Chapter 5. Platinum-alkyl and hydride complexes supported by the monoanionic tris(phosphino)borate ligand [PhB(CH₂PPh₂)₃]⁻

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5.1. Introduction

Trofimenko's tris(pyrazolyl)borate ligands[1] have been widely used in mechanistic C-H activation studies. Several reports of the noble group 9 metals (Rh and Ir) have exploited the scorpionates in this context, such as the recent works of Bergman and Harris,[2] as well mechanistic work from Jones' group.[3] Important advances in [Tp]-supported platinum C-H activation chemistry have also emerged ([Tp] = hydrotris(pyrazolyl)borate, [HB(pz)$_3$]$^-$). For example, Goldberg's group showed that the anionic complex K[[κ^2-Tp^{Me2}]PtMe$_2$] ([Tp^{Me2}] = hydrotris(3,5-dimethylpyrazolyl)borate) reacts with B(C$_6$F$_5$)$_3$ to generate an unobserved, presumed three-coordinate species, "[κ^2-Tp^{Me2}]PtMe," that then undergoes oxidative C-H bond addition to afford octahedral platinum(IV) alkyl hydride products, [κ^3-Tp^{Me2}]Pt(Me)(R)H.[4] A number of studies have followed this early report, including the isolation of a well-defined five-coordinate Pt(IV) species,[5] the synthesis of a rare η^2-benzene adduct of platinum(II),[6] and mechanistic investigations of reductive elimination from platinum(IV).[7,8]

Given the considerable momentum behind [Tp]-supported C-H activation studies, it seemed prudent to begin examining other tripodal borate ligands for comparison. Therefore, we have begun to develop the platinum chemistry of a related class of tris(phosphino)borate ligands (Figure 5.1).[9] These tris(phosphino)borate ligands resemble the classic scorpionates by virtue of having three donor arms covalently bound to a borate unit so that they bind most typically in a tripodal fashion. Despite these similarities, the (phosphino)borates appear to be electronically and sterically distinct from [Tp]-type ligands. For example, the monoanionic (phosphino)borate complexes of platinum feature an anionic borate unit that is more spacially separated from the

coordinated platinum center in both κ^3- and κ^2-binding modes by comparison to structurally related [Tp] complexes (*vide infra*). Moreover, the absence of simple resonance contributors that would efficiently distribute the anionic borate charge in these (phosphino)borate complexes suggests that they can be reasonably regarded as molecular zwitterions.[10] Such a description is not typically attributed to [Tp]-supported complexes, where resonance delocalization of the borate charge is normally presumed.[11]
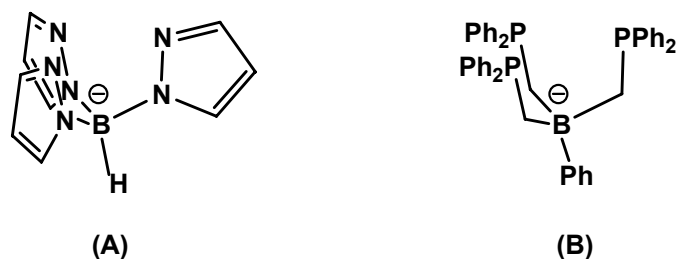

Figure 5.1. (A) [Tp] and (B) [PhBP$_3$] ligands.

In this chapter, we describe aspects of the platinum coordination chemistry of the tris(phosphino)borate ligand [PhB(CH$_2$PPh$_2$)$_3$]$^-$ ([PhBP$_3$], **5.1**). The synthesis and characterization of several methyl and hydride complexes of platinum supported by **5.1** are reported, emphasizing the electronic contribution that the anionic phosphine ligand provides. We compare these results to relevant [Tp]-platinum chemistry to provide a framework for understanding the similarities and differences between these related ligand platforms.
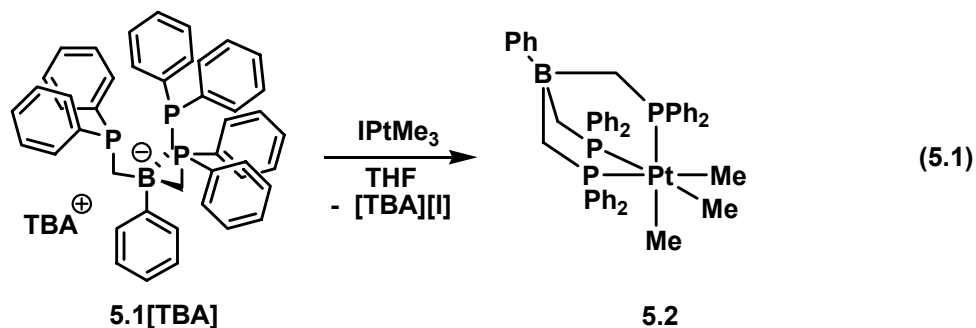
5.2. Results and discussion

5.2.1. Synthesis of a platinum(IV) trimethyl complex

The tridentate phosphine ligand **5.1** was initially reported as the lithium(TMEDA) salt, [PhB(CH$_2$PPh$_2$)$_3$][Li(TMEDA)] (**5.1**[Li(TMEDA)], TMEDA = *N,N′*-tetramethyl-ethylenediamine).[9a] Salt metathesis protocols developed in our laboratories have resulted in the useful thallium adduct, [PhB(CH$_2$PPh$_2$)$_3$]Tl (**5.1**[Tl])[12] and the

tetra(*n*-butyl)ammonium salt, [PhB(CH$_2$PPh$_2$)$_3$][TBA] (**5.1**[TBA]).[13] In general, it was

found that **5.1**[TBA] resulted in clean substitution onto platinum starting materials.

Reaction of **5.1**[TBA] in THF with IPtMe$_3$ led to the formation of a single

product, [PhBP$_3$]PtMe$_3$ (**5.2**), as a colorless, neutral, octahedral Pt(IV) complex (eq 5.1).

In solution, **5.2** exhibited C_{3v} symmetry based on the presence of a single resonance in the

^{31}P{^{1}H} NMR spectrum and a single resonance in the ^{1}H NMR spectrum attributed to the

platinum-methyl protons. Protons on the platinum-methyl groups showed coupling to

both platinum ($^2J_{\text{Pt-H}}$ = 55.5 Hz) and phosphorus ($^3J_{\text{P-H}}$ = 7.2 Hz) in the ^{1}H NMR

spectrum. Similarly, platinum coupling was seen for the ligand phosphines in the

^{31}P{^{1}H} NMR spectrum ($^1J_{\text{Pt-P}}$ = 1094 Hz). The only other *fac*-platinum(IV) trimethyl

complex supported by trialkyl phosphines that has been reported in the literature is

[(Me$_2$PhP)$_3$PtMe$_3$][PF$_6$].[14]

(5.1)

5.1[TBA]   5.2

An X-ray diffraction study carried out on a single crystal of **5.2** verified the

structure (Figure 5.2). The X-ray structure of **5.2** shows the tridentate *fac* coordination of

ligand **5.1**, with P-Pt-P bond angles being very close to 90º. Space-filling models of **5.2**

derived from the crystallographic data show that the phosphine-phenyl groups provide

sufficient steric bulk to force the platinum-methyl groups slightly away from octahedral,

as evidenced by the average C-Pt-C bond angle of 83.0º. Compared to the recently

structurally characterized [Tp^{Me_2}]PtMe$_3$,[15] the Pt-C bond lengths of **5.2** are longer (Pt-C(avg), **5.2**: 2.11 Å; [Tp^{Me_2}]PtMe$_3$: 2.05 Å), presumably due to the greater *trans* influence of the phosphine ligands. More importantly, the Pt-B distance (3.640 Å) in **5.2** is much larger than for its [Tp] analogue (3.184 Å), likely providing a better through space separation of charge for **5.2**.
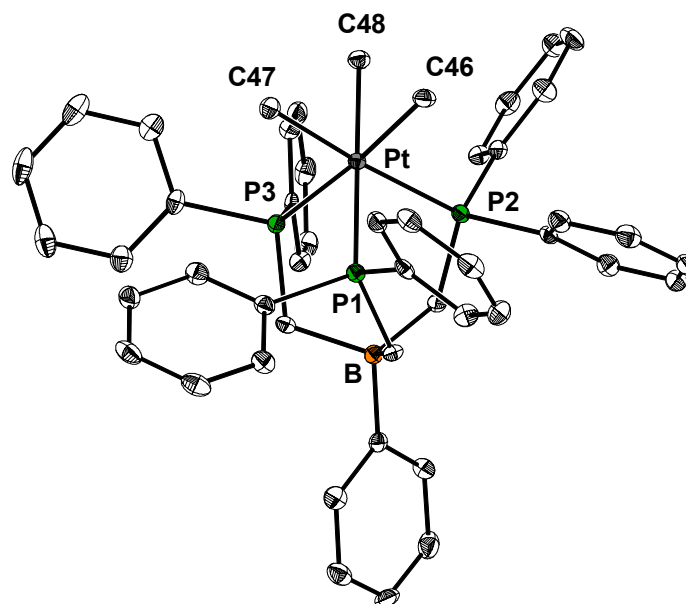

Figure 5.2. Displacement ellipsoid representation (50%) of [PhBP$_3$]PtMe$_3$·THF (**5.2·THF**). Hydrogen atoms and THF solvent molecule are omitted for clarity. Selected interatomic distances (Å) and angles (°): Pt-C46, 2.114(3); Pt-C47, 2.112(3); Pt-C48, 2.107(3); Pt-P1, 2.4044(7); Pt-P2, 2.3976(7); Pt-P3, 2.4307(7); Pt-B, 3.640(3); P-Pt-P (avg), 88.33; C-Pt-C (avg), 82.98; C-Pt-P (avg), 94.29.

Complex **5.2** is very robust, being stable to air, moisture, aqueous mineral acids (e.g., 12 M HCl (aq)), strong Lewis acids (e.g., B(C$_6$F$_5$)$_3$, [Ph$_3$C][BF$_4$]), and reductants (e.g., methyl lithium, sodium borohydride). Thermolysis of **5.2** in 1,3-dichlorobenzene showed that the complex was stable for several hours even at 170 ºC; however, thermal decomposition occurred relatively quickly (hours) at 180 ºC to provide a complex

mixture of uncharacterized products. The marked stability of **5.2** is comparable to that observed for $[(Me_2PhP)_3PtMe_3][PF_6]$ by Clark and Manzer. Interestingly, the authors observed high stability for $[Pt(CH_3)_3(OH_2)_3]^+$ and $[Pt(CH_3)_3(NC_5H_5)_3]^+$ as well, noting that the complexes "are quite stable and exhibit no tendency towards reductive decomposition" as compared to related platinum-trimethyl complexes containing inequivalent donor ligands. This stability may arise from the electronic nature of the three-fold symmetric octahedral molecules. The ability to dissociate a neutral ligand prior to reductive elimination appears to be favored for asymmetric donors.

5.2.2. Attempts to synthesize [PhBP$_3$]PtCl$_3$

To prepare a potentially more reactive Pt(IV) fragment, we attempted to synthesize a neutral Pt(IV) trichloride complex analogous to **5.2**. To our knowledge, no examples of trihalo Pt(IV) species have been reported for the [Tp] ligands. Reaction of **5.1**[TBA] or the previously described thallium(I) adduct, [PhBP$_3$]Tl, with various Pt(IV) chloride materials (e.g., $PtCl_4$, K_2PtCl_6, $[TBA]_2[PtCl_6]$) did not, however, lead to clean reactivity. In all cases, three or more products formed, as determined by $^{31}P\{^1H\}$ NMR, $^{11}B\{^1H\}$ NMR, and mass spectroscopies. In one case, a product was isolated by fractional crystallization from the reaction between [PhBP$_3$]Tl and $(CH_3CN)_2PtCl_4$ and was determined by X-ray diffraction to be $[PhB(Cl)(CH_2PPh_2)_2]_2Pt$ (**5.3**) (Figure 5.3). This product demonstrates a potential weakness of the (phosphino)borate carbon-boron linkage, as can be seen by the loss of one phosphine arm and its replacement by chloride. This reaction presumably occurs by oxidation of the (phosphino)borate ligand by Pt(IV), possibly through radical pathways. It is of note that the chlorides are organized in the structure of **5.3** to be in close proximity to the platinum center at distances of 3.3230(7) and 3.4511(7) Å. A somewhat related boron-halogen bond forming reaction of the

[PhBP$_3$]$^-$ ligand has been reported recently: when the complex [PhBP$_3$]IrCl$_2$ was thermolyzed in a 1:1 CCl$_4$/benzene mixture, the boron-phenyl bond was formally replaced by a boron-chloride bond.[9b]
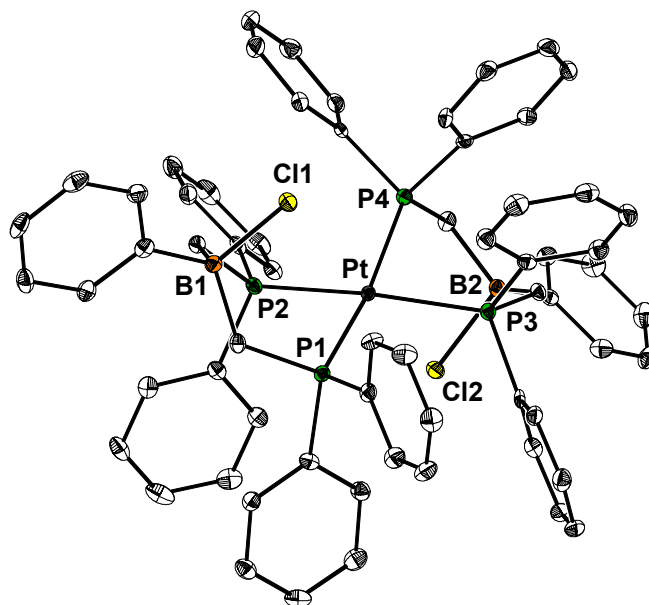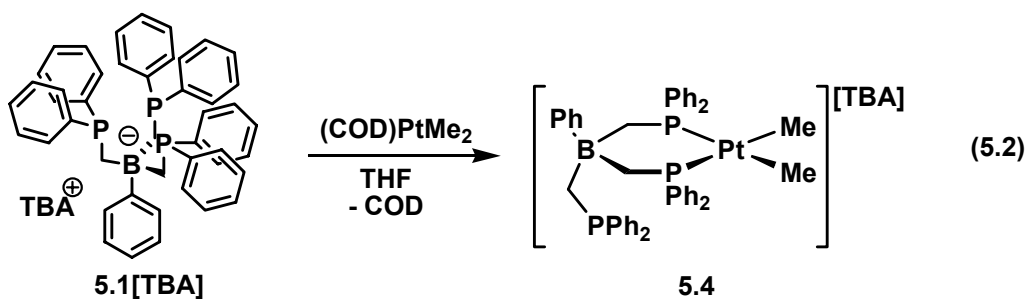

Figure 5.3. Displacement ellipsoid representation (50%) of [PhB(Cl)(CH$_2$PPh$_2$)$_2$]$_2$Pt·2THF (**5.3·2THF**). Hydrogen atoms and THF solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Pt-P1, 2.3801(8); Pt-P2, 2.3380(8); Pt-P3, 2.3621(8); Pt-P4, 2.3467(8); Pt-Cl1, 3.4511(7); Pt-Cl2, 3.3230(7); Pt-B1, 3.623(3); Pt-B2, 3.615(3); P1-Pt-P2, 84.55(3); P1-Pt-P3, 100.13(3); P2-Pt-P4, 93.19(3); P3-Pt-P4, 84.42(3).

5.2.3. Synthesis and reactivity of platinum(II) complexes

In addition to preparing platinum(IV) complexes, we also pursued the development of **5.1** coordinated to platinum(II). Formation of the platinum(II)-methyl compound [[κ^2-PhBP$_3$]PtMe$_2$][TBA] (**5.4**) proceeded cleanly at room temperature by the reaction of **5.1**[TBA] and (COD)PtMe$_2$ in THF solution (eq 5.2). The ability to use (COD)PtMe$_2$ as a reagent is consistent with previous results using phosphine donor

ligands and stands in contrast to (pyrazolyl)borate ligands which require more labile starting materials to achieve substitution.[16]

$$\textbf{5.1[TBA]} \qquad\qquad\qquad\qquad\qquad \textbf{5.4} \qquad\qquad\qquad (5.2)$$

Examination of the ^{1}H and ^{31}P$\{^1$H$\}$ NMR spectra of **5.4** shows the C_s symmetry of the platinum complex: the platinum-methyl protons are equivalent, with readily apparent coupling to platinum ($^2J_{\text{Pt-H}}$ = 67 Hz) and phosphorus ($^3J_{\text{P-H}}$ = 5 Hz). The coordinated phosphines in **5.4** have a very different ^{31}P$\{^1$H$\}$ NMR chemical shift and platinum coupling constant (δ 18.96, $^1J_{\text{Pt-P}}$ = 1885 Hz) from those in **5.2** (δ -26.01, $^1J_{\text{Pt-P}}$ = 1093 Hz), demonstrating a substantial change in the electronic character of the ligated phosphines between the Pt(II) and Pt(IV) states. In contrast to two related [[κ^2-Tp]PtMe$_2$]$^-$ complexes, **5.4** exhibits smaller methyl $^2J_{\text{Pt-H}}$ values ([[κ^2-Tp]PtMe$_2$]$^-$, $^2J_{\text{Pt-H}}$ = 86 Hz;[17] [[κ^2-Tp$^{\text{Me}_2}$]PtMe$_2$]$^-$, $^2J_{\text{Pt-H}}$ = 83 Hz), consistent with stronger *trans* influencing phosphine donors. Relative to a series of previously prepared bidentate phosphine platinum-dimethyl compounds,[18] [E(CH$_2$PPh$_2$)$_2$]Pt(CH$_3$)$_2$ (E = Ph$_2$B$^-$, Ph$_2$Si, H$_2$C), the phosphorus-platinum coupling constant of **5.4** is comparable to the anionic bis(phosphino)borate complex [[Ph$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] ($^1J_{\text{Pt-P}}$ = 1892 Hz), and both anionic complexes have larger platinum phosphorus coupling constants than similar neutral compounds. A structurally analogous neutral Pt(II) compound, (κ^2-Me-tripod)Pt(CH$_3$)$_2$ (Me-tripod = MeC(CH$_2$PPh$_2$)$_3$), has been previously prepared,[19] though it was not thoroughly characterized nor explored further.

Further examination of the $^{31}P\{^1H\}$ NMR spectrum of **5.4** showed two chemically inequivalent phosphine environments consistent with two phosphines ligated to a square planar platinum(II) center and one unligated phosphine. The pendant arm of the (phosphino)borate ligand in an analytically pure sample of **5.4** demonstrated unusual behavior. Two peaks were observed at -9.61 and -12.60 ppm whose integrated intensity corresponded to one phosphine relative to the two phosphines coordinated to platinum in the $^{31}P\{^1H\}$ NMR spectrum. Both of these signals are similar to the chemical shift of the uncoordinated ligand **5.1**[TBA] ($^{31}P\{^1H\}$ NMR (CD$_3$CN): δ -11.3). The two distinct signals suggest that there is a barrier to rotation about the phosphine-methylene (or the boron-methylene) carbon bond. The difference in chemical shifts between the two signals also suggests that a there is a modest change in the magnetic environment on the pendant phosphine depending on whether the phosphine lone pair is directed toward the metal or away from it. Two possible orientations are depicted in Figure 5.4.
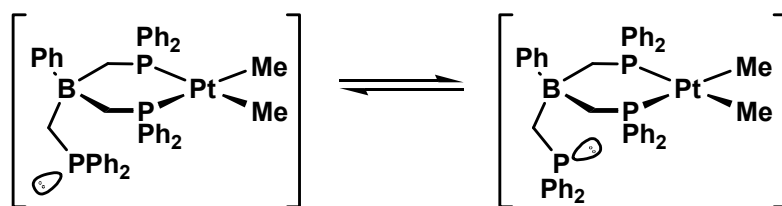

Figure 5.4. Possible orientations for the pendant phosphine arm in **5.4**.

An X-ray diffraction experiment confirmed the structure of **5.4** (Figure 5.5), showing that two arms of the tridentate ligand bind to platinum in a *cis* fashion to form a square planar dimethyl platinum complex while one arm of the ligand remains uncoordinated. The uncoordinated arm in the crystal lattice is oriented so that the phosphine lone pair is directed away from the metal. Examination of the bond angles around the platinum center reveals a square planar motif which has been slightly altered

complexes. It is interesting to note that for both **5.4** and $[[\kappa^2\text{-}Tp^{Me_2}]PtMe_2]^-$ the pendant

donor is directed away from the metal center in the solid state structure. Presumably,
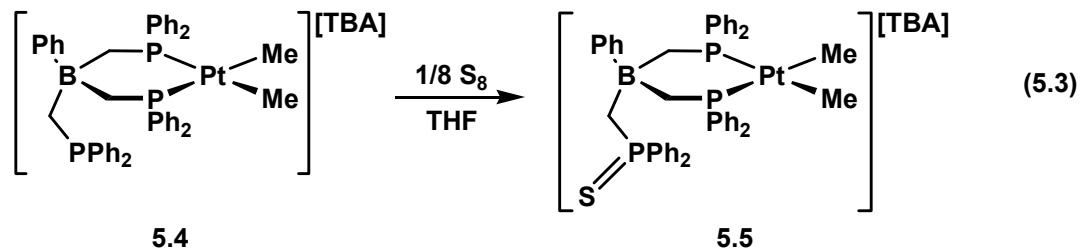
interactions between the donor lone pair and the occupied d_{z^2}-type orbital results in

electron-electron repulsion.

Complex **5.4** exhibited reactivity with dioxygen, water, protic and Lewis acids

(e.g., HCl in Et_2O, HOTf, $[Et_3NH][BPh_4]$, $B(C_6F_5)_3$), and small alkyl halides (e.g., CH_3I,

CH_2Cl_2, and $CHCl_3$). In most cases, complex product mixtures were formed, as

determined by $^{31}P\{^1H\}$ NMR spectroscopy. In particular, reactivity at the pendant

phosphine arm was frequently observed, as demonstrated by new signals in the $^{31}P\{^1H\}$

NMR spectrum without platinum satellites. Related $[[\kappa^2\text{-}Tp]PtMe_2]^-$ species also show a

wide variety of reactivity, including well-characterized reactions with H_2O, and protic

and Lewis acids.[4,16a-b,20] Reactivity at the uncoordinated pyrazolyl donor has been

primarily limited to protonation.[21] The apparent contrast in reactivity of the

uncoordinated donor in **5.4** is most likely attributed to its greater basicity and lower

oxidation potential.

5.2.4. Protection of the unchelated phosphine

In order to sidestep undesirable reactivity at the pendant phosphine arm,

phosphine protection strategies were considered. The pendant arm of the ligand reacted

with one equivalent of elemental sulfur to provide a single major product (eq 5.3),

assigned by NMR spectroscopy as $[[\kappa^2\text{-}PhB(CH_2P(S)Ph_2)(CH_2PPh_2)_2]PtMe_2][TBA]$

(**5.5**). The chemical shift of a singlet at 44.4 ppm ($^{31}P\{^1H\}$ NMR) suggests an oxidized

trialkylphosphine and is consistent with the $^{31}P\{^1H\}$ NMR chemical shifts of known

$R_3P=S$ compounds.[22] Additionally, the $^{31}P\{^1H\}$ NMR chemical shift (18.4 ppm) and

coupling ($^1J_{Pt-P}$ = 1875 Hz) of the coordinated phosphines do not change significantly upon modification of the pendant arm. The ^{1}H NMR spectra of **5.5** showed no significant changes as compared to **5.4**. Despite the difficulty in stoichiometric control of the sulfur addition, **5.5** was typically isolated in >95% purity. The addition of excess sulfur provides uncharacterized products.

$$(5.3)$$

A second protection strategy involved addition of the Lewis acid, $BH_3 \cdot SMe_2$. Using one equivalent of a 2.0 M solution of $BH_3 \cdot SMe_2$ in toluene ($BH_3 \cdot THF$ can also be used), clean formation of the BH_3-phosphine adduct **5.6** can be observed by $^{31}P\{^1H\}$ NMR spectroscopy (eq 5.4). $^{31}P\{^1H\}$ NMR spectra show the disappearance of the peaks at -9 and -12 ppm (*vide supra*) and the growth of a broad peak near 15 ppm. This downfield shift is expected for the formation of a phosphine-borane adduct due to the decreased shielding of the phosphorus nucleus upon borane complexation, and the broadness of the new peak results from unresolved coupling to the boron nucleus. Examination of **5.6** by $^{11}B\{^1H\}$ NMR spectroscopy confirmed the formation of the phosphine-borane adduct with the presence of a new upfield signal (-30.3 ppm) consistent with known phosphine-borane complexes. The resonances from the platinum-bound phosphines demonstrate virtually no change in their $^{31}P\{^1H\}$ NMR chemical shift and register only a slight change in their coupling to platinum ($^1J_{Pt-P}$(**5.6**) = 1870 Hz vs. $^1J_{Pt-P}$(**5.4**) = 1885 Hz).

5.4   **5.6**

    Protection of the pendant phosphine arm with BH_3 provides altered reactivity with various substrates relative to the reactivity found in **5.4**. For example, **5.4** begins to react immediately when dissolved in dichloromethane, providing a mixture of products over a period of hours. This is similar to observations for the unligated tris(phosphino)borate $[PhBP_3][TBA]$ which also demonstrates reactivity with halide-containing solvents such as CH_2Cl_2 and $CHCl_3$. In contrast, **5.6** shows no spectroscopic change over 2.5 hours when dissolved in dichloromethane. Additionally, **5.6** shows no reaction with air and water in THF solution over several hours. These examples show that the reactivity of complex **5.4** is dependent upon the pendant phosphine arm, either as a site of reactivity or as a neutral donor facilitating reactivity at the platinum center. Deprotection of the pendant phosphine·BH_3 adduct of **5.6** can be accomplished by heating **5.6** to 55 ºC for several hours in the presence of excess morpholine (approximately 200 equivalents), a common deprotection method.[23]

5.2.5. Formation of a dimeric platinum(I) bridged hydride complex

    If **5.6** is allowed to react with an additional equivalent of BH_3·SMe_2 (or BH_3·THF), then clean formation of a new product is observed (eq 5.5). NMR spectroscopy, mass spectrometry, and combustion analysis are consistent with the formation of the reduced platinum(I) dimeric species, $[[\kappa^2\text{-}PhB(CH_2P(BH_3)Ph_2)(CH_2PPh_2)_2]Pt(\mu\text{-}H)]_2[TBA]_2$ (**5.7**). BH_3 reagents are widely

known to act as reducing agents, and, in this case, it appears that BH_3 is serving as a reductant and H-atom donor. The fate of the methyl groups on platinum is unknown at this point: possible methyl containing products are methane or methylborane species, neither of which has been spectroscopically observed.
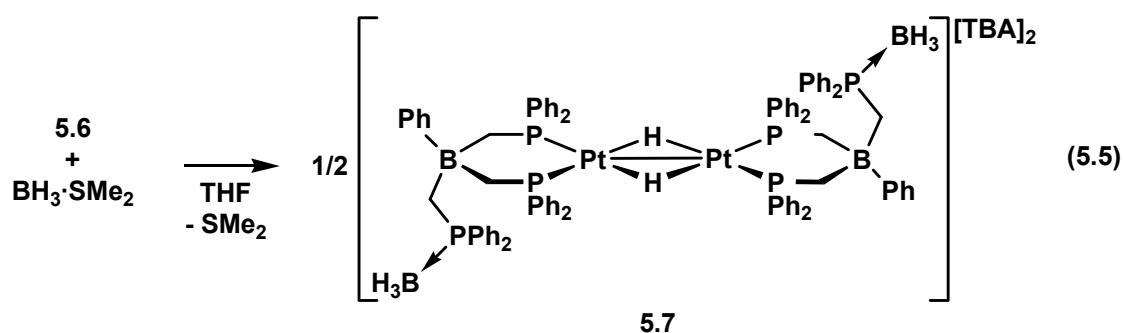
$$\textbf{5.6} + BH_3 \cdot SMe_2 \xrightarrow[- SMe_2]{THF} \tfrac{1}{2} \quad \textbf{5.7} \qquad (5.5)$$

Table 5.1. ^{1}H NMR and IR spectroscopic data for bis(phosphine) platinum(I) dimers.

Compound	δ, Pt-H (ppm)	$^1J_{Pt-H}$ (Hz)	$^2J_{P-H}$ (Hz)	ν_{Pt-H} (cm^{-1}, Nujol)	Ref.
5.7	-3.17	464	40	2003, 1966	-
[(dppe)PtH]$_2$	0.30	564	42	^{a}	25b
[(dippe)PtH]$_2$	0.49	516	40	1939, 1926	24
[(dcype)PtH]$_2$	0.49	512	40	1965, 1937	24
[(dtbpe)PtH]$_2$	0.05	570	42	1975, 1951	24
[(dfepe)PtH]$_2$	3.55	737	47	^{b}	26

^{a} IR data were not reported. ^{b} The authors did not observe Pt-H stretching bands in the IR spectrum (see footnote 7 of reference 26).

Bridging platinum(I) hydride dimers coordinated by chelating bis(phosphine) ligands have been previously described in detail by Schwartz and Andersen.[24] The NMR spectra of **5.7** are consistent with their observations and those of others,[24-26] including the unusual "quintet of quintets" signal for the hydrides (Table 5.1). The observed trends of the ^{1}H NMR spectroscopic data for several bisphosphine platinum(I) bridged hydrides suggest that the hydrides in **5.7** are *trans* to a more electron-rich bisphosphine ligand as compared to other neutral bisphosphine platinum(I) hydride dimers, based on the reduced Pt-H coupling constant. The IR data (Nujol) for **5.7** contain a broad peak at 2368 cm^{-1}

and two peaks at 2003 and 1966 cm^{-1}. The first of these peaks is consistent with previously observed BH$_3$-phosphine adducts, typically observed between 2450 and 2350 cm^{-1}.[27] The two peaks at 2003 and 1966 cm^{-1} are assigned as the Pt-H symmetric and asymmetric stretching modes.

5.3. Conclusions

Several platinum methyl and hydride complexes containing the monoanionic tris(phosphino)borate ligand **5.1** have been synthesized, and preliminary investigations into their chemistry have begun. In general, a zwitterionic description for complexes ligated by **5.1** seems more appropriate than for related [Tp]-containing systems, given that comparative structural data often shows similar binding modes for the two ligands but greater separation between the metal center and the anionic borate for [PhBP$_3$] systems. Although the binding modes are similar between [Tp] and [PhBP$_3$], particularly notable for **5.4** and its [Tp] analogue, we have found that much of the reactivity of the anionic dimethyl complex **5.4** is attributable to the unligated phosphine arm of the trisphosphine ligand. In comparison to related [Tp]-ligated platinum systems, the free phosphine donor readily participates in reactivity due to its greater basicity. Protection of the pendant phosphine arm can be achieved using either BH$_3$ or sulfur. The sulfur-protected complex **5.5** promises to be an interesting candidate for further reactivity studies based on its donor potential. Studies of the reactivity of the BH$_3$-protected compound **5.6** have shown it to be significantly less reactive than **5.4** under comparable conditions, demonstrating the role of the unbound phosphine in reactivity. Future studies of [PhBP$_3$]Pt systems will aim at further understanding the structural, electronic, and reactivity differences between analogous [Tp]- and [PhBP$_3$]-ligated complexes.

5.4. Experimental section

5.4.1. General considerations

Unless otherwise noted, general procedures were performed according to Section 2.4.1.

5.4.2. Starting materials and reagents

[PhBP$_3$][Li(TMEDA)],[9a] [PhBP$_3$]Tl, and (COD)PtMe$_2$[28] were prepared by literature methods.

5.4.3. Syntheses of compounds

[PhB(CH$_2$PPh$_2$)$_3$][^{n}Bu$_4$N] (5.1[TBA], [PhBP$_3$][TBA]). The previously reported compound [PhBP$_3$][Li(TMEDA)] (20.987 g, 25.952 mmol) was dissolved in MeOH in air (50 mL). The methanolic solution was quickly filtered through diatomaceous earth and added slowly to tetra-*n*-butyl ammonium bromide (9.603 g, 28.55 mmol) dissolved in water (300 mL), yielding a white gelatinous solid which dispersed into a coarse chunky powder upon addition of Et$_2$O (40 mL). The mixture was stirred for 5 minutes, and then the solids were collected by filtration and washed with sequentially with water (30 mL), Et$_2$O (30 mL), water (30 mL), and Et$_2$O (30 mL). The resulting white solids were dissolved in acetonitrile (100 mL), yielding a somewhat cloudy yellowish solution which was dried by stirring the reaction mixture over sodium sulfate for 10 min. The solution was then filtered over diatomaceous earth affording a clear yellow solution, which was concentrated by rotary evaporation and triturated with Et$_2$O, yielding white solid **5.1**[TBA] (16.453 g, 67.3%). This compound is not air or moisture stable and should be stored under inert atmosphere.

^{1}H NMR (400 MHz, CD$_3$CN): δ 7.48 (br, 2H, [*ortho*-C$_6$H$_5$BP$_3$]), 7.22 (m, 12H, aryl protons), 7.13 (m, 18H, aryl protons), 6.86 (t, 2H, [*meta*-C$_6$H$_5$BP$_3$]), 6.74 (t, 1H,

[*para*-C$_6$H$_5$BP$_3$]), 3.04 (m, 8H, [(CH$_3$CH$_2$CH$_2$C*H*$_2$)$_4$N]), 1.57 (m, 8H, [(CH$_3$CH$_2$C*H*$_2$CH$_2$)$_4$N]), 1.33 (m, 8H, [(CH$_3$C*H*$_2$CH$_2$CH$_2$)$_4$N]), 1.08 (br, 6H, [PhB(C*H*$_2$PPh$_2$)$_3$]), 0.96 (t, 12H, [(C*H*$_3$CH$_2$CH$_2$CH$_2$)$_4$N]). ^{31}P{^{1}H} NMR (161.9 MHz, CD$_3$CN): δ -11.31. Anal. Calcd. for C$_{62}$H$_{79}$BNP$_3$: C, 79.05; H, 8.45; N, 1.49. Found: C, 79.36; H, 8.52; N, 1.37.

[PhBP$_3$]PtMe$_3$ (5.2). Solid off-white [PhBP$_3$][TBA] (263.6 mg, 0.2840 mmol) and IPtMe$_3$ (104.5 mg, 0.2847 mmol) were dissolved in THF (7 mL). The reaction mixture was stirred for 2 h and then concentrated to 4 mL. Upon standing, white solids precipitated. The supernatent was decanted, and the solids were dried under reduced pressure. Benzene (6 mL) was added, and the reaction mixture was stirred for 10 min. The cloudy solution was filtered, and volatiles were removed under reduced pressure from the resulting solution, providing white solid **5.2** (193.2 mg, 73.5%). Clear, colorless block crystals suitable for X-ray diffraction were obtained from pentane diffusion into a THF solution of **5.2**.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.90 (d, 2H, (*ortho*-C$_6$H$_5$)B), 7.54 (t, 2H, (*meta*-C$_6$H$_5$)B), 7.36 (m, 13H, aryl protons), 6.85 (m, 18H, aryl protons), 2.01 (br, 6H, [PhB(C*H*$_2$PPh$_2$)$_3$]), 1.35 (d, 9H, Pt(C*H*$_3$)$_3$, $^2J_{Pt-H}$ = 55.5 Hz, $^3J_{P-H}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$): δ 136.9, 133.9, 132.4, 129.5, 128.9, 124.9, 15.8 (br, [PhB(C*H*$_2$PPh$_2$)$_3$]), 6.5 (dd, Pt(C*H*$_3$)$_3$, $^1J_{Pt-C}$ = 497 Hz, $^2J_{P-C}$ = 11, 111 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$): δ -26.01 ($^1J_{Pt-P}$ = 1094 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, C$_6$D$_6$): δ -11.9. Anal. Calcd. for C$_{48}$H$_{50}$BP$_3$Pt: C, 62.28; H, 5.44. Found: C, 62.44; H, 5.67.

[PhB(Cl)(CH$_2$PPh$_2$)$_2$]$_2$Pt (5.3). Solid orange [TBA]$_2$[PtCl$_6$] (24.2 mg, 27.1 μmol) was dissolved in CH$_3$CN (1 mL). While stirring, a CH$_3$CN solution (1 mL) of

$TlPF_6$ (19.0 mg, 54.4 μmol) was added. Precipitation of white and yellow-orange solids occurred immediately. After 10 min, the solids were collected by filtration and extracted with hot CH_3CN. Volatiles were removed from the yellow-orange solution under reduced pressure, providing crude $(CH_3CN)_2PtCl_4$ (10.3 mg, 24.6 μmol). Yellow-orange $(CH_3CN)_2PtCl_4$ was suspended in THF (2 mL). A THF solution (1 mL) of $[PhBP_3]Tl$ (21.9 mg, 24.6 μmol) was added, and the reaction was stirred. After 1 h, analysis of the pale yellow homogeneous reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed that the $[PhBP_3]Tl$ had been consumed, and two major platinum products had formed ($^{31}P\{^1H\}$ NMR (121.4 MHz, THF): δ 10.0 ($^1J_{Pt-P}$ = 3470 Hz), 4.3 ($^1J_{Pt-P}$ = 2460 Hz)). Crystallization of the reaction solution by vapor diffusion of petroleum ether into the THF solution provided colorless crystals which were determined by X-ray diffraction to be $[PhB(Cl)(CH_2PPh_2)_2]_2Pt$ (**5.3**).

[[κ^2-PhBP$_3$]PtMe$_2$][TBA] (5.4). Solid off-white $[PhBP_3][TBA]$ (1.6076 g, 1.732 mmol) was dissolved in THF (8 mL). A solution of $(COD)PtMe_2$ (577.0 mg, 1.731 mmol) dissolved in THF (1 mL) was added to the stirring $[PhBP_3][TBA]$ solution, forming a colorless to pale yellow solution. After stirring the reaction mixture for 4 h, the volume of the reaction was reduced by removal of volatiles under reduced pressure. Precipitation with pentane produced off-white to pale yellow solids which were repeatedly triturated under pentane. Drying the solids under reduced pressure resulted in off-white to pale yellow solid **5.4** (1.8024 g, 90.3%). Clear, colorless rectangular prism crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated toluene solution of **5.4**.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.64 (br, 4H), 7.44 (br, 4H), 6.86 - 7.28 (m, 24H), 6.63 (m, 3H), 3.36 (m, 8H, [(CH$_3$CH$_2$CH$_2$CH_2)$_4$N]), 1.76 (m, 8H, [(CH$_3$CH$_2$CH_2CH$_2$)$_4$N]), 1.55 (br, 4H, [[PhB(CH$_2$PPh$_2$)(CH_2PPh$_2$)$_2$]PtMe$_2$]), 1.39 (m, 8H, [(CH$_3$CH_2CH$_2$CH$_2$)$_4$N]), 0.96 (t, 12H, [(CH_3CH$_2$CH$_2$CH$_2$)$_4$N]), 0.65 (br, 2H, [[PhB(CH_2PPh$_2$)(CH$_2$PPh$_2$)$_2$]PtMe$_2$]), 0.08 (vt, 6H, Pt(CH_3)$_2$, $^2J_{Pt-H}$ = 67 Hz, $^3J_{P-H}$ = 5 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-d_6): δ 122-148 (aryl carbons), 59.9 ([(CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N]), 25.0 ([(CH$_3$CH$_2$CH_2CH$_2$)$_4$N]), 24 (br), 21.0 ([(CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N]), 14.6 ([(CH_3CH$_2$CH$_2$CH$_2$)$_4$N]), 6.7 (Pt(CH$_3$)$_2$, $^1J_{Pt-C}$ = 616 Hz, $^2J_{P-C}$ = 8.8, 103 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6): δ 18.96 (s, 2P, $^1J_{Pt-P}$ = 1888 Hz), -9.61 (s, 0.12P), -12.60 (s, 0.88P). ^{11}B{^{1}H} NMR (160.4 MHz, acetone-d_6): δ -14.10. Anal. Calcd. for C$_{63}$H$_{83}$BNP$_3$Pt: C, 65.86; H, 7.34; N, 1.20. Found: C, 65.51; H, 7.29; N, 1.06.

[[κ^2-PhB(CH$_2$P(S)Ph$_2$)(CH$_2$PPh$_2$)$_2$]PtMe$_2$][TBA] (5.5). Solid **5.4** (159.0 mg, 0.1379 mmol) was dissolved in THF (2 mL). While stirring the reaction mixture, a suspension of elemental sulfur (4.6 mg, 0.14 mmol of S atoms) in THF (1 mL) was added to the reaction. After 1 h, the sulfur had been visibly consumed and the reaction changed color from colorless to yellow. The reaction mixture was filtered, and volatiles were removed under reduced pressure, providing pale yellow solid **5.5** (160.7 mg, 97.2%) in >95% purity based on ^{31}P{^{1}H} NMR spectroscopy. Analytically pure **5.5** has not yet been isolated.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.62 (br, 4H), 7.46 (br, 4H), 6.8 - 7.3 (m, 24H), 6.62 (m, 3H), 3.36 (m, 8H, [(CH$_3$CH$_2$CH$_2$CH_2)$_4$N]), 1.76 (m, 8H, [(CH$_3$CH$_2$CH_2CH$_2$)$_4$N]), 1.6 (br, 4H, [[PhB(CH$_2$P(S)Ph$_2$)(CH_2PPh$_2$)$_2$]PtMe$_2$]), 1.39 (m,

8H, [(CH₃C*H₂*CH₂CH₂)₄N]), 0.96 (t, 12H, [(C*H₃*CH₂CH₂CH₂)₄N]), 0.73 (br, 2H,

[[PhB(C*H₂*P(S)Ph₂)(CH₂PPh₂)₂]PtMe₂]), 0.07 (vt, 6H, Pt(C*H₃*)₂, $^2J_{Pt-H}$ = 68 Hz, $^3J_{P-H}$ = 5

Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-*d₆*): δ 44.44 (s, 1P), 18.37 (s, 2P, $^1J_{Pt-P}$ = 1875

Hz).

[[κ²-PhB(CH₂P(BH₃)Ph₂)(CH₂PPh₂)₂]PtMe₂][TBA] **(5.6).** Solid **5.4** (241.2

mg, 0.2092 mmol) was added to a fresh 2.0 M solution of BH₃·SMe₂ (104.6 μL, 0.2092

mmol) in toluene/THF. After 5 min, concentration of the reaction mixture under reduced

pressure followed by addition of petroleum ether precipitated solid **5.6**. Analytically pure

5.6 was obtained from repeated washing of the solids with petroleum ether (237.6 mg,

97.3%).

^{1}H NMR (500 MHz, CD₂Cl₂): δ 7.72, 7.49, 7.0 - 7.4, 6.95, 6.54 (m, 35H, aryl

protons), 2.96 (m, 8H, [(CH₃CH₂CH₂C*H₂*)₄N]), 1.50 (m, 8H, [(CH₃CH₂C*H₂*CH₂)₄N]),

1.35 (m, 8H, [(CH₃C*H₂*CH₂CH₂)₄N]), 0.99 (t, 12H, [(C*H₃*CH₂CH₂CH₂)₄N]), 0.04 (vt, 6H,

Pt(C*H₃*)₂, $^2J_{Pt-H}$ = 67 Hz, $^3J_{P-H}$ = 5.5 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, CD₂Cl₂): δ 161

(br), 140.1 (m), 137.5 (d), 137.2 (d), 134.7 (m), 133.9 (m), 133.3, 132.4 (d), 129.0, 128.4,

128.0, 127.8 (d), 127.5, 127.1, 125.5, 122.3, 59.3 ([(CH₃CH₂CH₂C*H₂*)₄N]), 24.3

([(CH₃CH₂CH₂CH₂)₄N]), 23.5 (br), 22.5 (br), 20.2 ([(CH₃C*H₂*CH₂CH₂)₄N]), 13.9

([(C*H₃*CH₂CH₂CH₂)₄N]), 5.1 (dd, Pt(C*H₃*)₂, $^1J_{Pt-C}$ = 602 Hz, $^2J_{P-C}$ = 9.1, 102 Hz).

^{31}P{^{1}H} NMR (121.4 MHz, CD₂Cl₂): δ 18.01 (s, 2P, $^1J_{Pt-P}$ = 1878 Hz), 15.30 (br, 1P).

^{11}B{^{1}H} NMR (160.4 MHz, CD₂Cl₂): δ -14.8, -30.3. Anal. Calcd. for C₆₃H₈₆B₂NP₃Pt:

C, 65.09; H, 7.51; N, 1.19. Found: C, 64.69; H, 7.53; N, 1.02.

[[κ²-PhB(CH₂P(BH₃)Ph₂)(CH₂PPh₂)₂]Pt(μ-H)]₂[TBA]₂ (5.7). Solid **5.4** (277.4

mg, 0.2377 mmol) was dissolved in THF (2 mL). While stirring the reaction mixture, a

fresh 2.0 M solution of $BH_3 \cdot SMe_2$ in toluene/THF was added (250 μL, 0.500 mmol). After 15 min, the solution was concentrated to dryness under reduced pressure. The resulting solids were washed with petroleum ether (5 x 2 mL) and dried under reduced pressure, providing analytically pure **5.7** (268.4 mg, 99.2%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.97 (br), 7.83 (m), 7.76 (br), 7.54 (br), 7.45 (d), 7.04 (br), 6.93 (m), 2.66 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 2.10 (br, 4H, $PhB(CH_2P(BH_3)Ph_2)(CH_2PPh_2)_2Pt)$, 1.61 (br, 2H, $PhB(CH_2P(BH_3)Ph_2)(CH_2PPh_2)_2Pt)$, 1.15 (m, 16H, $[(CH_3CH_2CH_2CH_2)_4N]$ and $[(CH_3CH_2CH_2CH_2)_4N]$), 0.84 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$), -3.17 ("quintet of quintets," 2H, $[Pt(\mu\text{-}H)]_2$, $^1J_{Pt\text{-}H}$ = 464 Hz, $^2J_{P\text{-}H}$ = 40 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 161 (br), 142.5 (br d), 141.3 (br d), 138.2 (d), 137.5 (d), 134.6 (br m), 134.2 (d), 134.0, 133.2 (d), 133.0 (d), 129.4, 128.9 (m), 127.9 (m), 126.5, 123.1, 58.8 ($[(CH_3CH_2CH_2CH_2)_4N]$), 24.4 ($[(CH_3CH_2CH_2CH_2)_4N]$), 20.2 ($[(CH_3CH_2CH_2CH_2)_4N]$), 20 (br), 14.3 ($[(CH_3CH_2CH_2CH_2)_4N]$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 25.69 (s, 2P, $^1J_{Pt\text{-}P}$ = 2959 Hz, $^2J_{Pt\text{-}P}$ = 168 Hz), 16.06 (br, 1P). $^{11}B\{^1H\}$ NMR (160.4 MHz, C_6D_6): δ -15.3, -31.1. ES MS (CH_3CN, anion observe): calcd for $[C_{90}H_{90}B_4P_6Pt_2]^{2-}$: 1790.5, found: 1790.9 $[M^{2-} + H^+]$, 1777.1 $[M^{2-} + H^+ - BH_3]$, 1763.3 $[M^{2-} + H^+ - 2BH_3]$. IR (Nujol, cm^{-1}): ν 2368 ($R_3P:BH_3$), 2003 (Pt-H), 1966 (Pt-H). IR (THF, cm^{-1}): ν 2378 ($R_3P:BH_3$), 2010 (Pt-H), 1969 (Pt-H). Anal. Calcd. for $C_{122}H_{162}B_4N_2P_6Pt_2$: C, 64.64; H, 7.26; N, 1.22. Found: C, 64.26; H, 7.26; N, 1.46.

5.4.4. X-ray experimental information

The general X-ray experimental procedure was performed according to section 2.4.4. Crystallographic information is provided in Table 5.2.

Table 5.2. X-ray diffraction experimental details for **5.2·THF**, **5.3·2THF**, and **5.4**.

Compound	$[PhBP_3]PtMe_3$ ·THF **5.2·THF**	$[PhB(Cl)(CH_2PPh_2)_2]_2Pt$ ·2THF **5.3·2THF**	$[[\kappa^2\text{-}PhBP_3]PtMe_2]$ [TBA] **5.4**
CCDC ID	216189	216191	216190
Chemical formula	$C_{48}H_{41}BP_3Pt$ ·C_4H_8O	$C_{64}H_{58}B_2Cl_2P_4Pt$ ·$2(C_4H_8O)$	$C_{63}H_{83}BNP_3Pt$
Formula weight	925.72 · 72.11	1237.98 · 2(72.11)	1153.15
T (°C)	-175	-175	-175
λ (Å)	0.71073	0.71073	0.71073
a (Å)	12.1517(8)	12.733(1)	10.656(3)
b (Å)	13.4760(9)	14.320(1)	26.546(6)
c (Å)	15.218(1)	19.253(2)	20.462(5)
α (°)	88.345(1)	76.082(2)	90
β (°)	67.998(1)	81.292(2)	95.821(4)
γ (°)	71.325(1)	64.515(1)	90
V (Å^3)	2177.1(2)	3071.1(5)	5758(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	4
D_{calcd} (g cm^{-3})	1.522	1.495	1.330
μ (cm^{-1})	33.72	25.23	25.59
$R1$, $wR2$ [I>2σ(I)]	0.0263, 0.0557	0.0312, 0.0649	0.0695, 0.1258

$$R1 = \Sigma\,||F_o| - |F_c||\,/\,\Sigma\,|F_o|,\ wR2 = \{\,\Sigma\,[\,w(F_o^2 - F_c^2)^2\,]\,/\,\Sigma\,[\,w(F_o^2)^2\,]\,\}^{1/2}$$

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