{B(\underline{CH}^{Cy})_2(\underline{CH}_2^{nPr})(S)\}$ would be expected to be upfield shifted, this was not observed by VT 1H NMR spectroscopy.¹²

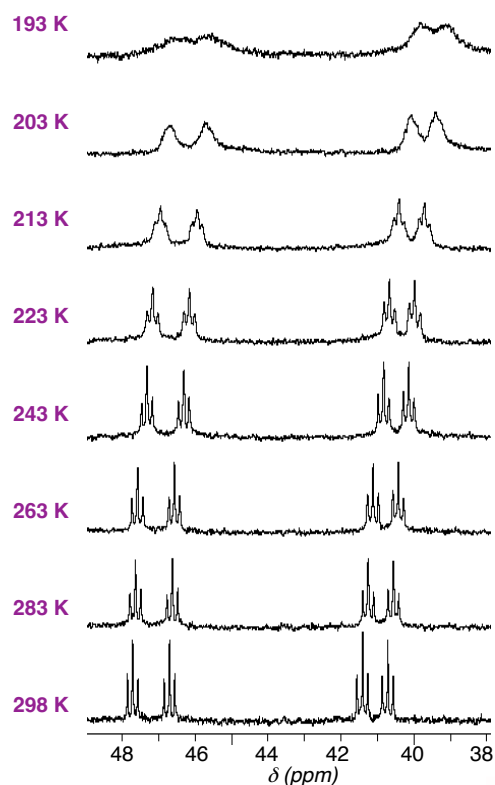


Figure 6. Variable temperature ^{31}P NMR spectroscopy of **2-S₂** (121 MHz, THF- d_8).

As a point of reference, other examples of boron-protected thiolate compounds, $\{[\text{M}]-\text{S}-\text{B}\}$ are known,^{19,20,21} though most interactions are fleeting (*e.g.*, in equilibrium with the unbound variant) and have been calculated to be uphill *e.g.*, interaction between $[\text{Ni}(\text{CO})_3(\text{SPh})]^-$ and BMe_3 provides $\Delta G(\text{B}-\text{S}) = +9 \text{ kcal mol}^{-1}$ ²² – a summary of related compounds (**I** – **IV**) and some of their interaction energies are provided in **Figure 7**.

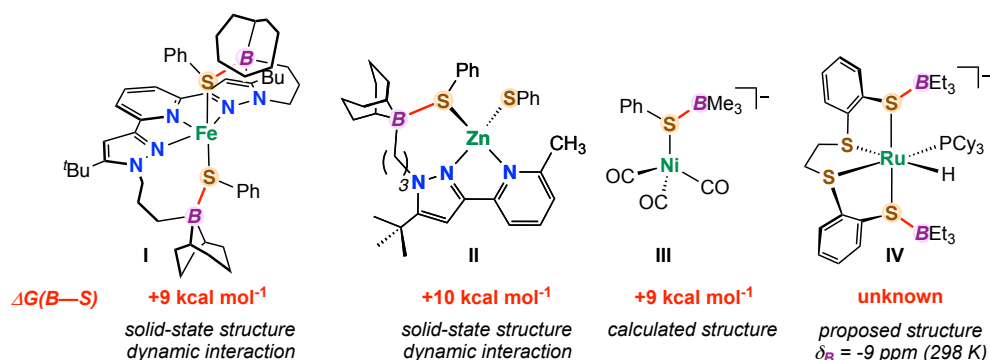


Figure 7. A sampling of compounds having $\{[\text{M}]-\text{S}-\text{B}\}$ interactions. $\Delta G(\text{B}-\text{S})$ refers to the free energy of adduct formation (endergonic in all cases).

3. Conclusion:

In summary, we have described here: the reactions of chalcogens (O_2 and S_8) with two compounds of the type $[Rh(\text{diphosphine})_2]^+$ where diphosphine bears $-CH_2CH_2CH_2-H$ (*dnppe*) or $-CH_2CH_2CH_2-BCy_2(P_2B^{Cy}_4)$ substituents to assess whether Lewis acidic secondary coordination spheres can be used to interact with bound chalcogenide molecules. By theory, monoboranyl candidate models having B--O interactions are calculated to be thermodynamically and kinetically viable, the B--S variant is not. By experiment, $[Rh(\text{dnppe})_2]^+$ reacts with O_2 or S_8 to give compounds of the type $[Rh(\text{dnppe})_2(\eta^2\text{-Ch})]^+$ (Ch = O or S). For O_2 , this reaction provides an equilibrium mixture, while for S_8 , goes to completion. For the $P_2B^{Cy}_4$ analogue, decomposition of the pendant boranyl arms was noted upon exposure to O_2 , likely stemming from O_2 insertion into B--R bonds. Reaction of $[Rh(P_2B^{Cy}_4)_2]^+$ with S_8 , however, cleanly produced $[Rh(P_2B^{Cy}_4)_2(\eta^2\text{-S}_2)]^+$. At 298 K this compound does not contain supporting B--S linkages, as examined by solution NMR spectroscopy – fluxionality at 193 K is observed, however, it is difficult to separate a possible B--S interaction from the ensemble of possible ligand motions. This report constrains hypotheses regarding Lewis acid/base interactions in such $\{[Rh]-CH_2-B\}$ units and provides a launchpad for the design of transition metal-ligand fragments which may cooperatively coordinate such ubiquitous chalcogen sources.

4. Experimental:

4.1 General Considerations:

All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents in a solvent purification system supplied by PPT, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective moisture removal. *ds*-THF was dried over molecular sieves and degassed by three freeze-pump-thaw cycles. $[Rh^I(\text{dnppe})_2]BPh_4^{12}$ and $[Rh^I(P_2B^{Cy}_4)_2]BPh_4^{12}$ were prepared using literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

4.2 Physical methods:

¹H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent *e.g.*, ¹H(THF-*d*₈): 3.58; ¹³C(THF-*d*₈): 67.21; coupling constants are reported in Hz. ¹³C, ¹¹B, and ³¹P NMR spectra were performed as proton-decoupled experiments and are reported in ppm.

4.2.1 Computational details:

All calculations were performed using version 4.2.1 of the ORCA computational package²³ and were run on the Graham cluster maintained by Compute Canada. All geometry optimizations and frequency calculations were performed at the BP86-D3(BJ)/def2-TZVP^{24–26} level of theory. The RI approximation was used to enhance computational efficiency, along with the auxiliary basis *def2/J*.²⁷ Convergence criteria were met using *Grid6* and *NoFinalGrid* integral grid sizes. Frequency calculations (*NumFreq*) were performed to confirm that each optimized geometry was a true minimum indicated by the absence of imaginary frequencies. Single-point calculations were performed at the BP86-D3(BJ)/def2-TZVP level of theory on optimized geometries using a Universal Solvation Model (*SMD*) of tetrahydrofuran (*THF*) to obtain thermochemical values in solvent. Accurate electronic energies were determined using CCSD(T) at the DLPNO-CCSD(T)/def2-TZVP^{28–30} level of theory. The RIJCOSX approximation was used to enhance computational efficiency, along with a *def2/J* auxiliary basis set. As well, a *def2-TZVP/C*³¹ auxiliary basis set was used. Potential energy surface scans were conducted on optimized geometries at the BP86-D3(BJ)/def2-TZVP level of theory. Starting points of each PES were the structure with the longest B-O bond distance.

4.3 Synthesis of Compounds:

4.3.1 {[Rh^I(*dnppe*)₂(*η*²-O₂)]BPh₄} (1-O₂; C₅₂H₈₄BP₄RhO₂, M_w = 978.5 g/mol): {[Rh^I(*dnppe*)₂]BPh₄} (**1**) (20 mg, 0.04 mmol, 1 equiv.) was weighed into a 20 mL scintillation vial and 500 μ L of THF-*d*₈ was added; the mixture was rapidly transferred to a J. Young NMR tube and freeze-pumped-thawed three times using a Schlenk line. At room temperature, O₂ (~ 1 atm) was added, and the sample was analyzed by multinuclear NMR spectroscopy, providing a mixture of **1** and **1-O₂** in a 1:2.74 ratio. **¹H NMR (300 MHz, THF-*d*₈, 298 K):** δ_{H} = 7.29 (br, 8H; BPh₄), 6.88 (t, ³J_{HH} = 7.3 Hz, 8H; BPh₄), 6.73 (t, ³J_{H,H} = 7.3 Hz, 4H; BPh₄), 2.15-1.27 (m, overlapping -CH₂- groups), 1.11-0.93 (m, overlapping -CH₃ groups). **³¹P{¹H} NMR (121 MHz, THF-*d*₈, 298 K):** δ_{P} = 49.6 (dt, ¹J_{Rh,P} = 89.0 Hz, ²J_{P,P} = 18.4 Hz), 47.3 (dt, ¹J_{Rh,P} = 125.0 Hz, ²J_{P,P} = 18.4 Hz). **¹¹B{¹H} NMR (96 MHz, THF-*d*₈, 298 K):** δ_{B} = - 6.54 (BPh₄).

4.3.2 {[Rh^I(dnppe)₂(η^2 -S₂)]BPh₄} (1-S₂; C₅₂H₈₄BP₄RhS₂, M_W = 1010.4 g/mol): {[Rh^I(dnppe)₂]BPh₄} (**1**) (31 mg, 0.03 mmol, 1 equiv.) was weighed into a 20 mL scintillation vial and 500 μ L of THF-d₈ was added. To the mixture was added octasulfur, S₈ (2 mg, 0.008 mmol, 0.25 equiv.) and all contents were transferred to a J. Young NMR tube for analysis by multinuclear NMR spectroscopy, providing evidence for **1-S₂** in 92% purity by ³¹P NMR spectroscopy – compound **1** was entirely consumed (*vide infra*). **¹H NMR (300 MHz, THF-d₈, 298 K):** δ_H = 7.29 (br, 8H; BPh₄), 6.88 (t, ³J_{HH} = 7.3 Hz, 8H; BPh₄), 6.74 (t, ³J_{H,H} = 7.3 Hz, 4H; BPh₄), 2.12-1.27 (m, 40H; -CH₂-), 1.11-0.90 (m, 24H; -CH₃). **¹³C{¹H} NMR (125 MHz, THF-d₈, 298 K):** δ_C = 165.1 (q, ¹J_{B,C} = 50.9 Hz; BPh₄), 137.1 (BPh₄), 125.5 (BPh₄), 121.6 (BPh₄), 35.1 (d, J = 25.6 Hz), 34.6 (d, J = 20.7 Hz), 30.4 (br), 26.2, 25.6, 19.8, 19.3, 18.4, 17.8, 16.2, 16.1, 15.8, 15.7, 15.6, 15.6. **³¹P{¹H} NMR (121 MHz, THF-d₈, 298 K):** δ_P = 47.5 (dt, ¹J_{Rh,P} = 123.9 Hz, ²J_{P,P} = 18.8 Hz), 41.2 (dt, ¹J_{Rh,P} = 84.6 Hz, ²J_{P,P} = 18.8 Hz). **¹¹B{¹H} NMR (96 MHz, THF-d₈, 298 K):** δ_B = - 6.54 (BPh₄). *N.B.* Compound **1-S₂** is 92% pure based on ³¹P NMR spectroscopy. An additional set of doublets of triplets (dt) was observed in the ³¹P NMR spectrum at δ_P = 37.1 ppm (dt, ¹J_{Rh,P} = 93.8 Hz, ²J_{P,P} = 16.5 Hz) and 32.8 ppm (dt, ¹J_{Rh,P} = 88.8 Hz, ²J_{P,P} = 16.5 Hz) (see ESI). We tentatively assign this by-product as another Rh-containing fragmentation product of S₈.³²

4.3.3 Attempted synthesis of {[Rh^I(P₂B^{Cy}₄)₂(η^2 -O₂)]BPh₄} (2-O₂; C₁₄₈H₂₅₂B₉P₄RhO₂, M_W = 2387.9 g/mol): {[Rh^I(P₂B^{Cy}₄)₂]BPh₄} (**2**) (20 mg, 0.04 mmol, 1 equiv.) was weighed into a 20 mL scintillation vial and 500 μ L of THF-d₈ was added; the mixture was rapidly transferred to a J. Young NMR tube and freeze-pumped-thawed three times using a Schlenk line. At room temperature, O₂ (~ 1 atm) was added, and the sample was analyzed by multinuclear NMR spectroscopy, resulting in decomposition providing unsymmetrical [Rh(diphosphine)₂]⁺ and/or [Rh(diphosphine)₂(η^2 -O₂)]⁺ complexes with decomposed boranyl units, giving Cy₂BOBCy₂ and (CyOB)₃, as examples. **³¹P{¹H} NMR (121 MHz, THF-d₈, 298 K):** δ_P = 53.0 ($\Delta_{1/2}$ \approx 80 Hz), 52.0 ppm ($\Delta_{1/2}$ \approx 80 Hz). **¹¹B{¹H} NMR (96 MHz, THF-d₈, 298 K):** δ_B = 52 (Cy₂BOBCy₂), 31 ((CyOB)₃), - 6.54 (BPh₄).

4.3.4 {[Rh^I(P₂B^{Cy}₄)₂(η^2 -S₂)]BPh₄} (2-S₂; C₁₄₈H₂₅₂B₉P₄RhS₂, M_W = 2419.9 g/mol): In the glovebox, {[Rh^I(dnppe)₂]BPh₄} (**1**) (62 mg, 0.026 mmol, 1 equiv.) was weighed into a 20 mL scintillation vial and 500 μ L of THF-d₈ was added. To the mixture was added octasulfur, S₈ (2 mg, 0.008 mmol, 0.25 equiv.) and all contents were transferred to a J. Young NMR tube for analysis by multinuclear NMR spectroscopy, providing evidence for **2-S₂** in 85% purity by ³¹P NMR spectroscopy – compound **2** was entirely consumed

(*vide infra*). ^1H NMR (300 MHz, THF- d_8 , 298 K): $\delta_{\text{H}} = 7.34$ (br, 8H; BPh $_4$), 6.92 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8H; BPh $_4$), 6.78 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 4H; BPh $_4$), 2.08 – 1.03 (multiple overlapping C(sp^3)—H resonances). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, THF- d_8 , 298 K): $\delta_{\text{C}} = 165.1$ (q, $^1J_{\text{B,C}} = 50.9$ Hz; BPh $_4$), 137.1 (BPh $_4$), 132.0 (allyl $\underline{\text{C}}\text{H}$), 125.5 (BPh $_4$), 121.6 (BPh $_4$), 36.5 (m), 35.4 (m), 29.9, 28.8, 28.6–27.5 (multiple ^{13}C resonances for $\underline{\text{C}}(sp^3\text{-H})$ carbons). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF- d_8 , 298 K): $\delta_{\text{P}} = 47.2$ (dt, $^1J_{\text{Rh,P}} = 123.4$ Hz, $^2J_{\text{P,P}} = 18.1$ Hz), 41.0 (dt, $^1J_{\text{Rh,P}} = 84.3$ Hz, $^2J_{\text{P,P}} = 18.0$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, THF- d_8 , 298 K): $\delta_{\text{B}} = 84$ ($\Delta_{1/2} = 2200$ Hz, -BCy $_2$), -6.54 (BPh $_4$). *N.B.* Compound 2-S $_2$ is 85% pure based on ^{31}P NMR spectroscopy. An additional set of doublets of triplets (dt) was observed in the ^{31}P NMR spectrum at $\delta_{\text{P}} = 35.8$ ppm (dt, $^1J_{\text{Rh,P}} = 93.9$ Hz, $^2J_{\text{P,P}} = 16.7$ Hz) and 33.2 ppm (dt, $^1J_{\text{Rh,P}} = 88.5$ Hz, $^2J_{\text{P,P}} = 16.5$ Hz) (see ESI). We tentatively assign this by-product as another Rh-containing fragmentation product of S $_8$.³²

Supplementary material:

^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and ^{11}B NMR spectra for all complexes. XYZ coordinates for DFT calculations.

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Notes and References:

- (1) Butter, S. A.; Chatt, J. Dihalogenodi-[1,2-Bis(Dimethylphosphino)Ethane]Rhodium(III) and Related Carbonyl- and Hydrido-Complexes. *J. Chem. Soc.* **1970**, 1411–1415.
- (2) Vaska, L.; Catone, D. L. A New Series of Four-, Five-, and Six-Coordinated Iridium Complexes. *J. Am. Chem. Soc.* **1966**, 88 (22), 5324–5325.
- (3) Sacco, A.; Nobile, C. F. Tetraco-Ordinated Complexes of Cobalt(I) and Iridium(I). *Chem. Commun. (London)* **1966**, 589–590.
- (4) Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. Disulfur and Diselenium Complexes of Rhodium and Iridium. *Inorg. Chem.* **1982**, 21 (10), 3666–3681.
- (5) McGinnety, J. A.; Payne, N. C.; Ibers, J. A. Role of the Metal Atom in the Reversible Uptake of Molecular Oxygen. The Structures of the Molecular Oxygen Complexes Formed by Bis[Bis(Diphenylphosphino)Ethane]Iridium(I)Hexafluorophosphate and Its Rhodium Analog. *J. Am. Chem. Soc.* **1969**, 91 (23), 6301–6310.
- (6) James, B. R.; Mahajan, D. Reactions of Bis(Ditertiaryphosphine) Complexes of Rhodium(I) with Carbon Monoxide, Dioxygen, Dihydrogen, and Hydrogen Chloride. *Can. J. Chem.* **1980**, 58 (10), 996–1004.
- (7) Ginsberg, A. P.; Lindsell, W. E. Ditertiary Phosphine Rhodium and Iridium Complexes Containing the Molecular Unit S₂ or Se₂ as a Ligand. *J. Chem. Soc. D* **1971**, 5, 232.
- (8) Ahijado Salomon, M.; Braun, T.; Penner, A. Stepwise Oxygenation of Pinacolborane by a Rhodiumperoxo Complex: Detection of an Intermediate Metal Borate and Perborate. *Angew. Chem.* **2008**, 120 (46), 8999–9003.
- (9) Baumgarth, H.; Meier, G.; von Hahmann, C. N.; Braun, T. Reactivity of Rhodium and Iridium Peroxido Complexes towards Hydrogen in the Presence of B(C₆F₅)₃ or [H(OEt)₂][B{3,5-(CF₃)₂C₆H₃}₄]. *Dalton Trans.* **2018**, 47 (45), 16299–16304.
- (10) Leonard, K.; Plute, K.; Haltiwanger, R. C.; DuBois, M. R. Reactions of Metal-Disulfur Complexes with Nucleophiles and Electrophiles. *Inorg. Chem.* **1979**, 18 (11), 3246–3251.
- (11) Arisawa, M.; Ichikawa, T.; Yamaguchi, M. Synthesis of Thiiranes by Rhodium-Catalyzed Sulfur Addition Reaction to Reactive Alkenes. *Chem. Commun.* **2015**, 51 (42), 8821–8824.
- (12) Zurakowski, J. A.; Austen, B. J. H.; Drover, M. W. Wrapping Rhodium in a Borane Canopy: Implications for Hydride Formation and Transfer. *Organometallics* **2021**, 40 (15), 2450–2457.
- (13) Ohishi, T.; Kashiwabara, K.; Fujita, J. Preparation and Reactivities of the Bis(1,2-Bis(Dimethylphosphino)Ethane)Peroxocobalt(III) Complex. *Chem. Lett.* **1984**, 13 (11), 1917–1918.
- (14) Ohishi, T.; Kashiwabara, K.; Fujita, J.; Ohba, S.; Ishii, T.; Saito, Y. Cobalt(III)-Peroxocomplexes Containing 1,2-Bis(dimethylphosphino)ethane (dmpe) or 1,3-Bis(dimethylphosphino)propane (dmpp). Molecular Structures of [Co(O₂)(dmpe)₂][B(C₆H₅)₄] and [Co(O₂)(dmpp)₂][BF₄·H₂O]. *Bull. Chem. Soc. Jpn.* **1986**, 59, 385–393.
- (15) Mahajan, D. Bis(Ditertiaryphosphine) Complexes of Rhodium, and Catalytic Asymmetric Hydrogenation. PhD Thesis. The University of British Columbia. Vancouver. 1976.

- (16) Zaremski, M. Yu.; Garina, E. S.; Gurskii, M. E.; Bubnov, Yu. N. Organoboranes-Atmospheric Oxygen Systems as Unconventional Initiators of Radical Polymerization. *Polym. Sci. Ser. B* **2013**, *55* (5–6), 304–326.
- (17) Zhang, Z.-C.; Chung, T. C. M. Reaction Mechanism of Borane/Oxygen Radical Initiators during the Polymerization of Fluoromonomers. *Macromolecules* **2006**, *39* (16), 5187–5189.
- (18) Zurakowski, J. A.; Bhattacharyya, M.; Spasyuk, D. M.; Drover, M. W. Octaboraneyl [Ni(H)(Diphosphine)₂]⁺ Complexes: Exploiting Phosphine Ligand Lability for Hydride Transfer to an [NAD]⁺ Model. *Inorg. Chem.* **2021**, *60* (1), 37–41.
- (19) Kiernicki, J. J.; Norwine, E. E.; Zeller, M.; Szymczak, N. K. Substrate Specific Metal-Ligand Cooperative Binding: Considerations for Weak Intramolecular Lewis Acid/Base Pairs. *Inorg. Chem.* **2021**, *60* (18), 13806–13810.
- (20) Kiernicki, J. J.; Shanahan, J. P.; Zeller, M.; Szymczak, N. K. Tuning Ligand Field Strength with Pendent Lewis Acids: Access to High Spin Iron Hydrides. *Chem. Sci.* **2019**, *10* (21), 5539–5545.
- (21) Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. Transition Metal Complexes with Sulfur Ligands. 130.¹ Synthesis, Structure, and Reactivity of the Sulfur-Rich Ruthenium Hydride Complexes [Ru(H)(PR₃)('S₄')]- and the h²-H₂ Complex [Ru(H₂)(PCy₃)('S₄')] (R = Ph, ⁱPr, Cy; 'S₄'²⁻ = 1,2-Bis((2-mercaptophenyl)thio)ethane(2-)) *Inorg. Chem.* **1998**, *37*, 3982–3988.
- (22) Shanahan, J. P.; Szymczak, N. K. Lewis Acid Effects on Calculated Ligand Electronic Parameters. *Organometallics* **2020**, *39* (23), 4297–4306.
- (23) Neese, F. Software Update: The ORCA Program System, Version 4.0. *WIREs Comput Mol Sci* **2018**, *8* (1). <https://doi.org/10.1002/wcms.1327>.
- (24) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.
- (25) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465.
- (26) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297.
- (27) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057.
- (28) Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. Sparse Maps—A Systematic Infrastructure for Reduced-Scaling Electronic Structure Methods. II. Linear Scaling Domain Based Pair Natural Orbital Coupled Cluster Theory. *J. Chem. Phys.* **2016**, *144* (2), 024109.
- (29) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural Triple Excitations in Local Coupled Cluster Calculations with Pair Natural Orbitals. *J. Chem. Phys.* **2013**, *139* (13), 134101.
- (30) Riplinger, C.; Neese, F. An Efficient and near Linear Scaling Pair Natural Orbital Based Local Coupled Cluster Method. *J. Chem. Phys.* **2013**, *138* (3), 034106.
- (31) Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W. Optimized Accurate Auxiliary Basis Sets for RI-MP2 and RI-CC2 Calculations for the Atoms Rb to Rn. *Theor. Chem. Acc.* **2007**, *117* (4), 587–597.
- (32) Kashiwabara, K.; Morikawa, A.; Suzuki, T.; Isobe, K.; Tatsumi, K. Oxidative Additions of Dichloromethane and Cyclo-Octasulfur to Rhodium(I) Complexes Containing (2-Aminoethyl)-Dimethylphosphine or -Diphenylphosphine. *J. Chem. Soc., Dalton Trans.* **1997**, No. 6, 1075–1082.