Intramolecular C–H Activation by Air-Stable Pt(II) Phosphite Complexes

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ABSTRACT: Air-stable L_2PtMe_2 complexes ligated by bulky aryl phosphite ligands were synthesized and characterized. The aryl phosphite ligands were prepared from substituted phenols and PCl_3 or $P(NMe_2)_3$ without the use of an external base. The steric environment of the phenol controlled the number of substitutions at $P(NMe_2)_3$, resulting in selective formation of $P(NMe_2)(O-2,6-Me_2C_6H_3)_2$. The phosphite ligands and their corresponding platinum(II) complexes were found to be air stable and robust. X-ray diffraction structures of the platinum(II) complexes were obtained in order to determine the steric environment around the metal centers. Thermolysis of the L_2PtMe_2 complexes in C_6D_6 at 100°C results in loss of methane and formation of one major platinum-containing product in high yield. The products of thermolysis were found to be a result of cyclometalation by C–H activation of a sp^3 C–H bond in the ligand to form a 6-membered ring, as confirmed by X-ray crystallography.

Keywords Organoplatinum(II) complexes; Phosphite ligands; X-ray crystallography; Cyclometallation

1. Introduction

Platinum complexes are effective catalysts for a variety of reactions, including C–H bond functionalization [1]. Alkane C–H bond functionalization is particularly useful because it can be used to transform inert bonds into valuable and versatile function groups such as olefins. Platinum complexes capable of C–H bond activation are commonly ligated by nitrogen donor ligands [2], and alkane functionalization reactions such as catalytic alkane transfer dehydrogenation have been reported [3]. The C–H activations that occur at the complexes supported by nitrogen-based ligands generally occur from the Pt(II) oxidation state. In comparison, C–H activation by phosphine-ligated Pt(II) complexes is relatively rare and is generally observed at sp^2 C–H bonds [4-10].

There is one report in the literature by Shinoda and coworkers wherein *acceptorless* cyclooctane dehydrogenation was observed at phosphite-ligated platinum complexes (Scheme 1) [11]. The reported complexes were coordinated by trialkyl phosphite ligands and trichlorostannate ligands. These two types of ligands are uncommon in C–H activation, but have been studied for hydrogenation and hydroformylation on platinum and other metals [12-14]. In the report, a turnover number (TON) of 10 was observed for $(P(OMe)_3)_3Pt(SnCl_3)_2$. Turnover frequencies were not measured and catalyst

decomposition was also observed, which clearly limits the utility of the reaction. The decomposition could be due to Michaelis-Arbuzov decomposition of the alkyl phosphites (Scheme 2) that has been observed to occur readily at very similar platinum complexes [15, 16].

Scheme 1. Acceptorless alkane dehydrogenation reported by Shinoda and coworkers.

Scheme 2. Michaelis-Arbuzov decomposition of alkyl phosphite ligands on platinum(II).

We seek to develop ligands that could be used to stabilize the platinum complexes and thus increase TON of the acceptorless alkane dehydrogenation reaction. Towards this end, we have explored aryl phosphites, which would not be capable of Michaelis-Arbuzov dealkylation. In addition, aryl phosphites are more π -accepting than alkyl phosphites [17], which may have beneficial effects in the activity of catalytic reactions. Similar bulky phosphite ligands have been used previously in hydroformylation and other catalytic transformations with rhodium [18]. Triphenylphosphite ($\text{P}(\text{OPh})_3$) can be cyclometallated at $\text{Pt}(\text{II})$ [19], and therefore substituents were added to the 2 and 6 positions on the aryl rings to obviate that unwanted reactivity. Herein we describe the synthesis and characterization of platinum(II) complexes of sterically bulky aryl phosphite ligands as well as their thermal reactivity.

2. Results and Discussion

2.1. Ligand Syntheses

Triaryl phosphite species can be synthesized via reaction of phenols with PCl_3 , often in the presence of a base. However, we were curious if the reaction could be simplified or if the toxic and caustic PCl_3 could be avoided. One strategy that has been used in the literature is the reaction of HOR groups with a P–N bond [20]. Therefore, 2,6-dimethylphenol was reacted with $\text{P}(\text{NMe}_2)_3$, a phosphine source that possesses internal bases (the formally anionic NMe_2 amide groups). One product was obtained by heating $\text{P}(\text{NMe}_2)_3$ in the presence of excess 2,6-dimethylphenol (>3 equiv.). This product possessed a ^1H NMR spectrum consistent with the di-substituted ligand $\text{P}(\text{NMe}_2)(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ (**L**¹) (Scheme 3). Presumably, the steric hindrance around the phosphorus center due to the two substituted phenoxy groups prevents the third phenoxy group from being installed. The less sterically hindered o-cresol has been heated with $\text{P}(\text{NMe}_2)_3$ to form $\text{P}(\text{O}-2\text{-MeC}_6\text{H}_4)_3$ [21]. Ligand **L**¹ possesses one signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta = 143.19$ ppm. The ligand was also characterized by elemental analysis and

X-ray crystallography. The crystal structure of **L**¹ is shown in Figure 1 and confirms the assignment based on spectroscopy. In the structure of **L**¹ the phosphorus is highly pyramidalized, whereas the nitrogen is nearly trigonal planar (with C–N–C and P–N–C angles of 115, 119, and 123°), consistent with delocalization of the nitrogen lone pair into an antibonding orbital with P–O character [22].

Scheme 3. Synthesis of aryl phosphite ligands **L**¹ and **L**².

Fig. 1. Molecular structure of **L**¹ obtained from X-ray crystallography with ellipsoids shown at 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–N1 = 1.6492(11), P1–O1 = 1.6590(7), P1–O2 = 1.6586(7); N1–P1–O1 = 98.20(5), O1–P1–O2 = 94.32(3), O2–P1–N1 = 102.93(5).

Notably, directly reacting PCl_3 and 2,6-dimethylphenol without a base leads to the previously reported tris-substituted $\text{P}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_3$ (**L**²) (Scheme 3). The increased reactivity of the P–Cl group as compared to the P– NMe_2 likely allows the third substitution to happen in this case. Both ligands **L**¹ and **L**² were isolated as crystalline solids that were stable to air over the course of 18 months at room temperature as judged by NMR spectroscopy.

Reacting the even more sterically hindered 2,6-diisopropylphenol with PCl_3 without a base did not proceed to the tri-substituted phosphite, but rather yielded $\text{PCl}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)_2$, as determined by

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = 173.8$ ppm, similar to literature data [23]). The known compound $\text{P}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)_3$ (L^3) was synthesized according to literature methods using triethylamine and PCl_3 [24]. Based on these observations, the direct synthesis of phosphite ligands without an external base from a phenol and PCl_3 or $\text{P}(\text{NMe}_2)_3$ is governed by steric hindrance around the phenol and the phosphorus as the substitutions occur. Further studies are ongoing in our laboratory to use this approach for the selective modular synthesis of $\text{P}(\text{OR})_3$ ligands with different R groups on the same ligand.

2.2 Syntheses of Platinum Complexes

With the phosphine ligands in hand, they were combined with soluble platinum(II) starting materials. Reactions with the commonly used chloride starting materials $(\text{COD})\text{PtCl}_2$ ($\text{COD} = 1,8\text{-cyclooctadiene}$) or $(\text{SEt}_2)_2\text{PtCl}_2$ led to multiple species as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction mixtures, and purification of the reactions were not attempted. However, reactions of the dimeric starting material $[(\text{SEt}_2)\text{PtMe}_2]_2$ with > 2 equivalents of L^1 or L^2 at 60°C led to one major species, **1** and **2** respectively (Scheme 4). Complexes **1** and **2** were both obtained as white, air-stable products. The $[(\text{SEt}_2)\text{PtMe}_2]_2$ compound was selected as a starting material because it is more thermally robust than the related $[(\text{SMe}_2)\text{PtMe}_2]_2$ [25]. Complexes **1** and **2** were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis, and X-ray crystallography (Figures 2 and 3). The X-ray crystal structure of **1** displays C_2 symmetry with the dimethylamino groups *anti* to each other and verifies a the *cis* ligand structure around the square planar $\text{Pt}(\text{II})$. The ligand P–O bond lengths have shortened, but the P–N bond and the angles around the nitrogen in **1** are similar to those in L^1 . The geometry around the platinum center in **2** is similar to that of **1**, but with a larger P–Pt–P angle, likely due to the increased steric bulk of L^2 .

Scheme 4. Synthesis of L_2PtMe_2 species **1** and **2**.

Fig. 2. Molecular structure of **1** obtained from X-ray crystallography with ellipsoids shown at 50% probability level and hydrogen atoms omitted for clarity. The two sides of the molecule are related by a C_2 axis. Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$): Pt–C1 = 2.098(2), Pt–P1 = 2.2596(5), P1–O1 = 1.6114(14), P1–O2 = 1.6400(15), P1–N1 = 1.646(2); C1–Pt–C1' = 82.38(14), C1–Pt–P1 = 88.15(7), P1–Pt–P1' = 102.06(3).

Fig. 3. Molecular structure of **2** obtained from X-ray crystallography with ellipsoids shown at 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$): Pt–P1 = 2.2505(9), Pt–P2 = 2.2471(9), Pt–C1 = 2.106(3), Pt–C2 = 2.099(3); P1–Pt–P2 = 104.40(3), P2–Pt–C2 = 86.17(10), C2–Pt–C1 = 82.15(13), C1–Pt–P1 = 87.68(10).

(P(OPh)₃)₂PtMe₂ has previously been synthesized [26], and the NMR spectral data was compared with the data for **1** and **2**. In solution, complexes **1**, **2**, and (P(OPh)₃)₂PtMe₂ all have ³¹P{¹H} NMR shifts in similar locations (130 with ¹J_{Pt–P} = 3054 Hz and 118 ppm with ¹J_{Pt–P} = 3158 Hz in C₆D₆ for **1** and **2**, respectively, and 120 ppm with ¹J_{Pt–P} = 3036 Hz for (P(OPh)₃)₂PtMe₂ in CDCl₃). The similar coupling constants indicate that the P–Pt bonding is similar among all of the complexes. These Pt–P coupling constants are higher than those observed at phosphine-based L₂PtMe₂ complexes because the phosphites

have additional bonding interactions from the back-bonding of the platinum d-orbitals in the P–O antibonding orbitals [27-29]. The proton NMR spectra of complexes **1** and **2** both exhibit similar features: broad signals for the CH₃ groups on the ligands and a triplet with ¹⁹⁵Pt satellites for the Pt–CH₃ signals. The coupling constants of the Pt–Me groups in **1** and **2** are similar to (P(OPh)₃)₂PtMe₂ (²J_{Pt-H} = 70.6 Hz in CDCl₃).

Attempts were made to synthesize the corresponding (L³)₂PtMe₂ complex. However, upon heating of L³ with [(SEt₂)PtMe₂]₂ in C₆D₆ at 60 °C for 14 h, only one major platinum-containing species was observed by ¹H NMR spectroscopy. The NMR spectra were consistent with a (L³)(SEt₂)PtMe₂ species; a coordinated SEt₂ group as well as two different Pt–Me groups were observed in the ¹H NMR spectrum (both were d with ¹⁹⁵Pt satellites: one at 0.43 ppm with ²J_{Pt-H} = 85.9 Hz and ³J_{P-H} = 8.9 Hz as well as one at 0.82 ppm with ²J_{Pt-H} = 65.6 Hz and ³J_{P-H} = 10.9 Hz) and a Pt–P group was observed in the ³¹P{¹H} NMR spectrum (114.78 ppm with ¹⁹⁵Pt satellites, ¹J_{P-Pt} = 3296 Hz). Continued heating of this sample lead to decomposition of the platinum species, as evidenced by black material plating on the sides and bottom of the reaction vessel. Therefore, it was concluded that L³ was too sterically hindered to allow formation of a (L³)₂PtMe₂ complex and the (L³)(SEt₂)PtMe₂ complex was not thermally stable towards decomposition at this temperature (Scheme 5).

Scheme 5. Attempted synthesis of (L³)₂PtMe₂.

2.3 Thermolysis Experiments of L₂PtMe₂ species

With pure samples of **1** and **2** in hand, their thermal stability was explored. When samples of **1** or **2** were heated at 100 °C in C₆D₆ in sealed medium-walled J.-Young style NMR tubes, signals for one new platinum compound (complexes **3** and **4**, formed from **1** and **2** respectively) were observed by NMR. These species were the only major product observed after 30 minutes of heating. The signal for methane-*d*₄ (CH₄) was observed by ¹H NMR [30], with no evidence for deuterated methane or other volatile products. No platinum black or deposited metal was observed to form on the sides of the tubes after continued heating at 100 °C for >1 day, indicating that complexes **3** and **4** were very stable at these temperatures.

Complex **3** displayed signals for a Pt–Me group (δ = 0.51 ppm, triplet with ¹⁹⁵Pt satellites, ²J_{Pt-H} = 68.8 Hz, ³J_{P-H} = 8.2 Hz) as well as sharp signals for ligand CH₃ groups, in stark contrast to the NMR spectra for **1**. A signal with platinum satellites was observed at 2.85 ppm. Similarly, complex **4** also displayed signals for one Pt–Me group (δ = 0.49 ppm, triplet with ¹⁹⁵Pt satellites, ²J_{Pt-H} = 70.4 Hz, ³J_{P-H} = 9.4) and

183 The X-ray structure of **4** confirms the NMR assignment of a cyclometallated structure. The six-
 184 membered ring is in a boat-like structure, with a Pt–C bond of 2.11 Å. The two phosphorus ligands are
 185 significantly different in their geometry, consistent with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. This
 186 Pt–P–O–C–C–C metallacycle is a rare motif, but appears to be very stable [31-33]. The mechanism for
 187 this C–H bond activation is not clear at this time, but it is apparent from the products that the platinum
 188 complex did not proceed through Pt(0) to reach **3** or **4**. No ethane, the product of C–C reductive
 189 elimination, was observed and a Pt–Me group is still present in the product. This suggests that the C–H
 190 activation occurs through a species of Pt(II) or Pt(IV) character via sigma-bond metathesis or an
 191 oxidative addition mechanism, respectively. Further experiments are planned to elucidate the
 192 mechanism.

193 3. Materials and Methods

194 3.1. General Considerations

195 Unless otherwise stated, all chemicals were used as provided by their respective manufacturers. All
 196 NMR spectra were collected using a Bruker Avance 300 MHz NMR spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$
 197 NMR spectra were referenced against residual solvent peaks and reported downfield of
 198 tetramethylsilane ($\delta = 0$ ppm). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced against an external 85% H_3PO_4
 199 standard ($\delta = 0$ ppm). Pentane and tetrahydrofuran (THF) were purified using an Innovative Technology
 200 PureSolv system under N_2 . $(\text{COD})\text{PtCl}_2$ and $(\text{SEt}_2)_2\text{PtCl}_2$ were synthesized according to literature
 201 methods [34, 35]. C_6D_6 was stored under vacuum over activated 3 Å molecular sieves and vacuum
 202 transferred to J-Young NMR tubes on a vacuum line. Activated 3 Å molecular sieves have been shown
 203 to be very effective at drying organic solvents [36]. Thermolysis reactions were performed with IKA C-
 204 MAG HS7 hotplates equipped with temperature controllers and Sil 180 Silicone oil to maintain constant
 205 temperatures. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. X-ray
 206 diffraction analyses were performed at the North Carolina State University Department of Chemistry X-
 207 ray Structural Facility by R. D. S.

208 3.2. Synthesis of $\text{P}(\text{NMe}_2)(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ (**L**¹)

209 A round bottom flask was charged with 15 mL of toluene. To this, 3 mL of
 210 tris(dimethylamino)phosphine (16.5 mmol) and 7.01 g (57.3 mmol) of 2,6-dimethylphenol were added.
 211 The solution was refluxed under N_2 atmosphere for 48 hours and the progress was tracked by $^{31}\text{P}\{^1\text{H}\}$
 212 NMR. The solvent was reduced under vacuum to produce white, needle-like crystals (identified as
 213 excess phenol starting material) and an oil. The crystals were collected by filtration and washed with
 214 cold pentane and acetone. The filtrate volume was reduced under vacuum to produce pale yellow oil.
 215 The oil was stored under vacuum for 5 days to produce a yellow liquid over large, white, cubic crystals.
 216 The crystals were filtered and washed with 40 mL of H_2O and 60 mL of cold pentane before being dried
 217 under vacuum for 30 minutes. The yield was 2.92 g (55.8%). The crystals were found suitable for single
 218 crystal X-ray analysis. ^1H NMR (C_6D_6): 6.97 (d, 4H), 6.87 (t, 2H), 2.86 (d, 6H, $^3J_{\text{H-H}} = 9.2$ Hz), 2.18 (s,
 219 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 151.31 (d, $J_{\text{P-C}} = 2.8$ Hz), 131.37 (d, $J_{\text{P-C}} = 2.9$ Hz), 129.60 (d, $J_{\text{P-C}} = 1.4$

220 Hz), 124.29 (d, $J_{\text{P-C}} = 2.0$ Hz), 35.29 (d, $J_{\text{P-C}} = 21.9$ Hz), 18.17 (d, $J_{\text{P-C}} = 5.7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6):
221 143.19. Elemental analysis – formula: $\text{C}_{18}\text{H}_{24}\text{NO}_2\text{P}$, Calculated: C 68.12%, H 7.62%, N 4.41%, Found:
222 C 68.16%, H 7.60%, N 4.57%.

223 3.3. Synthesis of $\text{P}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_3$ (L^2)

224 PCl_3 (1.6 mL, 20.1 mmol) was added to a solution of 2,6-dimethylphenol (2.52 g, 60.5 mmol) and 1 mL
225 toluene in a dropwise manner using a syringe under N_2 . The solution heated to reflux overnight under a
226 flow of N_2 . The resulting solution was initially dissolved in 25 mL of toluene, layered with 15 mL of
227 pentane, and placed in the freezer for several days, but no precipitate formed. The solvent was then
228 reduced under vacuum and the residue was allowed to cool in the freezer, yielding crystals and a liquid.
229 The crystals were filtered off and rinsed with cold pentane and dried 2.82 g (36%) of product. $^{31}\text{P}\{^1\text{H}\}$
230 NMR data matched literature values [37].

231 3.4. Synthesis of $\text{P}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)_3$ (L^3)

232 PCl_3 (0.8 mL, 9.2 mmol) was added dropwise to a solution of 2,6-diisopropylphenol (5.40 g, 30.3
233 mmol) and 5.6 mL triethylamine in 40.0 mL dichloromethane under N_2 . The solution was heated to
234 reflux for 48 hours under a flow of N_2 . A cloudy white precipitate was formed and the solvent was
235 reduced under vacuum. The crystals were filtered off and dried to yield 1.40 g (27%) of product from
236 the first crop. NMR data matched literature values [24].

237 3.5. Synthesis of $[(\text{SEt}_2)\text{PtMe}_2]_2$

238 This compound was synthesized according to a modification of a literature procedure.[38] $(\text{SEt}_2)_2\text{PtCl}_2$
239 (530 mg, 1.13 mmol) was suspended in 100 mL diethyl ether in a Schlenk flask under N_2 cooled with
240 an ice bath. To this a solution of MeLi (4.1 mL of 1.6 M in diethylether) was added via syringe. After
241 allowing the reaction to come to room temperature overnight, 2.1 mL of DI H_2O was added. The
242 solution was dried over $\text{Na}_2\text{SO}_4(\text{s})$ and extracted twice with 50 mL dichloromethane. The combined
243 organics were removed under vacuo and 205 mg (0.325 mmol, 57.5% yield) of the product was
244 obtained after multiple recrystallizations with acetone. NMR spectra matched literature values [38]. A
245 Barnstead International MEL-TEMP was used to find the decomposition temperature of $[(\text{SEt}_2)\text{PtMe}_2]_2$,
246 which was found to be 113–114 °C. This was significantly higher than the reported decomposition
247 temperature of $[(\text{SMe}_2)\text{PtMe}_2]_2$, 86 °C.

248 3.6. Synthesis of Complex 1

249 A glass reaction vessel equipped with a Teflon stopcock was charged with 10 mL of THF into which
250 130 mg (0.206 mmol) of $[(\text{SEt}_2)\text{PtMe}_2]_2$ and 315 mg (0.992 mmol) of $\text{P}[\text{O}-2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3]_2(\text{NMe}_2)$
251 (L^1) were added under N_2 . The flask was sealed and the solution was heated at 60 °C under N_2
252 atmosphere while stirring for 25 minutes. Excess solvent was removed under vacuum to produce a fine
253 gray powder which was washed with cold pentane before being dried under vacuum to yield 0.162 g
254 (91.5%) of product. ^1H NMR (CDCl_3): -0.31 (t with ^{195}Pt satellites, 6H, $^2J_{\text{Pt-H}} = 69.4$ Hz, $^3J_{\text{P-H}} = 7.9$
255 Hz), 2.48 (broad s, 24H), 2.62 (v. broad s, 12H), 6.90 (m, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 152.26,
256 130.66, 128.95, 123.76, 38.57, 19.26, -1.16 (dd w/ ^{195}Pt satellites, $J_{\text{P-C}} = 124.8$, 14.1 Hz, $J_{\text{Pt-C}} = 570$ Hz).

³¹P{¹H} NMR (CDCl₃): 130.35 (s w/ ¹⁹⁵Pt satellites, ¹J_{P-Pt} = 3054 Hz). Elemental analysis – formula: C₃₈H₅₄N₂O₄P₂Pt, Calculated: C 53.08%, H 6.33%, N 3.26%, Found: C 53.25%, H 6.41%, N 3.33%.

259

260 3.7. Synthesis of Complex 2

261 [(SEt₂)PtMe₂]₂ (24.5 mg, 0.174 mmol) and P[O-2,6-(CH₃)₂C₆H₃]₃ (**L**²) (68.8 mg, 0.0388 mmol) along
262 with 0.5 mL of C₆D₆ were added to a medium-walled J. Young NMR tube equipped with a Teflon
263 stopcock. The tube was evacuated with three freeze-pump-thaw cycles and then was heated at 60 °C for
264 two hours. The solvent was then removed under vacuum and the residue was taken up in 10 mL
265 pentane, which was allowed to cool in the freezer, yielding 35.4 mg (45%) of product. Evaporation of
266 the remaining pentane gave single crystals suitable for X-ray analysis. ¹H NMR (C₆D₆): 0.21 (t with
267 ¹⁹⁵Pt satellites, 6H, ²J_{Pt-H} = 69.5 Hz, ³J_{P-H} = 6 Hz), 6.79 (m, 18H), 2.65 (broad s, 24H), 1.70 (broad s,
268 12H), 0.21 (t, 6H). ¹³C{¹H} NMR (C₆D₆): 151.20, 131.70, 192.98, 125.27, 19.64, -1.91 (dd w/ ¹⁹⁵Pt
269 satellites, J_{P-C} = 146.6, 15.5 Hz, J_{Pt-C} = 570 Hz). ³¹P{¹H} NMR (C₆D₆): 118.28 (s w/ ¹⁹⁵Pt satellites, ¹J<sub>P-
270 Pt</sub> = 3158 Hz). Elemental analysis – formula: C₅₀H₆₀O₆P₂Pt, Calculated: C 59.22%, H 5.96%, Found: C
271 59.30%, H 6.07%.

272 3.8. Reaction of **L**³ with [(SEt₂)PtMe₂]₂

273 [(SEt₂)PtMe₂]₂ (10.0 mg, 0.158 mmol) and P[O-2,6-(CH(CH₃)₂)₂C₆H₃]₃(**L**³) (35.7 mg, 0.0634 mmol)
274 along with 0.5 mL of C₆D₆ were added to a medium-walled J. Young NMR tube equipped with a
275 Teflon stopcock. The tube was evacuated with three freeze-pump-thaw cycles and then was heated at 60
276 °C for 14 hours. The reaction did not go to completion and NMR indicated an intermediate complex was
277 formed, (**L**³)(SEt₂)PtMe₂. The species was not isolated and decomposition was observed upon continued
278 heating. Characteristic NMR data for (**L**³)(SEt₂)PtMe₂: ¹H NMR (C₆D₆): 0.43 (d with ¹⁹⁵Pt satellites,
279 3H, ²J_{Pt-H} = 85.9 Hz, ³J_{P-H} = 8.9 Hz), 0.82 (d with ¹⁹⁵Pt satellites, 3H, ²J_{Pt-H} = 65.6 Hz, ³J_{P-H} = 10.9 Hz).
280 ³¹P{¹H} NMR (C₆D₆): 114.78 (s w/ ¹⁹⁵Pt satellites, ¹J_{P-Pt} = 3296 Hz).

281 3.9. Thermolyses of **1** in C₆D₆

282 Thermolyses of **1** were performed according to the following procedure. A medium-walled J. Young
283 NMR tube was charged with complex **1** (8–10 mg) and 400–600 μL of C₆D₆ was added via vacuum
284 transfer. For reactions with an internal standard, the tube was opened, 1,4-dioxane (8–10 μL) was added
285 via syringe, and tube was sealed and subjected to three freeze-pump-thaw cycles. The tube was heated
286 to 100 °C for up to 20 hours with progress tracked by ¹H and/or ³¹P{¹H} NMR. Attempts were made to
287 grow crystals of **3** for X-ray crystallography, but were unsuccessful. Yields were quantitative (100 ±
288 5%) based on integration against the 1,4-dioxane standard. A similar yield was obtained when benchtop
289 C₆D₆ was used and the J-Young tube was sealed under air. ¹H NMR for compound **3** (C₆D₆): 0.51 (t
290 with ¹⁹⁵Pt satellites, 3H, ²J_{Pt-H} = 68.8 Hz, ³J_{P-H} = 8.2 Hz), 2.17 (s, 3H), 2.27 (s, 6H), 2.40 (s, 3H), 2.43 (s,
291 15H), 2.56 (s, 3H), 2.60 (s, 3H), 2.85 (m w/ ¹⁹⁵Pt satellites, 2H, ²J_{Pt-H} = 84 Hz), 6.7–7.0 (m, 12H).
292 ³¹P{¹H} NMR (C₆D₆): 126.3 (d w/ ¹⁹⁵Pt satellites, ²J_{Pt-P} = 3297 Hz, ³J_{P-P} = 7.45 Hz), 147.8 (broad s w/
293 ¹⁹⁵Pt satellites, ²J_{Pt-P} = 3243 Hz).

3.10. Thermolyses of **2** in C₆D₆

Thermolyses of **2** were performed according to the following procedure. A medium-walled J. Young NMR tube was charged with complex **1** (8–10 mg) and 400–600 μ L of C₆D₆ was added via vacuum transfer. For reactions with an internal standard, the tube was opened, 1,4-dioxane (8–10 μ L) was added via syringe, and tube was sealed and subjected to three freeze-pump-thaw cycles. The tube was heated to 100 °C for up to 20 hours with progress tracked by ¹H and/or ³¹P{¹H} NMR. Yields of **4** were quantitative (100 $\pm$ 5%) based on integration against the 1,4-dioxane standard. Crystals of **4** were obtained from the slow evaporation of a thermolysis sample. ¹H NMR for compound **4** (C₆D₆): 0.49 (t with ¹⁹⁵Pt satellites, 3H, ²J_{Pt-H} = 70.4 Hz, ³J_{P-H} = 9.4 Hz), 1.64 (s, 3H), 2.28 (br s, 15H), 2.37 (s, 15H), 2.80 (t w/ ¹⁹⁵Pt satellites, 2H, ³J_{P-H} = 13.4 Hz, ²J_{Pt-H} = 94.8 Hz), 6.6–7.1 (m, 18H). ³¹P{¹H} NMR (C₆D₆): 114.1 (d w/ ¹⁹⁵Pt satellites, ²J_{Pt-P} = 3455 Hz, ³J_{P-P} = 19.2 Hz), 140.2 (d w/ ¹⁹⁵Pt satellites, ²J_{Pt-P} = 3386 Hz).

3.11. X-Ray Crystallography

X-ray crystallographic analyses of **L**¹, **1**, **2**, and **4** were performed as follows. Single crystals suitable for structure analysis were selected from the bulk and mounted on a MiTeGen mounts. Data were collected on a Bruker-Nonius X8 Kappa Apex II diffractometer by ω and ϕ scans using MoK α radiation (λ = 0.71073 Å). Corrections for Lorentz and polarization effects, and absorption were made using SADABS [39]. All four structures were solved using direct methods, and refined using full-matrix least squares (on F²) using the SHELX [40] software package. All non-hydrogen atoms were refined anisotropically. H atoms were added at calculated positions, with coordinates and U_{iso} values allowed to ride on the parent atom. Selected crystallographic data are shown in Table 1.

Table 1. X-ray crystallization data for **L¹, **1**, **2**, and **4****

Compound	L ¹	1	2	4
chemical formula	C ₁₈ H ₂₄ NO ₂ P	C ₃₈ H ₅₄ N ₂ O ₄ P ₂ Pt	C ₅₀ H ₆₀ O ₆ P ₂ Pt	C ₄₉ H ₅₆ O ₆ P ₂ Pt · 0.5C ₆ D ₆
formula weight	317.35	859.86	1014.01	1040.04
temperature /K	110(2)	110(2)	110(2)	110(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> /Å	7.9544(2)	19.7508(14)	11.1065(4)	11.5915(3)
<i>b</i> /Å	8.4891(2)	11.3662(8)	18.6506(6)	14.9899(4)
<i>c</i> /Å	13.3798(4)	16.9566(13)	22.3667(8)	15.2035(4)

α /°	90	90	90	112.0250(7)
β /°	103.3140(10)	100.298(4)	103.3230(10)	104.9300(9)
γ /°	90	90	90	92.8200(8)
V Å ³	879.20(4)	3745.3(5)	4508.4(3)	2334.67(11)
Z	2	4	4	2
ρ_{calc} g/cm ³	1.199 g/cm ³	1.525 g/cm ³	1.494 g/cm ³	1.479 g/cm ³
$F(000)$	340	1744	2064	1054
θ range /°	2.63 to 35.78	2.08 to 32.57	1.87 to 28.34	2.01 to 35.11
reflections collected	28024	46059	69532	133346
data / restr. / parms.	7393 / 1 / 205	6821 / 0 / 220	11217 / 0 / 546	20698 / 138 / 553
R_{int}	0.0178	0.0605	0.0813	0.0280
Goodness-of-fit	1.044	1.029	1.004	1.044
R_1^a ($I > 2\sigma(I)$)	0.0278	0.0269	0.0328	0.0172
wR_2^b ($I > 2\sigma(I)$)	0.0754	0.0523	0.0549	0.0435

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, ^b $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$,
GOF = $\{\Sigma [w(F_o^2 - F_c^2)^2] / (\text{\#reflns} - \text{\#parms})\}^{1/2}$

4. Conclusions and Future Directions

Three air-stable phosphite ligands were synthesized by reaction of phenols with PCl₃ or P(NMe₂)₃. A new phosphite ligand, **L**¹, was synthesized from P(NMe₂)₃ and 2,6-dimethylphenol and characterized by NMR spectroscopy, elemental analysis and X-ray crystallography. The air-stable bulky aryl phosphite ligands were reacted with platinum starting materials to yield L₂PtMe₂ complexes. These species were also characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. While the species were stable on the bench at room temperature, thermolysis in C₆D₆ resulted in intramolecular C–H activation of sp³ bonds on the ligands, resulting in stable metallacycles. One of these complexes was characterized by X-ray crystallography, verifying the presence of a six-membered ring. Future work will explore ligand structures to facilitate *intermolecular* sp³ C–H activation instead of intramolecular sp³ C–H activation. In addition, the reactivity of complexes **1–4** with electrophiles and oxidants will be examined to determine if C–H bond functionalization can be achieved.

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Supporting Information

Cif files for **L**¹, **1**, **2**, and **4** have been deposited at the CCDC (CCDC structure numbers 1413718-1413721).

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ABSTRACT: Air-stable L_2PtMe_2 complexes ligated by bulky aryl phosphite ligands were synthesized and characterized. The aryl phosphite ligands were prepared from substituted phenols and PCl_3 or $P(NMe_2)_3$ without the use of an external base. The steric environment of the phenol controlled the number of substitutions at $P(NMe_2)_3$, resulting in selective formation of $P(NMe_2)(O-2,6-Me_2C_6H_3)_2$. The phosphite ligands and their corresponding platinum(II) complexes were found to be air stable and robust. X-ray diffraction structures of the platinum(II) complexes were obtained in order to determine the steric environment around the metal centers. Thermolysis of the L_2PtMe_2 complexes in C_6D_6 at $100^\circ C$ results in loss of methane and formation of one major platinum-containing product in high yield. The products of thermolysis were found to be a result of cyclometalation by C–H activation of a sp^3 C–H bond in the ligand to form a 6-membered ring, as confirmed by X-ray crystallography.

Air-stable phosphite ligands were synthesized without added external base. Organoplatinum(II) complexes of the air-stable bulky phosphite ligands have been synthesized and characterized. These compounds are very robust and can be stored on the bench without decomposition. Upon thermolysis at 100 °C, these complexes cyclometallate via intramolecular sp^3 C-H activation.