Chapter 3. Electronic studies of bis(phosphino)borate ligands on transition metals

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Thomas, J. C.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5055-5073.

Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870-8888.

3.1. Introduction

3.1.1. Background

A characteristic of transition metal complexes coordinated by (phosphino)borate ligands is the presence of an anionic borate charge in close proximity to the metal center (3.6 - 4.2 Å). As described in Chapter 1, the presence of the anionic borate presents a zwitterionic description for the metal complex. One of our fundamental interests in (phosphino)borate-metal complexes is to test the validity of this zwitterionic description. In particular, we are interested in the effects generated when a borate anion is covalently attached to the ligand framework. At the outset of this study, we considered several electronic consequences that may result from using (phosphino)borates. One possibility is that the borate anion would be insulated from the metal by the methylene links to the donor phosphines, thus having minimal electronic effect on the coordination sphere. Although potentially insulated, the presence of the borate may also generate discrete, measurable, through-space or electrostatic interactions. Alternatively, the anionic charge on the borate could be distributed throughout the ligand framework, resulting in a significantly more electron-donating ligand that would strongly impact electronics at a metal center. Ultimately, the true description likely lies between these extremes. Thus we have begun to examine (phosphino)borate-metal complexes to understand how the covalently attached borate interacts with the transition metal center.

3.1.2. Spectroscopic studies of metal complexes as electronic probes

To investigate the electronic nature of these systems, we have undertaken studies to measure the electronic effects that arise upon coordinating a (phosphino)borate ligand to a metal. These effects can be manifested in many possible aspects of a metal complex, such as the bond lengths of its ground state structure, its spectroscopic characteristics, and the reaction chemistry it exhibits. In particular, spectroscopic measurements can provide a sensitive evaluation of the electronic properties of a metal complex. In this chapter, we evaluate the NMR and infrared spectroscopic data of a series of platinum complexes coordinated by bis(phosphino)borates based on the presence of substituents with different electronic properties. The spectroscopic data for these complexes and also examples of structurally similar platinum and molybdenum complexes coordinated by neutral bis(phosphine) ligands provide insight into the electronic effects resulting from the covalent incorporation of a borate anion.

In examining the NMR spectroscopic data of platinum complexes, several parameters can be correlated to the electronic effects produced by the ligand. Both the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra provide resonances whose chemical shift and platinum coupling constants can be used. Previous work has demonstrated a correlation between platinum coupling constants and the electronic interaction between the platinum center and a ligated phosphine.[1] Particularly in situations where steric effects can be neglected (i.e., structurally similar or analogous complexes), an increase in the platinum-phosphorus coupling constant can be directly related to both a stronger Pt-P interaction and a more electron-rich phosphine. Similarly, the electronic effects on the chemical shifts of phosphine-coordinated metals have been studied.[1,2] These studies typically show a downfield shift in the $^{31}P\{^{1}H\}$ NMR spectrum for more electron-poor phosphines in structurally similar systems, consistent with a deshielding effect. The trends observed in these previous examinations provide a basis for studying similar effects in (phosphino)borate-ligated transition metal systems.

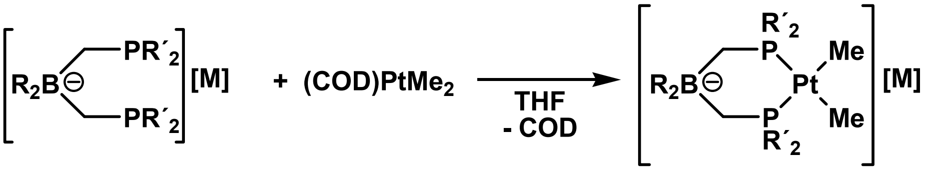
Historically, changes in the stretching frequencies of metal carbonyl complexes also have been used as an accessible electronic probe of the increase or decrease of electron density at a metal center resulting from the metal-ligand interaction.[3-9] These changes have been studied for a variety of cationic, neutral, and anionic metal complexes with many different donor ligands.[3-9] That numerous carbonyl complexes have been prepared represents a potentially consistent way to evaluate electronic effects across the periodic table. Herein, we apply this concept to a study of metal carbonyl complexes coordinated by (phosphino)borate ligands as well as structurally similar neutral bis(phosphine) ligands.

One approach to understanding the electronic effects that a ligand has on a transition metal complex is to study a series of substituted ligands in conjunction with their carbonyl complexes.[3-9] In these systems, the model proposed is that a more electron-donating ligand produces a more electron-rich metal center that is then able to back-bond to a bound carbonyl more effectively, resulting in greater electron density placed in the carbonyl π^* orbitals.[3-9] As a result, the C-O bond order is reduced: this is reflected in the infrared spectrum through a lowering of the C-O stretching frequency. Conversely, for more electron-poor ligands and less electron-rich metal centers, we predict an increase in the C-O stretching frequency. Thus, for a series of ligands substituted with electron-donating or electron-withdrawing groups, a trend may be observed that correlates the C-O stretching frequency with the electron-donating ability of a ligand.

3.2. Results and discussion

3.2.1. Preparation and characterization of neutral platinum methyl carbonyl complexes

In the context of this study, a series of square planar platinum methyl carbonyl complexes were prepared and spectroscopically examined. These platinum complexes were chosen for their monocarbonyl coordination, their diamagnetic nature, their ease of preparation, and their stability towards further reactivity. The dimethyl complexes $[[R_2B(CH_2PR'_2)_2]Pt(Me)_2][M]$ (**3.1-3.10**) that served as precursors to the monocarbonyl complexes were prepared by reaction of the appropriate bis(phosphine) ligand (**2.25-2.31**, **2.33-2.35**, **2.39-2.41**) with $(COD)PtMe_2$, which in most cases led to rapid and quantitative displacement of cyclooctadiene (eq 3.1). The sterically encumbered *tert*-butyl substituted phosphine ligands **2.40** and **2.41** failed to displace cyclooctadiene, even at elevated temperatures (80 °C). This lack of reactivity between *tert*-butyl substituted phosphines and $(COD)PtMe_2$ has been observed previously.[10]



(3.1)

2.25-2.33, 2.36

3.1-3.10

M = Li(THF)$_2^+$, Li(TMEDA)$_2^+$, ASN$^+$, ^{n}Bu$_4$N$^+$

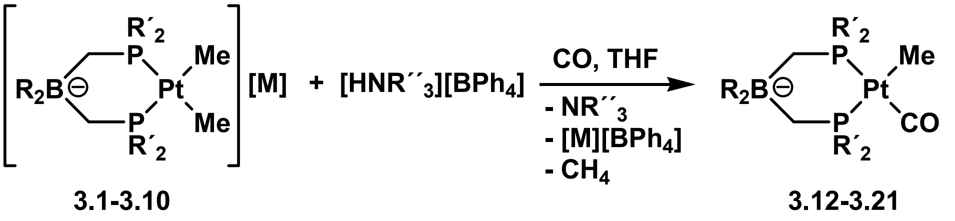
The dimethyl complexes **3.1-3.10** provided an opportunity to examine the effects of electronic substitutions on NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR resonances of **3.1-3.10** are presented in Table 3.1. A few trends related to the electronic substituents on the ligands are observed in the $^1J_{Pt-P}$ coupling constants. First, for the remotely *para*-substituted aryl borate series **3.1-3.5**, only the electron-withdrawing substituted derivative **3.5** shows a significant difference in $^1J_{Pt-P}$. This suggests that **3.1-3.4** are electronically very similar with regards to the metal-bis(phosphine) interaction. Second, changing the countercation from an alkyl ammonium to a lithium(TMEDA)$_x$ cation results in an increase in $^1J_{Pt-P}$. This is best seen for complexes **3.6-3.8**, which we would describe as having electronically similar ligands based on their corresponding carbonyl complexes **3.17-3.19** (*vide infra*). Finally, the expected trend for $^1J_{Pt-P}$ is that a more electron-poor ligand in a series of structurally analogous phosphines would result in a smaller coupling constant as a result of a weaker metal-ligand interaction. This trend is best seen here in the CF_3-substituted derivatives **3.5** and **3.9**, whose $^1J_{Pt-P}$ values (1880 and 1840 Hz, respectively) are notably smaller than derivatives containing more electron-donating groups ($^1J_{Pt-P}$ > 1890 Hz).

Table 3.1. $^{31}P\{^1H\}$ NMR data for platinum dimethyl complexes **3.1-3.10**.

Complex	$^{31}P\{^1H\}$ NMR δ ($^1J_{Pt-P}$, Hz) ^{a}
$[[Ph_2B(CH_2PPh_2)_2]Pt(Me)_2][ASN]$ (**3.1**)	20.60 (1892)
$[[(p\text{-}MePh)_2B(CH_2PPh_2)_2]Pt(Me)_2][ASN]$ (**3.2**)	20.70 (1895)
$[[(p\text{-}^tBuPh)_2B(CH_2PPh_2)_2]Pt(Me)_2][ASN]$ (**3.3**)	20.74 (1893)
$[[(p\text{-}MeOPh)_2B(CH_2PPh_2)_2]Pt(Me)_2][ASN]$ (**3.4**)	20.49 (1893)
$[[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2]Pt(Me)_2][ASN]$ (**3.5**)	19.33 (1880)
$[[Cy_2B(CH_2PPh_2)_2]Pt(Me)_2][Li(TMEDA)_2]$ (**3.6**)	17.39 (2037) ^{b}
$[[Ph_2B\{CH_2P(p\text{-}^tBuPh)_2\}_2]Pt(Me)_2][ASN]$ (**3.7**)	16.22 (1890) ^{b}
$[[(p\text{-}MeOPh)_2B\{CH_2P(p\text{-}^tBuPh)_2\}_2]Pt(Me)_2][Li(TMEDA)]$ (**3.8**)	15.95 (2033)
$[[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2]Pt(Me)_2][ASN]$ (**3.9**)	21.32 (1848) ^{c}
$[[Ph_2B(CH_2P^iPr_2)_2]Pt(Me)_2][^nBu_4N]$ (**3.10**)	24.75 (1961) ^{d}

^{a} acetone-d_6 ^{b} benzene-d_6 ^{c} CD_3CN ^{d} CD_2Cl_2

Subsequent protonation of each dimethyl complex **3.1-3.10** by $[HNEt_3][BPh_4]$ or $[HNEt^iPr_2][BPh_4]$ in THF, followed by introduction of an atmosphere of CO, cleanly generated the desired methyl carbonyl complexes $[R_2B(CH_2PR'_2)_2]Pt(Me)(CO)$ (**3.12-3.21**) (eq 3.2). Their IR spectra were recorded in CH_2Cl_2 solution (KBr cell) to provide the relevant CO stretching frequencies. These ν_{CO} data are presented in Table 3.2, along with the $^{31}P\{^1H\}$ NMR spectroscopic data for complexes **3.12**-**3.21**.



(3.2)

M = $Li(THF)_2^+$, $Li(TMEDA)_2^+$, ASN^+, $^nBu_4N^+$

Table 3.2. $^{31}P\{^1H\}$ NMR resonances (δ) and infrared carbonyl stretching frequencies (ν_{CO}, cm^{-1}) for bis(phosphino)borate platinum methyl carbonyl complexes **3.12**-**3.21**.

Complex	$^{31}P\{^1H\}$ NMR, δ ($^1J_{Pt\text{-}P}$, Hz)	ν_{CO}, cm^{-1} [c]
$[Ph_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.12**)	20.15 (3053), 15.53 (1637) [a]	2094
$[(p\text{-}MePh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.13**)	20.33 (3062), 15.92 (1645) [a]	2094
$[(p\text{-}{}^tBuPh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.14**)	20.00 (3044), 15.32 (1639) [b]	2094
$[(p\text{-}MeOPh)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.15**)	19.89 (3053), 15.43 (1640) [b]	2094
$[(p\text{-}CF_3Ph)_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.16**)	18.75 (3061), 14.24 (1631) [b]	2097
$[Cy_2B(CH_2PPh_2)_2]Pt(Me)(CO)$ (**3.17**)	20.42 (3037), 16.23 (1646) [a]	2092
$[Ph_2B\{CH_2P(p\text{-}{}^tBuPh)_2\}_2]Pt(Me)(CO)$ (**3.18**)	17.48 (3030), 12.68 (1641) [b]	2091
$[(p\text{-}MeOPh)_2B\{CH_2P(p\text{-}{}^tBuPh)_2\}_2]Pt(Me)(CO)$ (**3.19**)	17.65 (3034), 12.93 (1642) [a]	2091
$[Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2]Pt(Me)(CO)$ (**3.20**)	20.85 (3090), 16.84 (1616) [a]	2105
$[Ph_2B(CH_2P^iPr_2)_2]Pt(Me)(CO)$ (**3.21**)	40.28 (1666), 30.81 (2942) [b]	2079

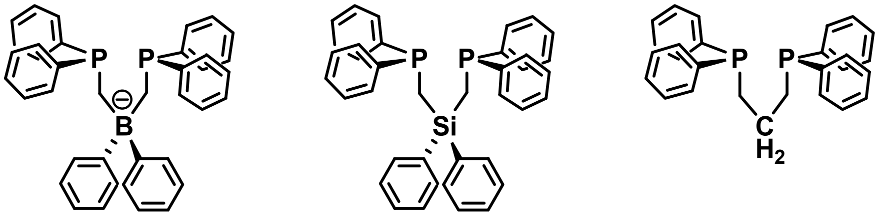
[a] $CDCl_3$ [b] CD_2Cl_2 [c] CH_2Cl_2

As can be seen from the infrared data (Table 3.2), variation of the borate backbone by systematic *para*-substitution on the phenyl ring (e.g., -H, $-CH_3$, $-{}^tBu$, -OMe, $-CF_3$) has a minimal effect on the observed CO stretching frequencies. Aside from the

CF_3-substituted derivative **3.16**, each of the complexes **3.12-3.15** provides an indistinguishable CO stretching frequency of 2094 cm^{-1}. The difference in the observed CO stretching frequency ($\Delta\nu_{CO}$) between the *p*-OMe-substituted (**3.15**) and the *p*-CF_3-substituted (**3.16**) derivatives is only 3 cm^{-1}. Replacement of the diaryl backbone by a dialkyl backbone, as in the Cy_2B-derivative **3.17**, provides a slightly more electron-releasing ligand in comparison (ν_{CO} = 2092 cm^{-1}). More pronounced effects are observed by *para*-substitution at the arylphosphine donor positions. For example, the electron-releasing *para*-*tert*-butyl substituted derivative **3.18** has a ν_{CO} at 2091 cm^{-1}, whereas the *para*-CF_3-substituted derivative **3.20** provides a ν_{CO} at 2105 cm^{-1} – a 14 cm^{-1} difference. Thus, the sensitivity of the CO stretching frequency as a function of variation at the borate backbone in these neutral complexes is quite small ($\leq$ 4 cm^{-1}). In contrast, variation at the phosphine donors has an appreciably more pronounced effect (up to 14 cm^{-1}). This outcome is consistent with describing the borate unit as electronically insulated to some degree. It is interesting to note that the subtle differences recorded for the IR data also appear in the respective $^{31}P\{^1H\}$ NMR chemical shifts of the methyl carbonyl complexes. The magnitude of the separation (between 4 and 5 ppm) between the two signals remains fairly constant across the series, and complexes with identical ν_{CO} stretches exhibit nearly identical ^{31}P NMR shifts as well as NMR coupling constants.

3.2.2. Synthesis and characterization of structurally analogous neutral and cationic platinum complexes

In addition to establishing the electronic effects of substitutions over a series of neutral complexes, we also want to understand the electronic effects resulting from changing the overall charge of the molecule. To address this issue, we chose to examine a series of structurally analogous but charge-differentiated platinum complexes. The three ligands that were used in this study are bidentate bis(phosphine) chelates containing a three atom backbone chain (Figure 3.1). The only structural difference between the three ligands is at the center of the backbone chain, where either a Ph_2B^- (**2.25**), a Ph_2Si (**3.22**), or a H_2C (**3.23**) unit resides. The synthesis of the anionic borate $[Ph_2BP_2]$[ASN] (**2.25**[ASN]) is described in Chapter 2, and 1,3-bis(diphenylphosphino)propane (dppp, **3.23**) is commercially available. As we desired a close structural analogue of anionic **2.25**, the neutral ligand $Ph_2Si(CH_2PPh_2)_2$ (Ph_2SiP_2, **3.22**) was prepared. Neutral **3.22** was synthesized readily by addition of two equivalents of Ph_2PCH_2Li(TMEDA) to Ph_2SiCl_2 (5.28 g, 82.3% yield). Attempts to prepare the structurally analogous carbon-based ligand $Ph_2C(CH_2Ph_2)_2$ by a similar route using Ph_2CCl_2 were unsuccessful. The chemical shifts ($^{31}P\{^1H\}$ NMR) for ligands **2.25**[ASN], **3.22**, and **3.23** are shown in Table 3.3.



2.25 **3.22** **3.23**

Figure 3.1. Ligands used for studying structurally similar metal complexes.

Dimethyl platinum(II) complexes of ligands **2.25**[ASN], **3.22**, and **3.23** were prepared by reacting the appropriate ligand with (COD)$PtMe_2$ in THF. The substitution reactions proceed cleanly to displace cyclooctadiene and generate $[[Ph_2BP_2]Pt(Me)_2]$[ASN] (**3.1**), $(Ph_2SiP_2)PtMe_2$ (**3.24**), and (dppp)$PtMe_2$ (**3.25**)[11,12] in high isolated yield (> 90%). Selected NMR data for these three complexes are also presented in Table 3.3.

Table 3.3. Selected NMR shifts (δ) and coupling constants (Hz) for ligands **2.25**[ASN], **3.22**, and **3.23**, and platinum dimethyl complexes **3.1**, **3.24**, and **3.25** (acetone-d_6).

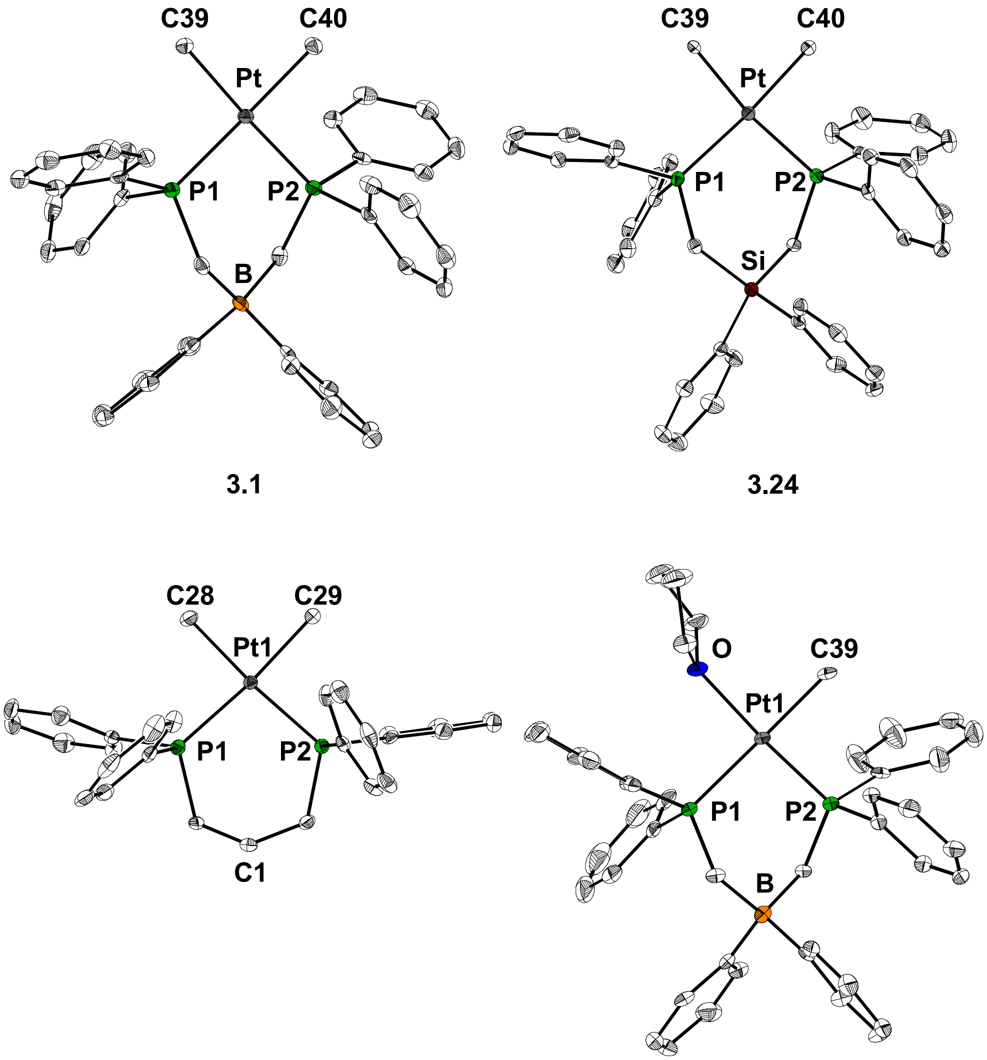
Compound	$^{31}P\{^1H\}$ NMR	$^1J_{Pt-P}$	^1H NMR, Pt-Me	$^3J_{P-H}$, Pt-Me	$^2J_{Pt-H}$, Pt-Me
$[Ph_2BP_2][ASN]$ (**2.25**[ASN])	-8.78	-	-	-	-
Ph_2SiP_2 (**3.22**)	-22.65	-	-	-	-
dppp (**3.23**)	-16.29	-	-	-	-
$[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**3.1**)	20.60	1892	0.08 (t)	12	68
$(Ph_2SiP_2)PtMe_2$ (**3.24**)	12.00	1848	0.17 (dd)	6.6, 8.1	69
$(dppp)PtMe_2$ (**3.25**)	5.47	1812	0.25 (dd)	5.4, 6.9	69

To prepare methyl carbonyl complexes for comparison, the precursor THF solvent adducts were synthesized. Protonation of the neutral dimethyl species **3.24** and **3.25** in dichloromethane in the presence of approximately 40 - 100 equivalents of THF with $[H(OEt_2)_2][B(C_6F_5)_4]$[13] resulted in the clean formation of the salts $[(Ph_2SiP_2)Pt(Me)(THF)][B(C_6F_5)_4]$ (**3.26**) and $[(dppp)Pt(Me)(THF)][B(C_6F_5)_4]$ (**3.27**) (> 90% isolated yield). In comparison to dimethyl complexes **3.24** and **3.25**, anionic $[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**3.1**) was readily protonated by weaker ammonium acids of the type $[HNR_3^+]$, consistent with **3.1** being a more electron-rich, anionic metal center. Thus, reacting **3.1** and $[HN^iPr_2Et][BPh_4]$ in THF for 15 min provided the neutral THF adduct $[Ph_2BP_2]Pt(Me)(THF)$ (**3.11**) after workup (> 95% isolated yield). The cationic methyl THF complexes **3.26** and **3.27** are markedly more stable to both vacuum and halogenated solvents than zwitterionic **3.11**. Complex **3.11** exhibits decomposition within minutes in dichloromethane at ambient temperature, whereas both **3.26** and **3.27** are stable for hours under similar conditions. Also, prolonged exposure of **3.11** to vacuum results in its degradation. Thus, to remove residual THF in the preparation of **3.11**, it is critical to dry the sample carefully with a gentle stream of dry nitrogen or argon.

3.2.3. Structural and NMR comparisons of 3.1, 3.24, 3.25, and 3.11

X-ray diffraction studies were carried out on crystals of the dimethyl complexes **3.1**, **3.24**, and **3.25** and the neutral complex [Ph_2BP_2]Pt(Me)(THF) (**3.11**) to confirm their structural analogy. Relevant structural representations are shown in Figure 3.2, and noteworthy bond lengths and angles are presented in Table 3.4. As anticipated, the solid-state structures of **3.1**, **3.24**, and **3.25** are very similar. The Pt-P and Pt-C bond lengths are nearly identical for the three derivatives. The modest deviation observed in the C-Pt-C and P-Pt-P bond angles present in **3.1**, **3.24**, and **3.25** may reflect the presence of a countercation in the unit cell of anionic [[Ph_2BP_2]Pt$(Me)_2$][ASN] (**3.1**) that is not present in neutral (Ph_2SiP_2)$PtMe_2$ (**3.24**) or (dppp)$PtMe_2$ (**3.25**). The extended lattice structure of **3.1** (Figure 3.3) shows that the ammonium cation packs within the wedge of a diphenylborate unit and is also in close proximity to the methyl ligands of an adjacent platinum anion. This solid-state arrangement of the cation of **3.1** may slightly alter the ligand conformation of [Ph_2BP_2] in **3.1** relative to **3.24** and **3.25**. For comparison, the solid-state structure of zwitterionic **3.11** reveals a P-Pt-P angle (91.96(3)°) that is closer to the bite angles observed for both **3.24** and **3.25**.

Another structural parameter of interest concerns the Pt-B distance in (phosphino)borate complexes [[Ph_2BP_2]Pt$(Me)_2$][ASN] (**3.1**) and [Ph_2BP_2]Pt(Me)(THF) (**3.11**). The borate anion in **3.1** is separated from the Pt-center at 4.117(1) Å in a twisted boat conformation of the chelate ligand. This compares well with the Pt-Si distance in neutral (Ph_2SiP_2)$PtMe_2$ (**3.24**) (4.192(1) Å), which contains a similar twisted boat configuration. Both of these distances are somewhat longer than the related Pt-C1 distance (3.838(1) Å) in (dppp)$PtMe_2$ (**3.25**) due to the boat conformation of the bis(phosphine) in the latter structure. The Pt-B distance contracts only slightly in moving from anionic **3.1** to zwitterionic **3.11** (Pt-B = 4.007(6) Å in **3.11**): the closer approach of the borate center to the metal may be an expected consequence of removing an electron-rich methyl ligand.



3.1

3.24

3.25

3.11

Figure 3.2. Displacement ellipsoid representations (50%) of $[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**3.1**), $(Ph_2SiP_2)PtMe_2$·toluene (**3.24**·toluene), $(dppp)PtMe_2$ (**3.25**), and $[Ph_2BP_2]Pt(Me)(THF)$·2THF (**3.11**·2THF). Hydrogen atoms, counterions (ASN, **3.1**), and solvent molecules (toluene, **3.24**; 2 THF, **3.11**) are omitted for clarity.

Table 3.4. Selected interatomic distances (Å) and angles (º) for complexes **3.1**, **3.24**, **3.25**, and **3.11**.

Complex	Pt-C	Pt-P	Pt-E	C-Pt-C	P-Pt-P
[[Ph_2BP_2]Pt(Me)$_2$][ASN] (**3.1**)	2.134(3), 2.132(3)	2.2829(7), 2.2776(7)	4.117(1) (Pt-B)	86.6(1)	90.64(2)
(Ph_2SiP_2)$PtMe_2$ (**3.24**)	2.142(3), 2.122(3)	2.2828(7), 2.2804(7)	4.192(1) (Pt-Si)	83.8(1)	94.63(3)
(dppp)$PtMe_2$ (**3.25**)	2.102(3), 2.113(3)	2.2724(8), 2.2714(8)	3.838(1) (Pt-C)	85.9(1)	94.30(3)
[Ph_2BP_2]Pt(Me)(THF) (**3.11**)	2.087(6)	2.313(2) [a]	4.007(6) (Pt-B)	91.2(1) [b]	91.94(6)

[a] P *trans* to methyl [b] C-Pt-O angle

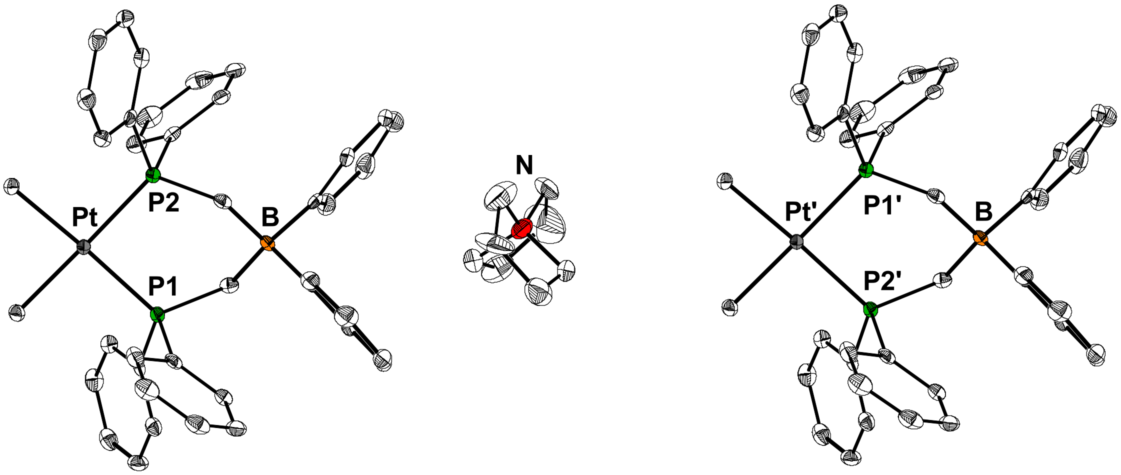


Figure 3.3. Packing diagram displaying the location of the [ASN] cation between adjacent platinum dimethyl and borate units of **3.1**.

Structural and NMR parameters potentially sensitive to electronic differences between the neutral and cationic systems include the relative Pt-Me and Pt-P bond lengths obtained from the X-ray structures of **3.1**, **3.24**, and **3.25** and the chemical shifts and coupling constants observed from their NMR spectra. These data can be used to gauge the relative *trans* influence of a ligand coordinated to a square planar platinum(II) center.[2b,10] Our data establish that the structural parameters are relatively insensitive to the placement of an anionic diphenylborate unit in [[Ph_2BP_2]Pt(Me)$_2$][ASN] (**3.1**) versus incorporation of a neutral diphenylsilane in $(Ph_2SiP_2)PtMe_2$ (**3.24**) or a neutral methylene in (dppp)$PtMe_2$ (**3.25**). The average Pt-C bond lengths between isostructural **3.1** and **3.24** are virtually indistinguishable (Pt-C ≈ 2.13 Å), as are their Pt-P bond distances (Pt-P ≈ 2.28 Å) (Table 3.4), consistent with structural data obtained for various $(Ar_3P)_2PtMe_2$ complexes that have been reported previously. In considering the comparative NMR data, the magnitudes of the $^2J_{Pt-H}$ coupling constants for **3.1**, **3.24**, and **3.25** are all very similar (68, 69, and 69 Hz, respectively, Table 3.3), as expected. NMR parameters that do show variation among the three systems are the $^{31}P\{^1H\}$ NMR chemical shifts, the $^1J_{Pt-P}$ coupling constants, the Pt-$(CH_3)_2$ chemical shifts in the ^1H NMR spectra, and the $^3J_{P-H}$ coupling constants (Table 3.3). The relationship between the electronic nature of a phosphine-coordinated $PtMe_2$ center and the coupling constant $^1J_{Pt-P}$ and the Pt-$(CH_3)_2$ chemical shift in the ^1H NMR spectrum has also been examined previously. The trends observed for *para*-substituted aryl phosphine adducts of dimethyl platinum(II) suggest that $^1J_{Pt-P}$ decreases and the Pt-$(CH_3)_2$ chemical shift moves downfield for less donating phosphines. Both of these trends are observed in the data presented here, consistent with the idea that the bis(phosphino)borate ligand **2.25** provides a platinum center that is more electron-rich than the isostructural derivatives supported by ligands **3.22** and **3.23**.

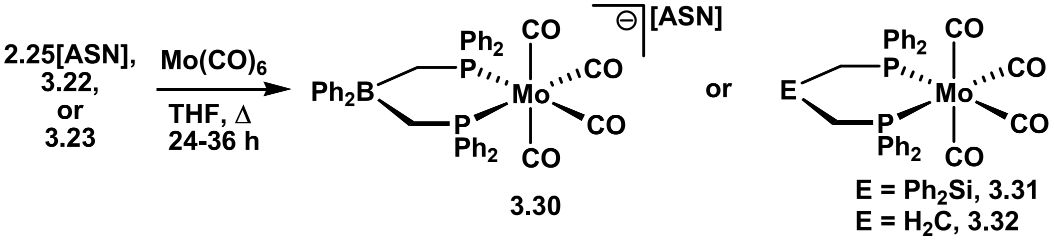
3.2.4. Synthesis and characterization of charge-differentiated metal carbonyl complexes

As an additional method for comparing the electronic differences arising from isostructural but charge-differentiated ligands, transition metal carbonyl complexes were prepared. Reaction of the THF adducts **3.11**, **3.26**, or **3.27** with excess carbon monoxide in THF ($[Ph_2BP_2]Pt(Me)(THF)$, **3.11**) or dichloromethane ($[(Ph_2SiP_2)Pt(Me)(THF)]^+$, **3.26**; $[(dppp)Pt(Me)(THF)]^+$, **3.27**) solution resulted in the rapid formation of neutral

$[Ph_2BP_2]Pt(Me)(CO)$ (**3.12**), and cationic $[(Ph_2SiP_2)Pt(Me)(CO)][B(C_6F_5)_4]$ (**3.28**), and $[(dppp)Pt(Me)(CO)][B(C_6F_5)_4]$ (**3.29**). Solution IR spectra for these derivatives were recorded in dichloromethane solution in a KBr cell (Table 3.5). The carbonyl stretching frequencies observed for the two cations are identical (**3.28**: 2118 cm^{-1}, **3.29**: 2118 cm^{-1}). The neutral complex **3.12**, however, shows a ν_{CO} vibration that is 24 cm^{-1} lower in energy (**3.12**: 2094 cm^{-1}). These data suggest that the metal center of the neutral complex **3.12** is more electron-rich and that the $[Ph_2BP_2]$ ligand is more electron-releasing than its neutral analogues.

Table 3.5. Comparative infrared carbonyl frequencies (cm^{-1}) for model platinum (**3.12**, **3.28**, **3.29**) and molybdenum (**3.30-3.32**) complexes (KBr cell in CH_2Cl_2 solution).

Complex	ν_{CO} (cm^{-1})
$[Ph_2BP_2]Pt(Me)(CO)$ (**3.12**)	2094
$[(Ph_2SiP_2)Pt(Me)(CO)][B(C_6F_5)_4]$ (**3.28**)	2118
$[(dppp)Pt(Me)(CO)][B(C_6F_5)_4]$ (**3.29**)	2118
$[[Ph_2BP_2]Mo(CO)_4][ASN]$ (**3.30**)	2005
$(Ph_2SiP_2)Mo(CO)_4$ (**3.31**)	2018
$(dppp)Mo(CO)_4$ (**3.32**)	2018



(3.3)

The phosphine ligands **2.25**[ASN], **3.22**, and **3.23** were also examined within the conventional $L_2Mo(CO)_4$ infrared model system. Crabtree has previously suggested that the highest frequency CO vibration, presumed to be an a_1 vibration, in tetracarbonyl molybdenum complexes is a reasonable gauge of the relative electron-releasing/accepting character for a bidentate chelate. Reaction of the appropriate bisphosphine ligand **2.25**[ASN], **3.22**, or **3.23** with $Mo(CO)_6$ in refluxing THF for 24-36 h provides the desired species $[[Ph_2BP_2]Mo(CO)_4][ASN]$ (**3.30**), $(Ph_2SiP_2)Mo(CO)_4$ (**3.31**), and $(dppp)Mo(CO)_4$[14] (**3.32**), respectively (eq 3.3). Measurement of their respective IR spectra in dichloromethane solution established a trend similar to that of the platinum system (Table 3.5). The highest frequency CO vibration for anionic **3.30** is 2005 cm^{-1}, whereas the same vibration for both **3.31** and **3.32** is 2018 cm^{-1}. Thus, the data for both the platinum and molybdenum systems support the notion that **2.25** results in a more electron-rich metal center.

3.2.5. Discussion of cationic versus neutral complexes

For complexes coordinated by a (phosphino)borate ligand, the term "zwitterionic" is often used to describe the separation between the anionic borate and the cationic metal center. This description emphasizes that the borate unit in these systems is not delocalized by conventional resonance structures to the phosphine donor atoms. However, charge in covalently linked molecules is often highly distributed and assigning a formal charge to any atom or unit may be inaccurate. Despite the possibility of distributed charge, we believe that the zwitterionic description for complexes of the type $[Ph_2BP_2]Pt(X)(L)$ is useful, especially when considering them in a comparative context with respect to formally cationic $[(P_2)Pt(X)(L)]^+$ complexes. In particular, the overall reactivity of the zwitterionic systems examined thus far compares well with their isostructural but cationic analogues for Pt, Pd, and Rh.[15-17]

To address the relative electrophilicity between the platinum centers of $[Ph_2BP_2]Pt(X)(L)$ and $[(P_2)Pt(X)(L)]^+$ type systems, the platinum(II) methyl carbonyl complexes **3.12**, **3.28**, and **3.29** were prepared and studied. A key assumption we make is that the relative energy of the CO vibration is a reasonable gauge of whether the $[Ph_2BP_2]^-$ ligand is more electron-releasing than its neutral relatives Ph_2SiP_2 and dppp.[3-8]

In reality, the absolute magnitude in $\Delta\nu_{CO}$ measured between a zwitterionic complex (e.g., $[Ph_2BP_2]Pt(Me)(CO)$, **3.12**) and a cationic complex (e.g., $[(Ph_2SiP_2)Pt(Me)(CO)][B(C_6F_5)_4]$, **3.28**) can be misleading. For cationic late metal carbonyls, where π-backbonding is relatively weak, strong polarization of the CO σ-bond by the cationic complex is anticipated.[9,18,19] This raises the energy of the force constant F_{CO} significantly, and, in extreme cases, polarization can dominate the observed F_{CO}. In this context, cationic fragments such as $[(Ph_2SiP_2)PtMe]^+$ are expected to have characteristically high force constants (F_{CO}) due to a strong polarization effect. This effect will be reduced for CO coordinated to a neutral $[Ph_2BP_2]PtMe$ fragment, regardless of whether or not its charge is described as a discrete zwitterion or as distributed throughout the metal complex. Therefore, the absolute magnitude of $\Delta\nu_{CO}$ may not be a reliable gauge of relative backbonding ability between complexes that are formally cationic and complexes that are formally neutral. Large differences in polarization between isostructural cationic and neutral complexes likely compete with the electronic factors of σ-donation, π-backbonding, and/or π-acceptor character that are typically relied upon to correlate measured $\Delta\nu_{CO}$ values to the electron releasing character of a ligand.

The issue of polarization is avoided by studying a series of electronically substituted neutral carbonyl complexes (Table 3.2). These ν_{CO} values are reflective of relative “electron-releasing” character and electronic distribution within the complex as a function of substitution. Infrared data recorded for the series of platinum complexes shown in Table 3.2 show the results of electronic effects at a position remote from the coordinated metal center. It is reasonable to conclude that electronic variation by substitution at the aryl borate unit of the bis(phosphino)borate ligands has only a small, if any, electronic impact on the electron-releasing character of the phosphine ligands. This view is consistent with the zwitterionic description of neutral complexes coordinated by (phosphino)borate ligands.

The modest differences observed upon substitution of the (phosphino)borate ligand are notable when compared to the large difference in the CO stretching frequencies ($\Delta\nu_{CO}$ = +24 cm^{-1}) between [PhBP$_2$]Pt(Me)(CO) (**3.12**) and its cationic analogue [(Ph$_2$SiP$_2$)PtMe(CO)][B(C$_6$F$_5$)$_4$] (**3.28**). Large $\Delta\nu_{CO}$ values also have been observed between many other isostructural cationic and neutral carbonyl complexes of several transition metals coordinated by both (phosphino)- and (amino)borate ligands (Table 3.6).[15-17,20-22] In all cases, the neutral systems display lower ν_{CO} frequencies, consistent with a more electron-rich metal center, in the absence of polarization effects.

Table 3.6. Select infrared data for structurally similar neutral and cationic carbonyl complexes.

Complex	ν_{CO} (cm^{-1}) [a]	Ref.
[Ph$_2$B(CH$_2$PPh$_2$)$_2$]Pd(CO)(C(O)Me)	2108 (CO), 1694 (C(O)Me)	16
[(dppp)Pd(CO)(C(O)Me)][B(3,5-(CF$_3$)$_2$Ph)$_4$]	2130 (CO), 1715 (C(O)Me)	16
[Ph$_2$B(CH$_2$PPh$_2$)$_2$]Rh(CO)$_2$	2080, 2029 (avg: 2055)	17
[(Ph$_2$Si(CH$_2$PPh$_2$)$_2$)Rh(CO)$_2$][PF$_6$]	2099, 2056 (avg: 2078)	17
[(dppp)Rh(CO)$_2$][PF$_6$]	2100, 2056 (avg: 2078)	17
[Ph$_2$B(CH$_2$NMe$_2$)$_2$]Rh(CO)$_2$	2070, 1992 (avg: 2031)	21
[(Ph$_2$Si(CH$_2$NMe$_2$)$_2$)Rh(CO)$_2$][PF$_6$]	2097, 2030 (avg: 2064)	21
[PhB(CH$_2$PPh$_2$)$_3$]Co(CO)$_2$	2008, 1932 (avg: 1970) [b]	20
[{MeC(CH$_2$PPh$_2$)$_3$}Co(CO)$_2$][BPh$_4$]	2030, 1972 (avg: 2001)	23
[PhB(CH$_2$PPh$_2$)$_3$]RuCl(CO)$_2$	2068, 2021 (avg: 2045)	22
[{MeC(CH$_2$PPh$_2$)$_3$}RuCl(CO)$_2$][PF$_6$]	2076, 2040 (avg: 2058) [c]	24

[a] CH$_2$Cl$_2$/KBr [b] Benzene/KBr [c] KBr (solid)

Considering all of the data collectively, one can anticipate a step-change in the relative electrophilicity of a metal center on moving from a neutral to a formally cationic system, regardless of whether the neutral system is formally zwitterionic. Because electrostatic factors contribute to the difference in CO stretching frequencies between charge-differentiated complexes, the absolute magnitude of $\Delta\nu_{CO}$ overemphasizes the differences between transition metals coordinated by either a (phosphino)borate or its neutral analogues. Thus, the absolute difference in electrophilicity between complexes such as **3.12** and **3.28** is likely not as large as might be suggested by carbonyl model complex studies. However, we also emphasize the ambiguity that arises if one tries to separate electrophilicity from electrostatic factors. In comparing neutral **3.12** and cationic **3.28**, the electrostatic effect on the force constant of the bound carbonyl does result in different carbonyl stretching frequencies. This measurable difference for carbonyls will also be reflected to some degree in other ligands bound to a metal center coordinated by a (phosphino)borate ligand, and we interpret this as an electronic change resulting in the reduction the electrophilicity of the metal. Therefore, we maintain that anionic (phosphino)borates *are* more electron-releasing than their neutral counterparts as a result of the anionic borate in close proximity and covalently linked to a transition metal; however, the degree to which the borate charge is distributed throughout the complex is overemphasized by infrared data that compares a cationic to a neutral system.

3.3. Conclusions

The transition metal carbonyl model complexes presented in this chapter have addressed the electron-releasing character of anionic (phosphino)borate ligands. Although we have not achieved a quantitative measurement of the change in electrophilicity, we conclude that (phosphino)borates are generally more electron-releasing than their neutral phosphine analogues, despite the fact that the borate unit is not delocalized by conventional resonance contributors. This conclusion suggests that neutral complexes supported by (phosphino)borate ligands will be more electron-rich than their cationic counterparts. An absolute measure of the comparative electrophilicities of these types of metal centers will require further investigation.

Whether a zwitterionic description is most appropriate for a neutral complex supported by a (phosphino)borate ligand depends on the degree of charge delocalization. Measuring the degree of charge delocalization and the electronic mechanism by which delocalization occurs is not done with absolute precision through infrared carbonyl studies. Such model studies do, however, provide information concerning the *relative* electron-richness of each complex discussed herein. At present, we suggest that a zwitterionic description is useful as it often predicts a complex's chemical reactivity. A diverse set of model studies have shown that neutral complexes supported by (phosphino)borate ligands will mediate transformations typical of their more conventional, cationic counterparts.[15-17] In this sense, our classification of these neutral complexes as "zwitterionic" is meaningful.

3.4. Experimental section

3.4.1. General considerations

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

3.4.2. Starting materials and reagents

The reagents (COD)$PtCl_2$,[25] (COD)$PtMe_2$,[26] [$HNEt_3$][BPh_4],[27] [$Li(OEt_2)_2$][$B(C_6F_5)_4$],[28] [$H(OEt_2)_2$][$B(C_6F_5)_4$], (dppp)$Mo(CO)_4$, and (dppp)$PtMe_2$[11,12] were prepared by previously described methods. [$HNEt_3$][BPh_4] was prepared by stirring an aqueous solution of $HNEt_3Cl$ and $NaBPh_4$. [$HNEt^iPr_2$][BPh_4][29] was prepared by acidifying an aqueous solution of NEt^iPr_2 with HCl (aq) and adding $NaBPh_4$. The resulting white precipitate was collected by filtration and dried under heat and vacuum for 24 h prior to use. The bis(phosphine) ligands **2.25-2.31**, **2.33-2.35**, and **2.39-2.41** were prepared as described in Chapter 2.

3.4.3. Syntheses of compounds

[[Ph_2BP_2]Pt(Me)$_2$][ASN] (3.1). Solid [Ph_2BP_2][ASN] (391.8 mg, 0.5680 mmol) was suspended in THF (6 mL). A solution of (COD)$PtMe_2$ (189.3 mg, 0.5679 mmol) in THF (2 mL) was added to the suspension, and the reaction homogenized as it stirred. A white precipitate formed after 1 h. The resulting mixture was concentrated under reduced pressure and triturated with pentane (2 x 2 mL). The off white solids were dried under reduced pressure, providing **3.1** as an off-white solid (511.2 mg, 98.4%). Crystals suitable for X-ray diffraction were grown by slow evaporation of an acetonitrile solution of **3.1**.

^1H NMR (300 MHz, acetone-d_6): δ 7.40 (m, 8H), 7.07 (m, 12H), 6.88 (m, 4H), 6.64 (m, 4H), 6.58 (m, 2H), 3.71 (m, 8H), 2.26 (m, 8H), 1.98 (br, 4H), 0.08 (vt, 6H, Pt-CH_3, $^3J_{P\text{-}H}$ = 12 Hz, $^2J_{Pt\text{-}H}$ = 68 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 167 (br), 140.1 (d), 134.4 (m), 133.5, 128.2, 127.3 (m), 126.3 (m), 122.0, 63.7, 22.9 (br), 22.8, 5.5 (dd, $^1J_{Pt\text{-}C}$ = 600 Hz, $^2J_{P\text{-}C}$ = 103 Hz, $^2J_{P\text{-}C}$ = 9.1 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 20.60 ($^1J_{Pt\text{-}P}$ = 1892 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -13.7. Anal. Calcd. for $C_{48}H_{56}BNP_2Pt$: C, 63.02; H, 6.17; N, 1.53. Found: C, 62.97; H, 5.90; N, 1.81.

General method A: preparation of bis(phosphino)borate platinum dimethyl complexes [[$R_2B(CH_2PR'_2)_2$]Pt(Me)$_2$][X] (3.2-3.10). A solution of CODPtMe_2 in THF was added to a stirring solution or suspension of one equivalent of the bis(phosphino)borate in THF. After 1 h, the reaction had gone to completion, as shown by a $^{31}P\{^1H\}$ NMR spectrum of the homogeneous reaction. The resulting solution was concentrated to dryness under reduced pressure. The resulting white or off-white solids were typically washed repeatedly with Et_2O or petroleum ether to remove residual cyclooctadiene and then were dried under reduced pressure. Purity was assessed by examination of the NMR spectra (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$). Yields are reported for compounds where greater than 100 mg were isolated.

[[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (3.2). Following General Method A, off-white solids (209.7 mg, 96.7%).

^1H NMR (300 MHz, acetone-d_6): δ 7.38 (m, 8H), 7.11 (m, 4H), 7.05 (m, 8H), 6.79 (d, 4H), 6.47 (d, 4H), 3.67 (m, 8H), 2.24 (m, 8H), 2.09 (s, 6H), 1.91 (br, 4H), 0.08 (t, 6H, Pt(CH_3)$_2$, $^3J_{P\text{-}H} = 6.0$ Hz, $^2J_{Pt\text{-}H} = 67$ Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 163 (q), 140.8 (d), 134.7, 134.1, 130.5, 128.5, 127.9, 127.6, 64.2, 23.4 (br), 23.3, 21.7, 5.9 (dd, Pt(CH$_3$)$_2$, $^1J_{Pt\text{-}C} = 600$ Hz, $^2J_{P\text{-}C} = 9.2$, 103 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 20.70 ($^1J_{Pt\text{-}P} = 1895$ Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -13.6. Anal. Calcd. for $C_{50}H_{60}BNP_2Pt$: C, 63.69; H, 6.41; N, 1.49. Found: C, 63.43; H, 6.74; N, 1.76.

[[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (3.3). Following General Method A, white solids (172.3 mg, 94.4%).

^1H NMR (300 MHz, acetone-d_6): δ 7.40 (tt, 8H), 7.06 (m, 12H), 6.83 (br d, 4H), 6.70 (d, 4H), 3.69 (m, 8H), 2.25 (m, 8H), 2.00 (br, 4H), 1.22 (s, 18H), 0.07 (vt, 6H, Pt(CH_3)$_2$, $^2J_{Pt\text{-}H} = 67$ Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 163 (br q), 144.3, 141.0, 135.2, 133.9, 129.0, 128.1, 123.9, 64.6, 35.2, 33.1, 23.8 (br), 23.7, 6.2 (dd, Pt(*C*H$_3$)$_2$, $^1J_{\text{Pt-C}}$ = 600 Hz, $^2J_{\text{P-C}}$ = 9, 100 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-*d*$_6$): δ 20.74 ($^1J_{\text{Pt-P}}$ = 1893 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-*d*$_6$): δ -14.2. Anal. Calcd. for $C_{56}H_{72}BNP_2Pt$: C, 65.49; H, 7.07; N, 1.36. Found: C, 65.68; H, 6.94; N, 1.30.

[[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (3.4). Following General Method A.

^{1}H NMR (300 MHz, acetone-*d*$_6$): δ 7.40 (m, 8H), 7.09 (m, 12H), 6.78 (br d, 4H), 6.28 (m, 4H), 3.63 (m, 8H), 3.62 (s, 6H), 2.21 (m, 8H), 1.90 (br d, 4H), 0.09 (dd, 6H, Pt-C*H*$_3$, $^2J_{\text{Pt-H}}$ = 68 Hz, $^3J_{\text{P-H}}$ = 6, 6 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, acetone-*d*$_6$): δ 159 (br), 140.8, 134.9, 134.7, 129.8, 128.7, 127.9, 112.9, 64.4, 55.7, 24 (br), 23.4, 6.1 (dd, Pt-*C*H$_3$, $^1J_{\text{Pt-C}}$ = 605 Hz, $^2J_{\text{P-C}}$ = 10, 100 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-*d*$_6$): δ 20.49 ($^1J_{\text{Pt-P}}$ = 1893 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, acetone-*d*$_6$): δ -13.7.

[[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][ASN] (3.5). Following General Method A.

^{1}H NMR (300 MHz, acetone-*d*$_6$): δ 7.40 (m, 8H), 7.10 (m, 12H), 6.95 (m, 8H), 3.74 (m, 8H), 2.27 (m, 8H), 2.01 (br, 4H), 0.07 (vt, 6H, Pt(C*H*$_3$)$_2$, $^2J_{\text{Pt-H}}$ = 68 Hz, $^3J_{\text{P-H}}$ = 6.3 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, acetone-*d*$_6$): δ 172 (br q), 139.4 (m), 134.2 (m), 133.3, 128.5, 127.4 (m), 124.0 (q), 122.7, 63.7, 22.8, 22.7 (br), 5.5 (dd, Pt(*C*H$_3$)$_2$, $^1J_{\text{Pt-C}}$ = 600 Hz, $^2J_{\text{P-C}}$ = 9.7, 103 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-*d*$_6$): δ 19.33 ($J_{\text{Pt-P}}$ = 1880 Hz). ^{19}F{^{1}H} NMR (282.1 MHz, acetone-*d*$_6$): δ -61.6. ^{11}B{^{1}H} NMR (128.3 MHz, acetone-*d*$_6$): δ -13.5.

[[Cy$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)$_2$][Li(TMEDA)$_2$] (3.6). Following General Method A.

^{1}H NMR (300 MHz, C_6D_6): δ 7.92 (m, 8H), 7.14 (m, 12H), 2.21 (s, 8H), 1.88 (m, 32H), 1.3-1.6 (m, 24H), 1.09 (m, 2H), 0.21 (br s, 6H, Pt-C*H*$_3$, $^2J_{\text{Pt-H}}$ = 54 Hz). ^{13}C{^{1}H}

NMR (75.4 MHz, C_6D_6): δ 141 (m), 135.0 (m), 128.9, 127.9 (m), 68.2, 56.3, 45.3, 39.8 (br), 33.5, 31.4, 19.7 (br), 2.2 (dd, Pt(CH$_3$)$_2$, $^1J_{Pt\text{-}C}$ = 530 Hz, $^2J_{P\text{-}C}$ = 8.9, 96 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 17.39 ($^1J_{Pt\text{-}P}$ = 2037 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, C_6D_6): δ -13.2.

[[Ph$_2$B{CH$_2$P(*p*-^{t}BuPh)$_2$}$_2$]Pt(Me)$_2$][ASN] (3.7). Following General Method A, white solids (108.5 mg, 98.6%).

^1H NMR (300 MHz, C_6D_6): δ 7.86 (t, 8H, J = 8.4 Hz), 7.24 (br d, 4H, J = 7.2 Hz), 7.17 (d, 8H, J = 7.8 Hz), 6.76 (m, 4H), 6.70 (m, 2H), 2.53 (br d, 4H), 1.65 (m, 8H), 1.29 (s, 36H), 0.85 (m, 8H), 0.65 (s, 6H, Pt(CH_3)$_2$, $^2J_{Pt\text{-}H}$ = 67 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 166.9 (q, $J_{B\text{-}C}$ = 54 Hz), 150.6, 137.0 (m), 134.6 (m), 133.2, 126.4, 124.3, 121.8, 62.3, 34.9, 32.0, 23.4 (br), 21.8, 6.6 (dd, Pt(CH$_3$)$_2$, $^1J_{Pt\text{-}C}$ = 595 Hz, $^2J_{P\text{-}C}$ = 9.7, 103 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 16.22 ($^1J_{Pt\text{-}P}$ = 1890 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, C_6D_6): δ -14.6. Anal. Calcd. for $C_{64}H_{88}BNP_2Pt$: C, 67.47; H, 7.79; N, 1.23. Found: C, 67.47; H, 7.55; N, 1.07.

[[(*p*-MeOPh)$_2$B{CH$_2$P(*p*-^{t}BuPh)$_2$}$_2$]Pt(Me)$_2$][Li(TMEDA)] (3.8). Following General Method A.

^1H NMR (300 MHz, acetone-d_6): δ 7.35 (8H, m), 7.10 (8H, d), 6.75 (4H, d), 6.25 (4H, d), 3.61 (6H, s), 2.36 (4H, s), 2.18 (12H, s), 1.88 (4H, br d), 1.29 (36H, s), 0.10 (t, 6H, Pt(CH_3)$_2$, $^2J_{Pt\text{-}H}$ = 67 Hz, $^3J_{P\text{-}H}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, acetone-d_6): δ 158 (br), 156.1, 150.4, 134.3 (m), 134.1, 124.1 (m), 112.1, 59.7, 46.2, 35.0, 31.9, 24 (br), 5.2 (dd, Pt(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 15.95 ($^1J_{Pt\text{-}P}$ = 2033 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, acetone-d_6): δ -14.2.

[[$Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2$]Pt(Me)$_2$][ASN] (3.9). Following General Method A.

^{1}H NMR (300 MHz, CD_3CN): δ 7.50 (m, 8H), 7.40 (m, 8H), 6.75 (br, 4H), 6.65 (m, 6H), 3.38 (m, 8H), 2.10 (m, 8H), 2.03 (br m, 4H), -0.06 (vt, Pt(CH_3)$_2$, $^2J_{Pt\text{-}H}$ = 68 Hz, $^3J_{P\text{-}H}$ = 5.7 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): δ 164 (br), 142.7 (m), 133.8 (m), 132.1, 129.4 (q), 126.0, 123.7 (m), 121.9, 117.5, 63.0, 22.0, 21 (br), 4.8 (dd, Pt(CH_3)$_2$, $^1J_{Pt\text{-}C}$ = 632 Hz, $^2J_{P\text{-}C}$ = 9.3, 102 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_3CN): δ 21.32 ($^1J_{Pt\text{-}P}$ = 1848 Hz). ^{19}F{^{1}H} NMR (282.1 MHz, CD_3CN): δ -63.1. ^{11}B{^{1}H} NMR (128.3 MHz, CD_3CN): δ -14.2.

[[$Ph_2B(CH_2P^iPr_2)_2$]Pt(Me)$_2$][^{n}Bu$_4$N] (3.10). Following General Method A, to the resulting THF solution was added one equivalent of ^{n}Bu$_4$NBr. After removal of the volatiles under reduced pressure, the white solids were washed with Et_2O (2 x 2 mL).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.50 (br, 4H), 6.97 (t, 4H), 6.77 (t, 2H), 2.82 (m, 8H), 2.15 (m, 4H), 1.2-1.5 (m, 20H), 1.04 (m, 24H), 0.93 (dd, 12H), 0.14 (t, 6H, $^2J_{Pt\text{-}H}$ = 64 Hz, $^3J_{P\text{-}H}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 169.2 (q, $^1J_{B\text{-}C}$ = 50 Hz), 132.1, 126.4, 121.9, 59.3 (N($CH_2CH_2CH_2CH_3$)$_4$), 24.6 (q), 24.4 (N($CH_2CH_2CH_2CH_3$)$_4$), 20.3 (N($CH_2CH_2CH_2CH_3$)$_4$), 19.8 (m), 18.8 (m), 14.0 (N($CH_2CH_2CH_2CH_3$)$_4$), 7.9 (br), 1.2 (dd, Pt(CH_3)$_2$, $^1J_{Pt\text{-}C}$ = 564 Hz, $^2J_{P\text{-}C}$ = 11.4, 102 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ 24.75 ($^1J_{Pt\text{-}P}$ = 1961 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): δ -15.7. Anal. Calcd. for $C_{44}H_{84}BNP_2Pt$: C, 59.05; H, 9.46; N, 1.57. Found: C, 59.10; H, 9.53; N, 1.61.

[Ph_2BP_2]Pt(Me)(THF) (3.11). Solid **3.1** (118.2 mg, 129.2 μmol) was dissolved in THF (1 mL). A THF solution (2 mL) of [^{i}Pr$_2$EtNH][BPh$_4$] (58.1 mg, 129 μmol) was added to the stirring solution of **3.1**. The clear, colorless reaction rapidly produced a white precipitate. The mixture was stirred for 15 min, and the white solids ([ASN][BPh_4]) were filtered away. The solution was concentrated under reduced pressure, and pentane (2 mL) was added, precipitating **3.11** as a spectroscopically pure white solid. The solids were collected by filtration, washed with petroleum ether (2 x 4 mL), dissolved in THF (4 mL), filtered, and concentrated under reduced pressure to 0.5 mL. Petroleum ether was added (4 mL), precipitating white solids. The solution was decanted. The collected solids were dried under a stream of dry gas (dinitrogen or argon) for 20 min, providing **3.11** (108.0 mg, 99.0%). Crystals suitable for X-ray diffraction were grown from THF at -35 ºC.

^{1}H NMR (300 MHz, C_6D_6): δ 7.64 (m, 4H), 7.48 (m, 4H), 7.24 (m, 4H), 7.00 (m, 18H), 2.90 (br, 4H), 2.51 (d, 2H, $^2J_{\text{P-H}}$ = 18 Hz), 2.37 (d, 2H, $^2J_{\text{P-H}}$ = 14 Hz), 0.71 (br, 4H), 0.35 (br d, 3H, Pt-CH_3, $^3J_{\text{P-H}}$ = 6 Hz, $^2J_{\text{Pt-H}}$ = 40 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, THF, -5 ºC): δ 160.3 (br), 134.1 (d), 130.9 (d), 130.8 (d), 130.1 (d), 129.7, 127.3, 126.9, 125.5 (d), 125.1 (d), 123.5, 119.2, 64.9, 22.6, 21.2 (br), 15.3 (br), 8.2 (dd, Pt-CH_3, $^2J_{\text{P-C}(trans)}$ = 85.5 Hz, $^2J_{\text{P-C}(cis)}$ = 4.8 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, THF): δ 33.44 (d, $^1J_{\text{Pt-P}}$ = 1820 Hz, $^2J_{\text{P-P}}$ = 22 Hz), 15.96 (d, $^1J_{\text{Pt-P}}$ = 4478 Hz, $^2J_{\text{P-P}}$ = 22 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 34.14 (d, $^1J_{\text{Pt-P}}$ = 1813 Hz, $^2J_{\text{P-P}}$ = 21 Hz), 16.09 (d, $^1J_{\text{Pt-P}}$ = 4453 Hz, $^2J_{\text{P-P}}$ = 21 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, THF): δ -14.5. Anal. Calcd. for $C_{43}H_{45}BOP_2Pt$: C, 61.07; H, 5.36. Found: C, 61.14; H, 5.32.

[Ph_2BP_2]Pt(Me)(CO) (3.12). A THF solution (2 mL) of [Et_3NH][BPh_4] (47.5 mg, 0.113 mmol) was added to a stirring THF solution (15 mL) of **3.1** (103.3 mg, 0.1129 mmol). Formation of a white precipitate occurred gradually over 15 min. The reaction was filtered, removing the white solids, and the solution was transferred to a 50 mL Schlenk flask and sealed with a septum and a needle valve. A stream of CO was passed through the flask for 5 min. The septum was exchanged for a stopper under an N_2 flow, and the volatiles were removed under reduced pressure. The resulting solids were dissolved in THF (10 mL), filtered, concentrated, triturated under pentane (2 x 2 mL), washed with Et_2O (3 x 2 mL), and dried under reduced pressure, providing **3.12** (78.1 mg, 86.3%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.34, 6.85-6.92, 6.72-6.83 (aryl protons), 2.14 (br, 2H, $^3J_{Pt\text{-}H}$ = 61 Hz), 2.09 (br, 2H, $^3J_{Pt\text{-}H}$ = 54 Hz), 0.45 (t, 3H, $^2J_{Pt\text{-}H}$ = 58 Hz, $^3J_{Pt\text{-}P}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 180.5 (dd, Pt-*C*O, $^1J_{Pt\text{-}C}$ = 1291 Hz, $^2J_{Pt\text{-}P(\mathit{trans})}$ = 131 Hz, $^2J_{Pt\text{-}P(\mathit{cis})}$ = 6.9 Hz), 162 (br), 136.2 (d), 133.5 (d), 132.5 (d), 132.3, 131.2 (d), 130.5 (d), 130.1 (d), 128.4 (d), 128.2 (d), 126.6, 122.8, 18.2 (br), 16.4 (br), -2.6 (d, $^2J_{P\text{-}C}$ = 60 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.15 (d, $^1J_{Pt\text{-}P}$ = 3053 Hz, $^2J_{P\text{-}P}$ = 31 Hz), 15.53 (d, $^1J_{Pt\text{-}P}$ = 1637 Hz, $^2J_{P\text{-}P}$ = 31 Hz). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$): δ -14.2. IR: (Nujol mull) ν_{CO} = 2087 cm^{-1}. IR: (CH_2Cl_2) ν_{CO} = 2094 cm^{-1}. Anal. Calcd. for $C_{40}H_{37}BOP_2Pt$: C, 59.94; H, 4.65. Found: C, 60.37; H, 5.27.

General method B: preparation of bis(phosphino)borate platinum methyl carbonyl complexes [$R_2B(CH_2PR'_2)_2$]Pt(Me)(CO) (3.13-3.21). A solution of bis(phosphino)borate platinum dimethyl anion (**3.2-3.10**) was dissolved in THF. A THF solution containing one equivalent of [Et_3NH][BPh_4] was added to the stirring reaction mixture. After 15-20 min, the solution was filtered into a flask with a sidearm, removing any solid precipitate ([X][BPh_4], X = TBA$^+$, ASN$^+$, Li(THF)$_2$$^+$, Li(TMEDA)$_2$$^+$). The flask was sealed with a septum. A stream of CO gas was introduced through the sidearm, and the flask was flushed with CO for 10 min. The sealed flask was then stirred for an additional 60 min, after which time volatiles were removed under reduced pressure.

[(*p*-MePh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (3.13). Following General Method B.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.21-7.44 (m, 20H), 6.94 (d, 4H), 6.74 (d, 4H), 2.27 (s, 6H), 2.13 (br m, 4H), 0.57 (t, 3H, Pt(C*H*$_3$), $^3J_{\text{P-H}}$ = 5.7 Hz, $^2J_{\text{Pt-H}}$ = 58 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ 180.6 (dd, Pt-*C*O, $^1J_{\text{Pt-C}}$ = 1286 Hz, $^2J_{\text{Pt-P}}$ = 7.4, 131 Hz), 159 (br, *ipso* B(C$_6$H$_5$)$_2$), 136.5 (d, $^1J_{\text{P-C}}$ = 48.5 Hz), 133.5, 132.5, 132.4, 131.7, 131.4 (d, $^1J_{\text{P-C}}$ = 57 Hz), 130.3, 129.9, 1283 (m), 128.1 (m), 127.5, 21.3, 18.0 (br), 16.8 (br), -2.8 (d, Pt(*C*H$_3$), $^2J_{\text{P-C}}$ = 61 Hz, $^1J_{\text{Pt-C}}$ = 416 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ 20.33 ($^1J_{\text{Pt-P}}$ = 3062 Hz, $^2J_{\text{P-P}}$ = 31 Hz), 15.92 ($^1J_{\text{Pt-P}}$ = 1645 Hz, $^2J_{\text{P-P}}$ = 31 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CDCl$_3$): δ -13.9. IR: (CH$_2$Cl$_2$) ν$_{\text{CO}}$ = 2094 cm^{-1}.

[(*p*-^{t}BuPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (3.14). Following General Method B.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.30 (m, 10H), 7.20 (m, 8H), 7.05 (t, 2H), 6.81 (m, 8H), 2.16 (m, 4H), 1.24 (s, 18H), 0.42 (t, 3H, Pt(C*H*$_3$), $^2J_{\text{Pt-H}}$ = 58 Hz, $^3J_{\text{P-H}}$ = 6.0 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$): δ 180.9 (dd, Pt(*C*O), $^2J_{\text{P-C}}$ = 7.4, 131 Hz), 159 (br), 145.1, 136.6 (d), 136.5, 134.0 (m), 133.2 (m), 131.8, 130.8 (d), 130.5 (d), 128.6 (d), 128.4 (d), 123.7, 34.3, 32.0, 19 (br), 17 (br), -2.8 (dd, Pt(*C*H$_3$)). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$): δ 20.00 ($^1J_{\text{Pt-P}}$ = 3044 Hz, $^2J_{\text{P-P}}$ = 32 Hz), 15.32 ($^1J_{\text{Pt-P}}$ = 1639 Hz, $^2J_{\text{P-P}}$ = 32 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, THF): δ 20.38 ($^1J_{\text{Pt-P}}$ = 3038 Hz, $^2J_{\text{P-P}}$ = 32 Hz), 15.94 ($^1J_{\text{Pt-P}}$ = 1645 Hz, $^2J_{\text{P-P}}$ = 32 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD$_2$Cl$_2$): δ -15.1. IR: (CH$_2$Cl$_2$) ν$_{\text{CO}}$ = 2094 cm^{-1}.

[(*p*-MeOPh)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (3.15). Following General Method B.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.2-7.4 (m, 16H), 7.04 (t, 2H), 6.89 (t, 2H), 6.78 (d, 4H), 6.39 (d, 4H), 3.69 (s, 6H), 2.09 (br m, 4H), 0.47 (t, 3H, Pt(C*H*$_3$)), $^2J_{\text{Pt-H}}$ = 58 Hz, $^3J_{\text{P-H}}$ = 5.7 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ 180.9 (dd, Pt(*C*O)), 154 (br), 136.5, 133.9 (m), 133.1, 132.9 (m), 130.8, 130.5, 128.7 (d), 128.5 (d), 126.4, 122.4, 112.6, 55.4, 18.8 (br), 17.1 (br), -2.8 (dd, Pt(*C*H$_3$)). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ 19.89 ($^1J_{\text{Pt-P}}$ = 3053 Hz, $^2J_{\text{P-P}}$ = 32 Hz), 15.43 ($^1J_{\text{Pt-P}}$ = 1640 Hz, $^2J_{\text{P-P}}$ = 32 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): δ -14.6. IR: (CH_2Cl_2) ν_{CO} = 2094 cm^{-1}.

[(*p*-CF$_3$Ph)$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (3.16). Following General Method B.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.15-7.45 (m, 20H), 7.01 (d, 4H), 6.92 (d, 4H), 2.21 (br m, 4H), 0.44 (t, $^2J_{\text{Pt-C}}$ = 58 Hz, $^3J_{\text{P-C}}$ = 6.0 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ 180.5 (dd, Pt(*C*O), $^1J_{\text{Pt-C}}$ = 1288 Hz, $^2J_{\text{P-C}}$ = 6.8, 132 Hz), 167 (br q), 135.9 (d), 134.0 (d), 132.9 (d), 132.3, 131.2 (d), 131.0 (d), 129.5, 128.9 (d), 128.6 (d), 125.1 (q), 123.4, 19 (br), 17 (br), -2.6 (dd, Pt(*C*H$_3$), $^1J_{\text{Pt-C}}$ = 415 Hz, $^2J_{\text{P-C}}$ = 4.3, 61 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ 18.75 ($^1J_{\text{Pt-P}}$ = 3061 Hz, $^2J_{\text{P-P}}$ = 31 Hz), 14.24 ($^1J_{\text{Pt-P}}$ = 1631 Hz, $^2J_{\text{P-P}}$ = 31 Hz). ^{19}F{^{1}H} NMR (282.1 MHz, CD_2Cl_2): δ -62.8. ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): δ -14.7. IR: (CH_2Cl_2) ν_{CO} = 2097 cm^{-1}.

[Cy$_2$B(CH$_2$PPh$_2$)$_2$]Pt(Me)(CO) (3.17). Following General Method B.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 8H), 7.14 (t, 8H), 6.99 (t, 4H), 2.02 (br, 2H), 1.86 (br, 2H), 1.45 (m, 8H), 1.30 (m, 8H), 0.88 (m, 4H), 0.67 (m, 2H), 0.45 (dd, 3H, Pt(C*H*$_3$), $^2J_{\text{Pt-H}}$ = 58 Hz, $^3J_{\text{P-H}}$ = 6, 6 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 181.0 (dd, Pt(*C*O), $^2J_{\text{P-P}}$ = 9, 130 Hz), 138.8, 138.4, 133.9 (d), 132.9 (d), 130.4 (d), 130.1 (d), 128.6 (d), 128.3 (d), 56.4 (br), 45.7 (br), 38.7 (br), 16.3 (br), 14.4 (br), -2.0 (dd, Pt(*C*H$_3$), $^1J_{\text{Pt-C}}$ = 413 Hz, $^2J_{\text{P-C}}$ = 4, 62 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 20.42 ($^1J_{\text{Pt-P}}$ =

3037 Hz, $^{2}J_{\text{P-P}}$ = 31 Hz), 16.23 ($^{1}J_{\text{Pt-P}}$ = 1646 Hz, $^{2}J_{\text{P-P}}$ = 31 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, $CDCl_3$): δ -13.3. IR: (CH_2Cl_2) ν_{CO} = 2092 cm^{-1}.

[$Ph_2B\{CH_2P(p\text{-}{}^tBuPh)_2\}_2$]Pt(Me)(CO) (3.18). Following General Method B.

^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ 180.8 (d, $^{2}J_{\text{P-C}}$ = 130 Hz), 162.5 (br), 153.5, 153.3, 133.3 (m), 133.2 (m), 132.3 (m), 132.2 (m), 131.9, 126.4, 125.2 (d), 125.0 (d), 122.5, 34.7, 34.6, 31.2, 31.1, 18.7 (br), 16.8 (br), 2.4 (dd, Pt(*C*H$_3$), $^{1}J_{\text{Pt-C}}$ = 410 Hz, $^{2}J_{\text{P-C}}$ = 4.3, 62 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ 17.48 ($^{1}J_{\text{Pt-P}}$ = 3030 Hz, $^{2}J_{\text{P-P}}$ = 32 Hz), 12.68 ($^{1}J_{\text{Pt-P}}$ = 1641 Hz, $^{2}J_{\text{P-P}}$ = 32 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): δ -14.7. IR: (CH_2Cl_2) ν_{CO} = 2091 cm^{-1}.

[(p-MeOPh)$_2$B{$CH_2P(p\text{-}{}^tBuPh)_2$}$_2$]Pt(Me)(CO) (3.19). Following General Method B.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5 (b, 4H), 7.1 (m, 8H), 6.91 (m, 4H), 6.67 (d, 4H), 6.28 (d, 4H), 3.57 (s, 6H), 1.98 (br, 2H), 1.93 (br, 2H), 1.23 (s, 36H), 0.35 (dd, 3H, Pt(C*H*$_3$), $^{2}J_{\text{Pt-H}}$ = 58 Hz, $^{3}J_{\text{P-H}}$ = 5.7, 5.7 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 180.8 (dd, Pt-*C*O, $^{2}J_{\text{P-C}}$ = 130 Hz, $^{1}J_{\text{Pt-C}}$ = 1278 Hz), 163.0 (q, $^{1}J_{\text{C-B}}$ = 51 Hz), 153.4, 153.1, 133.3 (m), 132.9, 132.3 (m), 128.6, 127.2, 125.2 (d), 125.0 (d), 123.3, 112.2, 55.2, 35.0, 34.9, 31.5, 31.4, 18.8 (br), 17.4 (br), -2.5 (dd, Pt(*C*H$_3$), $^{2}J_{\text{P-C}}$ = 4.3, 62 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 17.65 ($^{1}J_{\text{Pt-P}}$ = 3034 Hz, $^{2}J_{\text{P-P}}$ = 31 Hz), 12.93 ($^{1}J_{\text{Pt-P}}$ = 1642 Hz, $^{2}J_{\text{P-P}}$ = 31 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, $CDCl_3$): δ -14.8. IR: (CH_2Cl_2) ν_{CO} = 2091 cm^{-1}.

[$Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2$]Pt(Me)(CO) (3.20). Solid [[$Ph_2B\{CH_2P(p\text{-}CF_3Ph)_2\}_2$]$PtMe_2$][ASN] (**3.9**) and [$Et_3NH$][$BPh_4$] were dissolved in THF (2 mL). After 15 min, the cloudy mixture was filtered into a J. Young NMR tube and placed under reduced pressure. An atmosphere of CO was introduced to the tube. The reaction was heated at 55 ºC for 4 h, after which $^{31}P\{^1H\}$ NMR spectroscopic analysis verified that the reaction had gone to completion. Volatiles were removed under reduced pressure. Dissolution in benzene (2 mL), filtration, and removal of volatiles under reduced pressure provided **3.20**.

^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 6H), 7.39 (m, 8H), 6.81 (m, 12H), 2.23 (m, 4H), 0.53 (t, 3H, Pt(CH_3), $^2J_{Pt\text{-}H}$ = 57 Hz, $^3J_{P\text{-}H}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 179.5 (dd, Pt(CO), $^2J_{P\text{-}C}$ = 7.3, 132 Hz, $^1J_{Pt\text{-}C}$ = 1296 Hz), 160 (br m), 139.7, 139.3, 133.7 (d), 132.7 (d), 131.8, 127.0, 125.5 (m), 125.2 (m), 123.4, 18.3 (br), 16.3 (br), -1.9 (dd, Pt(CH$_3$), $^1J_{Pt\text{-}C}$ = 408 Hz, $^2J_{P\text{-}C}$ = 4.1, 61 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, $CDCl_3$): δ -64.0, -64.1. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.85 ($^1J_{Pt\text{-}P}$ = 3090 Hz, $^2J_{P\text{-}P}$ = 32 Hz), 16.84 ($^1J_{Pt\text{-}P}$ = 1616 Hz, $^2J_{P\text{-}P}$ = 32 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ -14.3. IR: (CH_2Cl_2) ν_{CO} = 2105 cm^{-1}.

$[Ph_2B(CH_2P^iPr_2)_2]Pt(Me)(CO)$ (3.21). Following General Method B.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.38 (br, 4H), 7.04 (t, 4H), 6.87 (t, 2H), 2.38 (d of septet, 2H), 2.17 (d of septet, 2H), 1.53 (br m, 4H), 1.10 (dd, 12H), 1.02 (dd, 6H), 0.97 (dd, 6H), 0.79 (dd, 3H, Pt(CH_3), $^2J_{Pt\text{-}H}$ = 57 Hz, $^3J_{P\text{-}H}$ = 5.7, 4.8 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 183.1 (dd, Pt(CO), $^2J_{P\text{-}C}$ = 7, 123 Hz, $^1J_{Pt\text{-}C}$ = 1222 Hz), 164.2 (q, $^1J_{C\text{-}B}$ = 50 Hz), 132.0, 127.1, 123.2, 28.9 (m), 28.7 (m), 26.0 (m), 25.7 (m), 20.3 (m), 19.9 (m), 18.8 (m), 18.7 (m), 9.0 (br), 5.5 (br), -8.6 (dd, Pt(CH$_3$), $^1J_{Pt\text{-}C}$ = 406 Hz, $^2J_{P\text{-}C}$ = 6.2, 61 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 40.28 ($^1J_{Pt\text{-}P}$ = 1666 Hz, $^2J_{P\text{-}P}$ = 26 Hz), 30.81 ($^1J_{Pt\text{-}P}$ = 2942 Hz, $^2J_{P\text{-}P}$ = 26 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, CD_2Cl_2): δ -14.6. IR: (CH_2Cl_2) ν_{CO} = 2079 cm^{-1}.

$Ph_2Si(CH_2PPh_2)_2$ (Ph_2SiP_2, 3.22). Solid pale yellow Ph_2PCH_2Li(TMEDA) (7.1300 g, 22.119 mmol) was suspended in diethyl ether (100 mL) in a 250 mL Schlenk flask with a stirbar and a septum. The flask was cooled to -78 ºC in a dry ice/acetone bath. Separately, diphenyldichlorosilane (2.7981 g, 11.051 mmol) was dissolved in diethyl ether (10 mL) and was transferred by syringe to the cold reaction flask. The mixture was allowed to stir and warm gradually over 7 h. Volatiles were removed under reduced pressure, and the resulting solids were collected on a sintered glass frit and washed with diethyl ether (3 x 10 mL), removing yellow impurities and leaving white solids. The solids were dissolved in dichloromethane (50 mL), and the hazy solution was filtered over Celite on a sintered glass frit. Volatiles were removed under reduced pressure from the resulting clear, colorless solution, providing white solid $Ph_2Si(CH_2PPh_2)_2$ (5.2838 g, 82.3%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.46 (dd, 4H), 7.31 (m, 8H), 7.05 (m, 6H), 6.97 (m, 12H), 1.89 (s, 4H, $Ph_2Si(CH_2PPh_2)_2$). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 141.6, 136.0, 133.3, 129.8, 128.8, 128.2, 116.7, 12.4 (dd, $Ph_2Si(CH_2PPh_2)_2$, $^1J_{P\text{-}C}$ = 33 Hz, $^3J_{P\text{-}C}$ = 4.8 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ -23.29. $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-*d*$_6$): δ -22.65. $^{29}Si\{^1H\}$ NMR (99.3 MHz, THF): δ -10.42 (t, $^2J_{Si\text{-}P}$ = 17.0 Hz). Anal. Calcd. for $C_{38}H_{34}P_2Si$: C, 78.59; H, 5.90. Found: C, 78.89; H, 5.78.

(Ph_2SiP_2)$PtMe_2$ (3.24). Solid **3.22** (199.7 mg, 0.3439 mmol) and $CODPtMe_2$ (114.4 mg, 0.3432 mmol) were dissolved in THF (4 mL). After 30 min, volatiles were removed under reduced pressure. The resulting solids were triturated under petroleum ether (4 mL), and the solution was decanted. The resulting off-white solids were dried under reduced pressure, providing **3.24** (253.9 mg, 91.6%). Crystals suitable for X-ray diffraction were grown from petroleum ether vapor diffusion into a toluene solution of **3.24**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (m, 8H), 7.2-7.3 (m, 14H), 7.06 (t, 4H), 6.95 (dd, 4H), 2.29 (d, 4H, $^2J_{P\text{-}H}$ = 9.9 Hz, $^3J_{Pt\text{-}H}$ = 25 Hz), 0.31 (dd, 6H, $^3J_{P\text{-}H}$ = 8.7 Hz, $^3J_{P\text{-}H}$ = 6.3 Hz, $^2J_{Pt\text{-}H}$ = 68 Hz). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.56 (m, 8H), 7.2-7.3 (m, 14H), 7.08 (m, 8H), 2.41 (d, 4H, $^2J_{P\text{-}H}$ = 9.9 Hz, $^3J_{Pt\text{-}H}$ = 25 Hz), 0.17 (dd, 6H, $^3J_{P\text{-}H}$ = 8.1 Hz, $^3J_{P\text{-}H}$ = 6.6 Hz, $^2J_{Pt\text{-}H}$ = 69 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 135.4 (m), 134.9 (m), 134.1, 133.5 (m), 129.8, 129.4, 127.9 (m), 127.9, 10.5 (m), 5.7 (dd, $^2J_{P\text{-}C}$ = 101 Hz, $^2J_{P\text{-}C}$ = 7.9 Hz, $^1J_{Pt\text{-}C}$ = 596 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 14.35 ($^1J_{Pt\text{-}P}$ = 1822 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 12.00 ($^1J_{Pt\text{-}P}$ = 1848 Hz). $^{29}Si\{^1H\}$ NMR (99.3 MHz, THF): δ -13.57. Anal. Calcd. for $C_{40}H_{40}P_2PtSi$: C, 59.62; H, 5.00. Found: C, 59.36; H, 5.07.

$[(Ph_2SiP_2)Pt(Me)(THF)][B(C_6F_5)_4]$ (3.26). Solid white $(Ph_2SiP_2)PtMe_2$ (320.0 mg, 397.1 μmol) was dissolved in dichloromethane (2 mL) with THF (0.5 mL). Separately, $[H(OEt_2)_2][B(C_6F_5)_4]$ (324.9 mg, 397.0 μmol) was dissolved in dichloromethane (3 mL) and added slowly to the stirring solution of $(Ph_2SiP_2)PtMe_2$, evolving gas. After addition was complete, the reaction was stirred for 10 min. Volatiles were removed under reduced pressure, and the mixture was triturated and washed using petroleum ether (2 x 2 mL). The resulting white solids were dried under reduced pressure, providing off-white **3.26** (574.2 mg, 93.8%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.31 (m, 4H), 7.20 (m, 4H), 7.04 (m, 6H), 6.96 (m, 8H), 6.87 (t, 4H, J = 7.6 Hz), 6.63 (d, 4H, J = 6.7 Hz), 2.91 (m, 4H), 2.07 (d, 2H, J = 2.4 Hz), 1.19 (d, 4H, J = 12.2 Hz), 0.81 (m, 4H), 0.32 (dd, 3H, $^3J_{P\text{-}H}$ = 1.8, 7.3 Hz, $^2J_{Pt\text{-}H}$ =

41.5 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 150.2, 148.3, 140.0, 138.1, 136.2, 133.7, 132.9 (m), 132.1, 132.0, 131.7, 131.6, 130.1, 129.0 (d), 128.7 (d), 127.5, 125.2 (br), 72.3, 24.4, 12.1 (dd, $J_{Pt\text{-}C}$ = 903 Hz, $^2J_{P\text{-}C}$ =11, 59 Hz), 11.6 (m), 7.3 (m). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 26.48 (d, $^1J_{Pt\text{-}P}$ = 1808 Hz, $^2J_{P\text{-}P}$ = 15.9 Hz), 5.09 (d, $^1J_{Pt\text{-}P}$ = 4694 Hz,$^2J_{P\text{-}P}$ = 15.9 Hz), $^{19}F\{^1H\}$ NMR (282.1 MHz, C_6D_6): δ -132.2, -162.9 (t, J = 21.4 Hz), -166.5 (t, J = 17.1 Hz). Anal. Calcd. for $C_{67}H_{45}BF_{20}OP_2PtSi$: C, 52.19; H, 2.94. Found: C, 53.52; H, 2.91.

[(dppp)Pt(Me)(THF)][B(C_6F_5)$_4$] (3.27). Solid (dppp)PtMe$_2$ (155.1 mg, 243.3 μmol) was dissolved in dichloromethane (1 mL) with THF (0.5 mL). Separately, [H(OEt_2)$_2$][B(C_6F_5)$_4$] (199.0 mg, 243.2 μmol) was dissolved in dichloromethane (3 mL) and added slowly to the stirring solution of (dppp)PtMe$_2$, evolving gas. After addition was complete, the reaction was stirred for 10 min. Volatiles were removed under reduced pressure, and the mixture was triturated and washed using petroleum ether (2 x 2 mL). The resulting white solids were dried under reduced pressure, providing analytically pure **3.27** (323.1 mg, 96.7%).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.30-7.65 (20H, aryl protons), 2.65 (m, 4H), 1.92 (m, 2H), 1.28 (m, 2H), 0.86 (m, 2H), 0.42 (dd, 3H, Pt-CH_3, $^3J_{P\text{-}H}$ = 1.5, 7.0 Hz, $^2J_{Pt\text{-}H}$ = 38.0 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 149.7, 147.8, 139.8, 137.8, 135.9, 133.4 (br m), 132.6 (br m), 129.7 (br m), 127.9, 127.4, 125.0 (br m), 73.3 ((CH_2CH_2)$_2$O, $^2J_{Pt\text{-}C}$ = 96 Hz), 26.9, 25.3, 19.0, 13.4 (dd, Pt-CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 17.25 (d, $^1J_{Pt\text{-}P}$ = 1680 Hz, $^2J_{P\text{-}P}$ = 23.2 Hz), 2.28 (d, $^1J_{Pt\text{-}P}$ = 4550 Hz, $^2J_{P\text{-}P}$ = 23.2 Hz). $^{19}F\{^1H\}$ NMR (282.1 MHz, CD_2Cl_2): δ -133.6, -164.0 (t), -167.8. $^{11}B\{^1H\}$ NMR (128.3

MHz, CD_2Cl_2): δ -17.2. Anal. Calcd. for $C_{56}H_{37}BF_{20}OP_2Pt$: C, 48.96; H, 2.71. Found: C, 49.36; H, 2.77.

[(Ph_2SiP_2)Pt(Me)(CO)][B(C_6F_5)$_4$] (3.28). Solid [(Ph_2SiP_2)Pt(Me)(THF)][B(C_6F_5)$_4$] (48.2 mg, 31.3 μmol) was dissolved in dichloromethane (5 mL) in a round bottom flask containing a stirbar and sealed with a septum. The flask was purged with carbon monoxide gas for 5 min, and allowed to stir for 1 h under carbon monoxide. The flask was dried under a stream of dinitrogen. The resulting film was triturated and washed with petroleum ether (2 x 2 mL) and dried under reduced pressure, providing [(Ph_2SiP_2)Pt(Me)(CO)][B(C_6F_5)$_4$] as white solids (43.4 mg, 92.6%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.28-7.52 (m, 22H, aryl H), 7.11 (t, 4H, J = 7.5 Hz), 6.91 (d, 4H, J = 6.9 Hz), 2.51 (d, 2H, $^2J_{P\text{-}H}$ = 14.1 Hz, $^3J_{Pt\text{-}H}$ = 28.2 Hz), 2.43 (dd, 2H, J = 3.3 Hz, $^2J_{P\text{-}H}$ = 15.3 Hz, $^3J_{Pt\text{-}H}$ = 46.2 Hz), 0.62 (dd, 3H, Pt-C*H*$_3$, $^3J_{P\text{-}H}$ = 6.0 Hz, $^2J_{Pt\text{-}H}$ = 56.4 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 177.5 (dd, Pt-*C*O, $^2J_{P\text{-}C}$ = 137.9 Hz, $^2J_{P\text{-}C}$ = 8.2 Hz), 148.7 (d), 138.8 (d), 136.9 (d), 134.0, 133.8 (d), 133.2 (d), 132.6 (m), 132.5 (m), 131.0, 130.0 (d), 129.8 (d), 128.9, 127.5 (m), 126.7 (m), 9.2 (m), 7.2 (m), -1.2 (dd, Pt-*C*H$_3$, $^2J_{P\text{-}C}$ =5.2, 61.6 Hz, $^1J_{Pt\text{-}C}$ = 400 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ 10.31 (d, $^2J_{P\text{-}P}$ = 29.3 Hz, $^1J_{Pt\text{-}P}$ = 3238 Hz), 7.16 (d, $^2J_{P\text{-}P}$ = 29.3 Hz, $^1J_{Pt\text{-}P}$ = 1665 Hz). ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): δ -16.9. ^{19}F{^{1}H} NMR (282.1 MHz, CD_2Cl_2): δ -133.5, -163.9 (t), -167.7. IR: (CH_2Cl_2/KBr) ν_{CO} = 2118 cm^{-1}. Anal. Calcd. for $C_{64}H_{37}BF_{20}OP_2PtSi$: C, 51.32; H, 2.49. Found: C, 51.44; H, 2.26.

[(dppp)Pt(Me)(CO)][B(C_6F_5)$_4$] (3.29). Solid off-white [(dppp)Pt(Me)(THF)][B(C_6F_5)$_4$] (54.0 mg, 39.3 μmol) was dissolved in dichloromethane (2 mL) in a round bottom flask containing a stirbar and sealed with a septum. The flask was purged with carbon monoxide gas for 15 min, and subsequently dried under reduced pressure. The resulting film was triturated under petroleum ether (2 mL) and dried under reduced pressure, providing [(dppp)Pt(Me)(CO)][B(C_6F_5)$_4$] as a white solid (50.2 mg, 96.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.65 (20H, aryl protons), 2.69 (m, 4H), 2.17 (m, 2H), 0.76 (vt, $^3J_{P-H}$ = 6.00 Hz, $^2J_{Pt-H}$ = 57.3 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 176.9 (dd, Pt-*C*O, $^2J_{P-C}$ = 134.0 Hz, $^2J_{P-C}$ = 8.6 Hz, $^1J_{Pt-C}$ = 1320 Hz), 150.0, 146.8, 140.0, 138.1, 136.7, 134.8, 133.2, 132.7, 132.3, 129.9, 124.8, 124.0, 24.6, 24.1, 18.8, -0.9 (dd, Pt-*C*H_3, $^2J_{P-C}$ = 59.8 Hz, $^2J_{P-C}$ = 4.6 Hz, $^1J_{Pt-C}$ = 396 Hz). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -132.9 (d), -163.2 (t), -166.9 (t). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 2.32 (d, $^2J_{P-P}$ = 34.8 Hz, $^1J_{Pt-P}$ = 3126 Hz), -4.88 (d, $^2J_{P-P}$ = 34.8 Hz, $^1J_{Pt-P}$ = 1547 Hz). $^{11}B\{^1H\}$ NMR (128.3 MHz, $CDCl_3$): δ -17.1. IR: (CH_2Cl_2/KBr) ν_{CO} = 2118 cm^{-1}. Anal. Calcd. for $C_{53}H_{29}BF_{20}OP_2Pt$: C, 47.88; H, 2.20. Found: C, 47.89; H, 1.99.

[[Ph_2BP_2]Mo(CO)$_4$][ASN] (3.30). Solid Mo(CO)$_6$ (53.4 mg, 202 μmol) and solid [Ph_2BP_2][ASN] (133.0 mg, 192.8 μmol) were dissolved in THF (3 mL). The sealed vessel was placed under partial vacuum and heated to 65 ºC for 36 h. The resulting pale yellow solution was cooled to room temperature, and volatiles were removed under reduced pressure. The pale yellow solids were washed with petroleum ether (3 x 2 mL) and dried under reduced pressure, providing analytically pure [[Ph_2BP_2]Mo(CO)$_4$][ASN] (168.5 mg, 97.3%).

^{1}H NMR (300 MHz, CD_3CN): δ 7.36 (m, 8H), 7.11 (m, 12H), 6.94 (br d, 4H), 6.69 (m, 4H), 6.61 (m, 2H), 3.37 (m, 8H), 2.11 (m, 8H), 1.98 (br, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3CN): δ 220.0 (m), 213.6 (m), 166 (br), 143.6 (m), 133.6, 133.0 (m), 128.6, 128.1, 126.6, 122.6, 63.8, 23.9 (br), 22.7. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3CN): δ

29.37. $^{11}B\{^{1}H\}$ NMR (128.3 MHz, CD_3CN): δ -14.1. IR: (CH_2Cl_2/KBr) ν_{CO} = 2005, 1896, 1849 cm^{-1}. Anal. Calcd. for $C_{50}H_{50}BMoNO_4P_2$: C, 66.90; H, 5.61; N, 1.56. Found: C, 67.04; H, 5.82; N, 1.52.

$(Ph_2SiP_2)Mo(CO)_4$ (3.31). Solid $Mo(CO)_6$ (50.3 mg, 191 μmol) and solid $Ph_2Si(CH_2PPh_2)_2$ (108.2 mg, 186.3 μmol) were dissolved in THF (3 mL). The sealed vessel was placed under partial vacuum and heated to 65 ºC for 36 h. The resulting colorless solution was cooled to room temperature, and volatiles were removed under reduced pressure. The off-white solids were washed with petroleum ether (3 x 2 mL) and dried under reduced pressure, providing analytically pure $(Ph_2SiP_2)Mo(CO)_4$ (139.5 mg, 95.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (m, 8H), 7.26 (m, 12H), 7.21 (m, 2H), 7.05 (t, 4H, $J_{H\text{-}H}$ = 7.8 Hz), 6.95 (dd, 4H, $J_{H\text{-}H}$ = 1.5, 7.8 Hz), 2.29 (d, 4H, $^{2}J_{P\text{-}H}$ = 7.8 Hz). $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 215.4 (dd, Mo-*C*O, $^{2}J_{P\text{-}C}$ = 7.6, 7.6 Hz), 210.8 (t, Mo-*C*O, $^{2}J_{P\text{-}C}$ = 8.5 Hz), 139.3 (m), 134.6 (m), 134.3, 131.9 (m), 129.6, 129.5, 128.4 (m), 127.9, 13.6 (m). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): δ 23.50. IR: (CH_2Cl_2/KBr) ν_{CO} = 2018, 1922, 1896 cm^{-1}. Anal. Calcd. for $C_{42}H_{34}MoO_4P_2Si$: C, 63.96; H, 4.35. Found: C, 64.15; H, 4.09.

3.4.4. X-ray experimental information

The general X-ray experimental procedure was performed according to section 2.4.4. Crystallographic information is provided in Table 3.7.

Table 3.7. X-ray diffraction experimental details for **3.1**, **3.11·2THF**, **3.24·toluene**, and **3.25**.

	3.1	**3.11·2THF**	**3.24·toluene**	**3.25**
CCDC ID	151640	156632	198492	198491
Chemical formula	$[C_{40}H_{40}BP_2Pt]$ $[N(C_4H_8)_2]$	$C_{43}H_{45}P_2Pt$ $\cdot\ 2(OC_4H_8)$	$C_{40}H_{40}P_2PtSi$ $\cdot\ C_7H_8$	$C_{29}H_{32}P_2Pt$
Formula weight	914.78	845.65 · 2(72.11)	805.86 · 92.14	637.58
T (ºC)	-175	-175	-175	-175
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	14.7979(6)	12.210(4)	12.4923(9)	15.4697(10)
b (Å)	15.9490(7)	12.803(4)	21.3358(16)	16.0349(10)
c (Å)	17.6093(7)	16.205(5)	14.6898(11)	20.7479(13)
α (º)	90	109.614(5)	90	90
β (º)	91.488(1)	104.361(5)	90.021(1)	90
γ (º)	90	96.489(5)	90	90
V (Å^3)	4154.6(3)	2257.6(12)	3915.3(5)	5146.6(6)
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
Z	4	2	4	8
D_{calcd} (g cm^{-3})	1.462	1.456	1.523	1.646
μ (cm^{-1})	34.88	32.20	37.29	55.92
$R1$, $wR2$ ($I>2\sigma(I)$)	0.0273, 0.0514	0.0422, 0.0789	0.0272, 0.0546	0.0203, 0.0446

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

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