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CO Binding

The Coordination Chemistry of Pentafluorophenylphosphino Pincer Ligands to Platinum and Palladium

Bradley G. Anderson* and John L. Spencer[a]

Abstract: The synthesis of electron-poor PCP pincer ligands 1,3-$((C_6F_5)_2PO)_2C_6H_4$, 1,3-$((C_6F_5)_2PCH_2)_2C_6H_4$, and 1-$((C_6F_5)_2PO)$-3-$(t\mathrm{Bu}_2PCH_2)C_6H_4$, and their coordination chemistry to platinum and palladium is described. The most electron-poor ligand 1,3-$((C_6F_5)_2PO)_2C_6H_4$ (POCOPH) reacts with Group 10 metal chloride precursors to form a range of unusual *cis*, *trans*-dimers of the type κ^2-P,P-[(POCOPH)MCl(L)]$_2$ (M = Pt, Pd; L = Cl, Me), which undergo metallation to form [(POCOP)MCl] pincer complexes only under prolonged thermolysis. The formation of such *cis*,*trans*-dimers during pincer complex formation can be mitigated through the use of starting materials with more strongly binding ancillary ligands, improving the overall rate of ligand metallation. Carbonyl complexes of the type $[(\mathrm{PCP})M(CO)]^+$ were synthesised from the pincer chloride complexes by halide abstraction, and displayed large ν(C–O) values, from 2170–2111 cm^{-1}, confirming the electron-poor nature of the compounds. The $[(\mathrm{PCP})Pd(CO)]^+$ complexes also demonstrated the ability to reversibly bind carbon monoxide both in solution and the solid state, with the rate of decarbonylation increasing with increasing wavenumber for the C–O stretch.

Introduction

Over recent years, the pincer ligand motif has become an increasing popular design for synthetic chemists. Their planar, tridentate coordination geometry confers upon them high stability, whereas the ability to incorporate different functionalities while possessing the same general structure allows for substantial variety within the pincer ligand class.[1] These ligands have been employed with great success in catalysis; pincer complexes of ruthenium and iridium excel in acceptorless dehydrogenation,[2] and are at the forefront of research into alkane metathesis.[3] Pincer complexes of Group 10 metals, especially those of palladium, are also effective catalysts for the allylation of electrophiles, and cross-coupling reactions.[4]

Much of the research involving transition metal pincer complexes has utilised very electron-rich, strongly donating ligands, such as di-*tert*-butyl phosphines, along with the phosphorus-carbon-phosphorus (PCP) coordination motif. The use of poorly donating pincer ligands has so far been sparse, but has revealed that electron-poor pincer ligands in some cases possess a vastly different coordination chemistry to that of their more electron-rich analogues.[5] The electronic character of the pincer ligand also affects the reactivity and catalytic activity of these compounds. An electron-poor iridium pincer complex has displayed the ability to undergo ligand exchange and catalytic hydrogenation within a single crystal,[6] while catalysts with poorly donating ligands have demonstrated high activities in a variety of addition reactions.[7] The choice of electron-withdrawing group on the donor atoms can also impart other beneficial properties to the resultant complexes; for example, the presence of pentafluorophenylphosphino groups can dramatically increase solubility in supercritical CO_2, a property useful for “green” chemistry.[8] Thus, we aimed to synthesise a range of PCP pincer ligands bearing $P(C_6F_5)_2$ donor groups, and assess how their electronic nature affected their coordination chemistry, as well as the properties of the resultant pincer complexes.

Herein, we report the synthesis of the poorly donating PCP pincer ligands 1,3-$((C_6F_5)_2PO)_2C_6H_4$ (POCOPH, **1a**), 1,3-$((C_6F_5)_2PCH_2)_2C_6H_4$ (PCCCPH, **1b**), and 1-$((C_6F_5)_2PO)$-3-$(t\mathrm{Bu}_2PCH_2)C_6H_4$ (POCCPH, **1c**), and their coordination chemistry to platinum and palladium metal centres. Owing to the difficulty in metallating ligands **1a**–**1c**, we observed the formation of a range of dimeric structures with κ^2-P,P bridging ligands, and isolated a number of rare examples of *cis*,*trans*-dimers. Prolonged thermolysis of these *cis*,*trans*-dimers yielded metallated PCP pincer complexes; however, metallation could be made significantly more facile by choosing ancillary ligands that disfavoured dimer formation. We also describe the synthesis of the platinum and palladium carbonyl complexes of metallated ligands **1a**–**1c**, and report facile, reversible carbon monoxide coordination to the electron-poor palladium metal centres.

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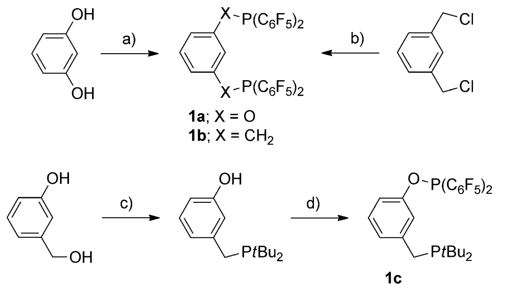


Scheme 1. Synthesis of the pincer ligands **1 a**–**1 c**. Reagents and conditions: a) NEt_3, Et_2O; $(C_6F_5)_2PBr$, Et_2O, 0 °C–RT; b) $[Mg(anth)(THF)_3]$, THF; $(C_6F_5)_2PBr$, THF, −78 °C–RT; c) PBr_3, THF/CH_2Cl_2, 0 °C–RT; HP*t*Bu$_2$, acetone, reflux; NEt_3, Et_2O; d) NEt_3, THF; $(C_6F_5)_2PBr$, THF, 0 °C–RT.

Results and Discussion

Synthesis of pincer ligands 1 a–1 c

The synthesis of pincer ligands **1 a**–**1 c** is summarised in Scheme 1. These ligands were chosen as synthetic targets as they offered a series of electron-poor ligands with similar steric bulk, which varied slightly in electronic character. We were also particularly interested the configuration of **1 c**, as it would possess mutually *trans* electron-donating and electron-withdrawing donors once metallated. Moreover, the formation of bis(pentafluorophenyl)phosphinito donors (such as in **1 a** and **1 c**) was desirable from a synthetic perspective, as the synthesis of fluoroarylphosphine ligands can often be more difficult than for the corresponding arylphosphine or alkylphosphine analogues.[9] Therefore, by connecting the $P(C_6F_5)_2$ moiety to the ligand backbone with a phosphinite linkage, this synthetic difficulty could be circumvented.

The synthesis of the POCOPH ligand **1 a** was carried out by the treatment of the phosphine halide $(C_6F_5)_2PBr$ with resorcinol, as is typical for the formation of phosphinite compounds.[4c] Ligand **1 a** was isolated as a white solid, and displayed a quintet in the ^{31}P NMR spectrum at 87.1 ppm ($^3J_{P-F} = 35.0$ Hz).

The PCCCPH ligand **1 b** has previously been prepared by the treatment of $(C_6F_5)_2PBr$ with the bis-Grignard reagent 1,3-$(ClMgCH_2)_2C_6H_4$.[10] In replicating this procedure, the preparation of the Grignard reagent was found to be difficult and unreliable; however, using $[Mg(anthracene)(THF)_3]$[11] to generate the bis-Grignard reagent resulted in consistently greater yields of PCCCPH than for reactions in which the Grignard reagent was generated using activated magnesium turnings. Purification of the reaction mixture by column chromatography in air afforded **1 b** as a white solid ($\delta = -46.3$ ppm), which was observed to oxidise only gradually under ambient conditions.

The unsymmetrical POCCPH pincer ligand **1 c** was prepared in a similar manner to that of the two previously published examples of phosphine-phosphinite pincer ligands.[12] The P*t*Bu$_2$ moiety was first installed by nucleophilic attack of di-*tert*-butylphosphine at the benzylic carbon of 3-hydroxybenzyl bromide, followed by formation of the phosphinite P–O linkage by treatment of the phenol functionality with $(C_6F_5)_2PBr$, in an almost identical manner to the synthesis of **1 a**. Ligand **1 c** was isolated as a pale yellow oil, which solidified into a cream-coloured solid on cooling to −15°. The ^{31}P NMR spectrum of **1 c** displayed a quintet for the pentafluorophenyl phosphinite moiety at 82.9 ppm ($^3J_{P-F} = 35.5$ Hz), and a singlet for the di-*tert*-butyl phosphine group at 34.3 ppm.

Ligands **1 a** and **1 c** represent the only incorporation of the bis(pentafluorophenyl)phosphinite moiety into the pincer ligand framework to date.

Formation of dimeric metal complexes

Coordination chemistry of the most electron-poor ligand, POCOPH ligand **1 a**, was initially explored with platinum(0). There have been no reports on the reaction of PCP pincer ligands with Pt^0 precursors. We were interested both in the coordination mode of the electron-poor ligand **1 a** with Pt^0 metal centres, and whether the species formed could be forced to oxidatively add the C–H bond at C-2 of the ligand backbone to form a metallated κ^3-PCP pincer complex.

Reactions between **1 a** and $[Pt(nb)_3]$ (where nb = norbornene) produced predominantly the κ^2-P,P-bridged dimer, $[(POCOPH)Pt(nb)]_2$ (**2**), along with minor amounts of a spectroscopically similar product, presumed to be a higher oligomer on the basis of its low solubility in common solvents. The ^{31}P NMR data of **2** revealed one phosphorus environment, with a large Pt–P coupling constant indicative of phosphorus coordination *trans* to the norbornene ($\delta = 100.5$ ppm, $^1J_{Pt-P} = 4623$ Hz). Compound **2** was confirmed as a dimer by high resolution mass spectrometry (HRMS), with $[M-nb+Na]^+$ observed at *m/z* 2087 amu. Attempts to promote oxidative addition of the ligand backbone to produce the pincer species [(POCOP)PtR] (where R = norbornyl or H) by thermolysis, protonolysis, or by treatment of **2** with base were all unsuccessful.

Crystals of **2** suitable for single crystal X-ray diffraction were grown from a dichloromethane solution layered with methanol. The structure revealed two trigonal planar platinum cores, bridged by two POCOPH ligands in a *cis*-κ^2-P,P fashion, with the norbornene bound "in-plane" in a conventional η^2 manner (Figure 1). When compared to other structures possessing the $[P_2Pt(nb)]$ coordination motif,[13] **2** displays a slightly shortened norbornene C=C bond (1.434(3) Å, compared to 1.460(11) and 1.469(8) Å for reported structures), and slightly elongated Pt–C bond (average of 2.146(4) Å, compared to 2.109(15) and 2.113(10) Å). This can be seen as a consequence of the poorly donating $P(C_6F_5)_2$ substituents reducing the amount of metal–norbornene π-backbonding that can occur, leading to a more weakly bound norbornene ligand when compared to structures with more electron-donating phosphine substituents. The ^{13}C NMR spectrum of **2** also supports the notion of a weakened metal–norbornene interaction, displaying a $^1J_{Pt-C}$ coupling of 259 Hz, significantly lower than the corresponding value of 344 Hz reported for the *tert*-butyl-substituted compound [(dtbpe)Pt(nb)] (where dtbpe = *t*Bu$_2$PCH$_2$CH$_2$P*t*Bu$_2$).[13b]

The solid-state structure of **2** also displays a folding of the aryl backbones to generate favourable "parallel displaced" π–π interactions[14] (interplanar angle = 0.0°, interatomic distance = 3.321(3) Å). This is somewhat unusual, as all similar *cis*-dimers

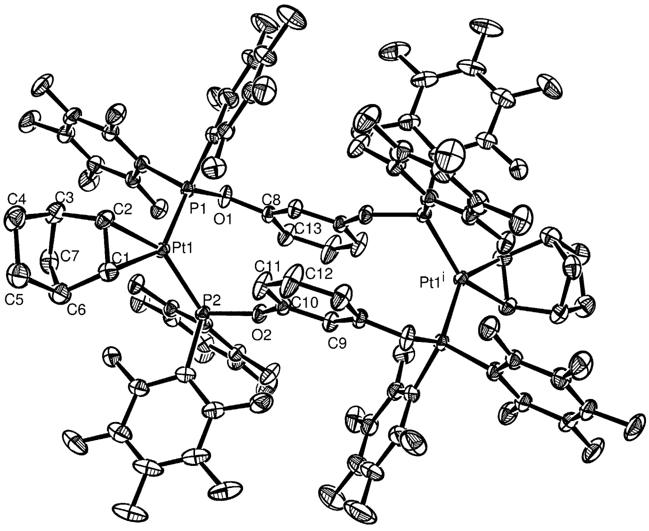


Figure 1. Crystal structure of $[(POCOPH)Pt(nb)]_2$ (**2**), with 50 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Atoms denoted by the superscripted "i" are generated from the asymmetric unit by inversion. Selected bond lengths [Å] and angles [°]: Pt1–C1, 2.153(2); Pt1–C2, 2.139(2); Pt1–P1, 2.110(6); Pt1–P2, 2.2224(5); C1–C2, 1.434(3); P1-Pt1-P2, 108.04(2).

reported have aromatic backbones canted towards each other by at least 18.6°, with the degree of canting seemingly independent of the steric bulk of the phosphorus donor.[15] The presence of π–π interactions in **2** may confer additional stability to the dimeric structure, and account for the observation that oligomeric species initially present in reaction mixtures appeared to rearrange to form the dimer **2** over time.

The coordination chemistry of ligand **1 a** with $[PtMe_2(hex)]$ (where hex = 1,5-hexadiene) was also explored, with reactions at room temperature yielding mixtures of the dimer *cis*-$[(POCOPH)PtMe_2]_2$ (**3**), and a higher oligomer *cis*-$[(POCOPH)PtMe_2]_x$ (**4**). Unlike many similar oligomeric species, **4** was sufficiently soluble in CD_2Cl_2 for spectroscopic data to be obtained. Compounds **3** and **4** possessed similar ^{31}P NMR spectra, with small Pt–P coupling values indicating coordination of phosphorus *trans* to the methyl groups (**3**, $\delta = 89.9$ ppm, $^1J_{Pt-P} = 2202$ Hz; **4**, $\delta = 90.9$ ppm, $^1J_{Pt-P} = 2150$ Hz). HRMS confirmed that **3** was dimeric, with the $[M+Na]^+$ ion observed at m/z 2147 amu. The nuclearity of **4** could not be determined by HRMS or LC-HRMS, but was assumed to be a higher oligomer ($x > 2$) on the basis of its lower solubility than **3**. As was observed for reactions with $[Pt(nb)_3]$, longer reaction times in toluene (rather than dichloromethane) favoured the formation of the dimer **3** over the oligomer **4**. Proton NMR spectroscopy indicated the π-stacking present in the crystal structure of **2** also occurs in solution: the proton environment H2 of dimers **2** and **3** appeared at about $\delta = 6.4$ ppm in $[D_6]$acetone, significantly upfield from that of the oligomer **4** ($\delta = 7.1$ ppm), which is unable to display π-stacking of ligand backbones (Figure 2). Similar shielding of aromatic protons by π-stacking has been observed for organic compounds,[16] and in this instance the shielding of H2 allows for ready discrimination between dimeric and oligomeric products. As for **2**, subjecting **3** and **4** to thermolysis did not yield significant quantities of the desired [(PCP)PtMe] pincer complexes.

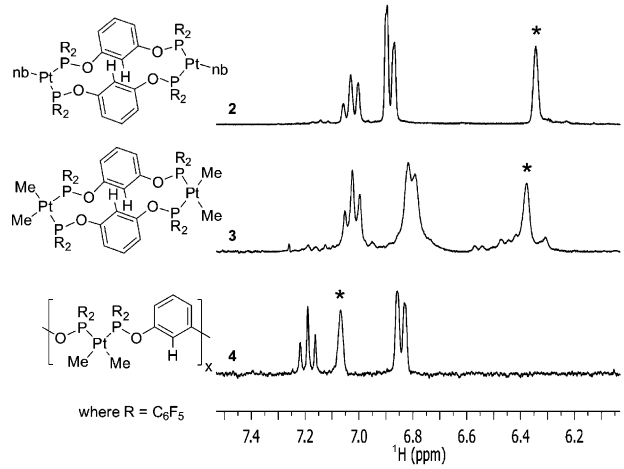
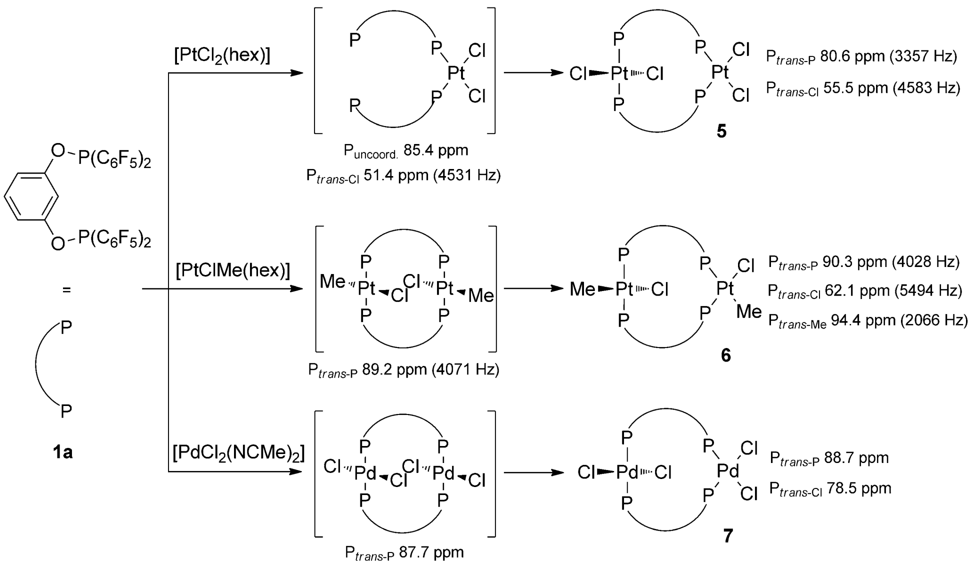


Figure 2. ^1H NMR spectra showing the effect of π–π interactions on the chemical shift of the H2 proton environment of compounds **2**, **3**, and **4** in $[D_6]$acetone.

Owing to the failure of $[Pt(nb)_3]$ and $[PtMe_2(hex)]$ to generate compounds that served as precursors to pincer complexes, reactions with metal chloride precursors were examined, as these have been shown to readily afford pincer complexes.[17] Reactions between **1 a** and $[PtCl_2(hex)]$, [PtClMe(hex)], and $[PdCl_2(NCMe)_2]$, at low temperatures all yielded unusual κ^2-P,P-bridged dimers possessing one *cis*-coordinated metal centre and one *trans*-coordinated metal centre. This coordination motif is very rare; only a handful of *cis*,*trans*-dimers have been reported to date.[18]

These *cis*,*trans*-dimers were found to be the thermodynamic product in each of the reactions, with in situ monitoring by NMR spectroscopy revealing the formation of an initial coordination complex, then rearrangement or further reaction to give the *cis*,*trans*-dimer (Scheme 2). None of the transient intermediate species was isolated, and structures have been tentatively proposed on the basis of ^{31}P NMR data (Scheme 2). The initial formation of a *cis*-species for the reaction with $[PtCl_2(hex)]$ was likely due a mutually *trans*-coordination being disfavoured for the π-accepting phosphinite groups, due to antisymbiotic effects.[19] The P-*trans*-P coordination was then observed in the initial products of the [PtClMe(hex)] and $[PdCl_2(NCMe)_2]$ reactions due to the preference of the methyl group (with a strong *trans*-influence) to coordinate *trans* to the group with the weakest *trans*-influence (the chloride), and also due to the greater ionic character of metal–ligand bonding on palladium disfavouring *cis*-dichloride compounds due to electrostatic repulsion.[20]

The complexes *cis*,*trans*-$[(POCOPH)PtCl_2]_2$ (**5**), *cis*,*trans*-$[(POCOPH)PtMeCl]_2$ (**6**), and *cis*,*trans*-$[(POCOPH)PdCl_2]_2$ (**7**), were all confirmed as dimers by HRMS, and displayed similar NMR spectra to each other. The mutually *trans* phosphorus environment of the compounds appeared at a ^{31}P chemical shift close to that of the free ligand **1 a**, at $\delta = 80.6$, 90.3, and 88.7 ppm for **5**, **6**, and **7**, respectively, and displayed Pt–P coupling con-



Scheme 2. Reaction between ligand **1a** and metal chloride precursors led to the formation of *cis*,*trans*-dimers **5**–**7**. In each reaction a transient intermediate species was observed, for which structures have been proposed on the basis of the ^{31}P NMR spectroscopy data shown. Numbers in brackets are $^{1}J_{\text{Pt-P}}$ values.

sistent with mutually *trans* phosphorus donors ($^{1}J_{\text{Pt-P}}=3357$ Hz for **5**, 4028 Hz for **6**). The phosphorus environment *trans* to a chloride was shifted significantly upfield for each compound, and appeared at $\delta=55.5$, 62.1, and 78.5 ppm, respectively, with large Pt–P coupling values signifying coordination of the phosphorus *trans* to the low *trans*-influence chloride ($^{1}J_{\text{Pt-P}}=4582$ Hz for **5**, 5494 Hz for **6**). The phosphorus coordinated *trans* to the methyl group in **6** appeared at $\delta=94.4$ ppm with a $^{1}J_{\text{Pt-P}}=2066$ Hz, spectroscopically similar to the phosphorus environments in the PtMe$_2$ *cis*-dimer **3** ($\delta=89.9$ ppm, $^{1}J_{\text{Pt-P}}=2066$ Hz). In this instance, $^{1}J_{\text{Pt-P}}$ coupling values were extremely useful in establishing the coordination geometry around each metal centre, with the palladium compound **7** assigned by analogy to the platinum compounds **5** and **6**. The structures of these *cis*,*trans*-dimers were confirmed by ^{1}H,^{31}P HMBC experiments, which established the connectivity of each of the phosphorus donors to the aromatic ligand backbone. Conventional ^{1}H,^{13}C HSQC and HMBC experiments were then used to establish the connectivity around the ligand backbone, and confirmed that both the *cis*- and *trans*-coordinated donors were in the same compound.

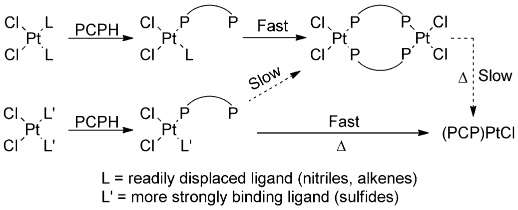
The preference of platinum and palladium dimers of the type [(POCOPH)M(L)$_2$]$_2$ to adopt a stable *cis*,*trans* configuration is interesting, especially considering that **5**, **6**, and **7** represent complexes both with and without a strongly *trans*-directing methyl group, and are able to rearrange to form these asymmetric dimers from both *cis* and *trans* complexes. For coordination complexes of the phosphinite ligand **1a** the *cis*,*trans*-dimeric structure must offer a balance between antisymbiotic and electrostatic effects that is energetically favourable for all compounds, despite the differences in metal centre and ancillary ligand. It may be pertinent to note that all *cis*,*trans*-dimers reported to date possess at least one diphenyl pnictogen donor;[18] as aryl substitution decreases the σ-donor ability of pnictogens,[21] poorly donating ligands may assist in the rearrangement to form *cis*,*trans*-dimers from the initial kinetic products formed in reaction mixtures.

Toluene solutions of *cis*,*trans*-dimers **5**, **6**, and **7** underwent thermolysis to cleanly produce the desired [(PCP)MCl] pincer compounds. This phenomenon has not been widely reported: examples of dimers undergoing metallation possess either ligands that favour metallation (through steric bulk[15c] or internal base functionality[22]), or poorly donating ligands that may be susceptible to rearrangement to configurations from which metallation is facile.[15a] Where the ligands do not aid metallation, dimers have been obtained as relatively inert by-products formed during the attempted synthesis of pincer compounds.[15b,23]

Synthesis of PCP pincer complexes 8a–8c, 9a–9c

From investigation of the coordination chemistry of **1a** with platinum and palladium starting materials, it was clear that the metal chloride starting materials offered the most successful route to the metallated pincer complex. Ligand metallation studies were performed with **1a** and [PtCl$_2$(hex)], [PtCl$_2$(COD)] (where COD = 1,5-cyclooctadiene), and [PtCl$_2$(SEt$_2$)$_2$] to investigate the effect of the ancillary ligand on both dimer and pincer complex formation. After 120 h at reflux in toluene, NMR spectroscopy revealed that the [PtCl$_2$(SEt$_2$)$_2$] reaction was complete, the [PtCl$_2$(COD)] reaction contained approximately 75% product, and the [PtCl$_2$(hex)] reaction contained approximately 50% metallated product. In situ NMR studies of the metallation reaction revealed that the dimeric intermediate **5** was formed more slowly and in smaller quantities for the faster reactions. This indicated that the ancillary ligand had a significant effect on the rate of reaction, with the order of reactivity being SEt$_2$ > COD > hexadiene. This reactivity series also correlated well with the binding strength of S-donors and alkenes on platinum.[24] Competitive displacement reactions between [PtCl$_2$(COD)] and SEt$_2$, and [PtCl$_2$(SEt$_2$)$_2$] and COD were performed, and qualitatively confirmed that SEt$_2$ was more effective at displacing COD than COD was at displacing SEt$_2$. However, exact data were difficult to obtain owing to the low solubility of [PtCl$_2$(COD)] in [D$_6$]benzene.

Strongly binding ancillary ligands are likely to aid the metallation reaction by stabilising κ^1-[(POCOPH)PtCl$_2$L] intermediate species, with more strongly binding ligands displaced from the metal centre at temperatures closer to those required for metallation, minimising the build-up of dimer in solution



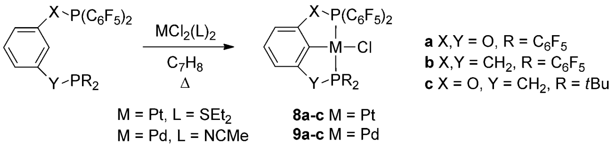
Scheme 3. Effect of ancillary ligand binding strength on dimer formation. Ligands that are more readily displaced from the κ^1-[(PCPH)$PtCl_2$(L)] intermediate will favour dimer formation (top), while less readily displaced ligands will favour monomer formation (bottom). Ligand metallation to form the pincer complex is more facile from the monomer than the dimer.

(Scheme 3). Dimeric species, such as **5**, hinder the metallation reaction; since metallation is unlikely to occur readily from a dimeric configuration, additional energy is required to rearrange from the thermodynamically stable dimer into an arrangement from which metallation can readily occur. The formation of dimeric/oligomeric species during pincer complex synthesis is less problematic when using ligands with fluoro-alkyl or -aryl phosphine donors, as such ligands will have a lower energy barrier to rearrangement than ligands with more basic phosphine donors. This has been reported in the literature, as starting materials with strongly binding PPh_3 ligands have resulted in greater yields of pincer complex and less oligomer formation than reactions proceeding from MX_2 or [MX_2(nitrile)$_2$] precursors.[25] Although the ancillary ligand effect has been little discussed and often overlooked, by choosing starting materials with less readily displaced ancillary ligands, oligomer/dimer formation can be minimised, while pincer complex formation can be made more facile.

Preliminary investigations into the effect of concentration on the reactivity of the κ^1-[(POCOPH)$PtCl_2$(SEt_2)] intermediate show that it does not react significantly faster when the concentration is doubled. While it may be anticipated that concentration would play a greater role, the coordination of the $P(C_6F_5)_2$ moiety likely increases the affinity of the metal centre for the remaining SEt_2 ligand, making any dimerisation dependent on SEt_2 dissociation rather than the availability of uncoordinated phosphinite donors in solution.

The nature of the ionic ligand on the metal precursor has a large effect on the ease of pincer complex formation; the use of a platinum starting material with an internal base has been shown to significantly lower the temperatures required for ligand metallation.[26] However, such starting materials are more difficult to prepare than [$PtCl_2(L)_n$] complexes. The methyl chloride precursor [PtClMe(COD)] has been used to good effect for the synthesis of [(PCP)PtCl] complexes,[15a, 17a] and we found that in reactions with **1 a**, [PtClMe(hex)] produced the desired pincer complex in less than half the time required when using dichloride precursor [$PtCl_2$(hex)] (48 h compared to >120 h). The efficacy of [PtClMe(hex)] as a starting material was somewhat surprising, considering that reactions between **1 a** and [$PtMe_2$(hex)] only yielded trace amounts of the desired [(PCP)PtMe] pincer complex. It is possible that in these reactions the chloride assists with proton transfer from the C–H bond being cleaved on to the leaving group, as Albrecht has published a crystal structure of a *trans*-κ^2-P,P-[(PCPH)PtCl(L)]$_2$ species in which the chloride ligands interact strongly with the proton on C-2 of the ligand backbone, resulting in a weakened C–H bond.[22] Such H···Cl interactions have also been calculated to be favourable in the breaking of C–H bonds in Shilov reactions.[27]

The effect of the ligand on the metallation reaction was also evaluated. The rate of ligand metallation was observed to increase as the phosphine donors became more basic. In reactions with [$PdCl_2$(NCMe)$_2$] at reflux in toluene, metallation of the phosphinite ligand **1 a** was complete after 80 h, whereas metallation of the phosphine ligand **1 b** took just 48 h. Replacing a pentafluorophenylphosphino substituent of **1 a** with a di-*tert*-butylphosphine (to give ligand **1 c**) allowed complete metallation after just 20 h. This is consistent with a recent study of nickellation rates with PCP pincer ligands, in which more electron-rich ligands were observed to metallate much more readily than electron-poor ligands.[28] Reactions between ligands **1 a**–**1 c** and platinum and palladium precursors gave the [(PCP)MCl] pincer complexes **8 a**–**8 c** and **9 a**–**9 c** in moderate to good yields (Scheme 4).

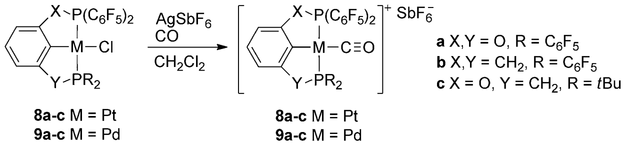


Scheme 4. Synthesis of [(PCP)MCl] complexes.

The NMR spectra of complexes **8 a**–**8 c** and **9 a**–**9 c** were all consistent with the formation of tridentate pincer complexes; ^{31}P NMR spectra displayed signals shifted downfield from those of the free ligand and unmetallated intermediates, consistent with deshielding of the phosphorus atoms upon coordination to the metal centre, followed by the loss of an electron-rich chloride from the metal centre upon metallation. The $^1J_{Pt-P}$ values for **8 a**, **8 b**, and **8 c** ranged from 3088 to 3663 Hz, indicative of mutually *trans*-coordinated phosphorus donors. Complexes **8 c** and **9 c**, possessing the asymmetric POCCP ligand **1 c**, displayed large $^2J_{P-P}$ values (460–470 Hz), significantly greater than the 388 Hz reported for a similar POCCP pincer complex,[12a] suggesting the mutually *trans* arrangement of donating and accepting ligands may provide a synergy that strengthens the phosphorus–phosphorus coupling interaction. The loss of a signal for the H2 proton environment was also evident in the ^{1}H NMR spectra of all compounds.

Synthesis and reactions of pincer carbonyl complexes 10 a–10 c, 11 a–11 c

To quantify the electronic effect of ligands **1 a**, **1 b**, and **1 c** on the metal centre, carbonyl complexes **10 a**–**10 c**, **11 a**–**11 c** were prepared from the parent pincer chloride complexes **8 a**–**8 c**, **9 a**–**9 c** by chloride abstraction with $AgSbF_6$ followed by treatment with CO (Scheme 5). As expected, the observed magni-



Scheme 5. Synthesis of $[(PCP)M(CO)]^+$ complexes.

Table 1. Spectroscopic data for carbonyl complexes **10a**–**10c**, **11a**–**11c**.

Compound	ν(C–O) [cm^{-1}]	^{13}C δ(CO) (ppm)[a]	^{19}F $\Delta\delta_{m,p}$ (ppm)[b]
10a	2145	177.5	15.8
10b	2127	180.6[c]	13.3
10c	2111	180.1	13.8
11a	2170	176.0	15.1
11b	2148	177.9	13.4
11c	2140	179.7	13.9

[a] Recorded in [D$_2$]dichloromethane. [b] Values are for the [(PCP)MCl] compounds, to reflect that $\Delta\delta_{m,p}$ values may be used in lieu of carbonyl C–O stretches. [c] Recorded in [D$_6$]acetone.

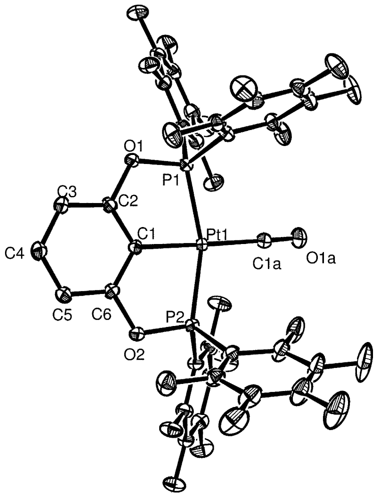


Figure 3. Crystal structure of $[(POCOP)Pt(CO)][SbF_6]$ (**10a**), with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1, 2.2748(6); Pt1–P2, 2.22829(6); Pt1–C1, 2.008(2); Pt1–C1a, 1.962(2); C1a–O1a, 1.117(3); P1-Pt1-P2, 157.73(2); C1-Pt1-C1a, 178.72(9); Pt1-C1a-O1a, 179.2(2).

tude of ν(C–O) followed the pattern POCOP > PCCCP > POCCP; the enhanced π-acceptor ability of the phosphinite POCOP generated the most electron-poor metal centres, while the strong σ-donor ability of the *tert*-butyl phosphine in POCCP resulted in the most electron-rich metal centres (Table 1). Of note is that ν(C–O) values for compounds **10a**, **11a**, and **11b** were greater than that of free CO (2143 cm^{-1}), suggesting that negligible M–CO π-backbonding is present in these carbonyl complexes.[29]

Compounds **10a**, **11a**, and **11b** all possess ν(C–O) values higher than for any previously reported pincer complex, (2141 cm^{-1} for a $[(POCOP)Pd(CO)]^+$ complex,[30] and 2143 cm^{-1} for a $[(PCCCP)Pt(CO)]^+$ complex),[15a] and are close to the 2174 cm^{-1} reported for the highly electrophilic $[(dfepe)Pt(Me)(CO)]^+$ (where dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$).[31] As expected the chemical shift of the carbonyl carbon in the ^{13}C NMR spectra of **10a**–**10c** and **11a**–**11c** is in broad agreement with the corresponding C–O stretching frequency; the greater the C–O stretching frequency the less electron density removed from the C–O bond by back-donation to the metal, and so the more shielded (and further upfield) the resonance in the ^{13}C NMR spectrum. A further measure of electronic character for pentafluorophenyl-containing compounds is $\Delta\delta_{m,p}$, the chemical shift difference between *meta* and *para* fluorine environments on the pentafluorophenyl ring.[10,32] This parameter has been proposed as an approximation of the electronic character of the phosphorus donor, and therefore may be able to provide insight into the electronic nature of these complexes without having to synthesise the carbonyl derivatives. However, for the platinum and palladium pincer complexes the $\Delta\delta_{m,p}$ values of the [(PCP)MCl] complexes do not correlate well with the observed ν(C–O) values of the carbonyl analogues (Table 1).

Single crystals of **10a** suitable for single crystal X-ray diffraction were grown by slow evaporation from a dichloromethane solution of at room temperature. Compound **10a** represents the first example of a crystallographically characterised Group 10 $[(POCOP)M(CO)]^+$ complex. The solid-state structure revealed a C-Pt-CO angle close to the expected 180° (178.72(9)°), and a P-Pt-P angle of 157.73(2)°, smaller than that commonly observed for platinum PCP pincer complexes (typically 161–168°,[15a,33] due to the steric constraints of the PCP chelate; Figure 3). The small P-Pt-P angle in **10a** was likely to be due to the electron-poor phosphorus atoms polarising and shortening the P–O bonds (average bond length of 1.607(4) Å, compared to 1.644(10) Å in a more electron-rich platinum phosphinite),[33c] resulting in more strained five-membered chelate rings. A similar effect is observed in iridium carbonyl pincer complexes.[6] The C–O and Pt–C bond lengths for the carbonyl ligand of **10a** (1.117(3) and 1.962(2) Å) were consistent with the IR data, and indicated CO coordination to an electron-poor metal centre. Similar values were reported for an electron-poor trifluoromethyl phosphine pincer compound (1.114(6), 1.964(4) Å, and 2143 cm^{-1}, respectively),[15a] with a sufficiently shorter C–O bond and longer Pt–C bond than in the more electron-rich isopropyl phosphine pincer complex (1.131(4), 1.919(3) Å, and 2080 cm^{-1}).[33e]

All of the palladium carbonyl compounds underwent gradual loss of bound carbon monoxide, as has been noted in the literature for similar palladium species.[30,34] The decarbonylated adducts of **11a**–**11c**, $[(PCP)Pd][SbF_6]$ (**12a**–**12c**) gradually formed over the course of months under ambient conditions in the solid state. Infrared spectroscopy revealed that aside from the absence of a C–O stretch, these compounds were almost identical to their parent carbonyl complexes, with the observation of Sb–F stretches (ν(Sb–F) approx. 650 cm^{-1}) suggesting the continued presence of the hexafluoroantimonate counterion in **12a**–**12c** (Figure 4).

The IR of **12b** also displayed a sharp O–H stretch at 3671 cm^{-1} (see the Supporting Information for IR spectra of

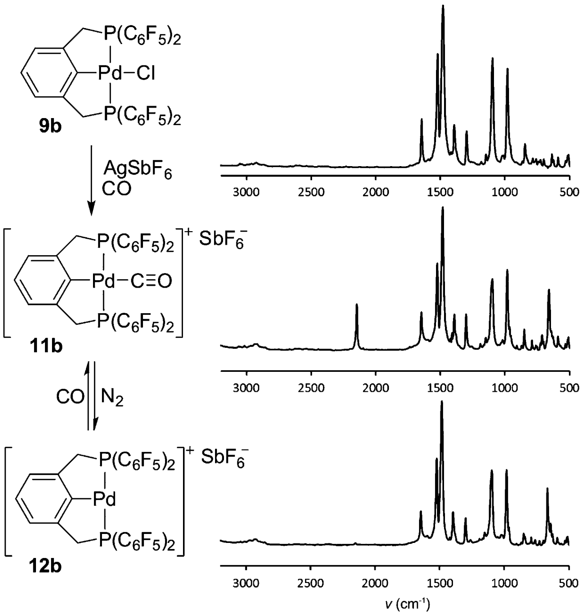


Figure 4. IR spectra showing the formation and subsequent decarbonylation of **11 b**. The C–O stretch of **11 b** appears at 2148 cm^{-1}, and Sb–F stretches are observed around 650 cm^{-1} for **11 b** and **12 b**, but not for the starting material **9 b**.

11 b and **12 b**) indicating that in the solid state adventitious water had replaced the CO on the palladium centre. However, for solutions of **12 b** in CD_2Cl_2 NMR spectroscopy revealed no indication of water coordination to the palladium, or of C–F···Pd interactions from the pentafluorophenyl substituents stabilising the decarbonylated species. Synthesis of the BF_4 adduct of **12 b** from $AgBF_4$ revealed no evidence of BF_4 coordination to the metal centre in the ^{19}F NMR spectrum ($\delta = -153$ ppm: values of around -160 ppm have been reported for coordinated BF_4^-),[35] making it likely that compounds **12 a**–**12 c** are stabilised by solvent coordination in solution.

Quantitative regeneration of the palladium carbonyl complexes **11 a**–**11 c** was achieved by passage of CO through CD_2Cl_2 solutions of the decarbonylated species **12 a**–**12 c** for 15 min at room temperature. This carbonylation was reversible, with the CO displaced upon passage of inert gas (Ar, N_2, or CH_4) through solution; however, decarbonylated species **12 a**–**12 c** slowly decomposed over time in solution, leading to palladium black formation.

While the exchangeable binding of small gaseous molecules (H_2, N_2, O_2, NH_3, and C_2H_4) in the solid state has previously been reported for an electron-poor PCP iridium complex,[6] carbon monoxide was unable to be displaced from the metal centre. This work, therefore, represents the first report of reversible carbon monoxide uptake for a pincer complex.

The ease of decarbonylation of each of the carbonyl complexes **12 a**–**12 c** was investigated by passage of N_2 through CD_2Cl_2 solutions of carbonyl complexes **11 a**–**11 c** for 30 min. The proportion of decarbonylated species present was then assessed by NMR spectroscopy. The ease of carbonyl displacement was in broad agreement with ν(C–O) values for **11 a**–**11 c**; the larger the C–O stretching frequency, the more readily the decarbonylation occurred (Figure 5). However, while **11 b** and **11 c** have ν(C–O) values that differ by only 8 cm^{-1} (2148 and 2140 cm^{-1}, respectively), **11 c** proved substantially harder to decarbonylate than **11 b**. This highlights the dramatic effect that the electron-rich di-*tert*-butylphosphine group has in facilitating π-backbonding and stabilising the carbonyl ligand.

Carbon monoxide-releasing molecules (CO-RMs) are of pharmaceutical significance,[36] as in vivo release of CO allows its beneficial anti-inflammatory effects to be magnified, while reducing its toxicity.[37] Whilst **11 a**–**11 c** are not suited for use as CO-RMs due to their high molecular weight and low water solubility, they indicate that the use of electron-deficient ligands may be beneficial in the design of molecules with labile CO ligands.

Conclusion

In this work, three electron-poor PCP pincer ligands **1 a**–**1 c** have been synthesised, and their coordination chemistry to platinum and palladium examined. The electronic character of ligands **1 a**–**1 c** inhibited the cyclometallation reaction to form the desired tridentate pincer complexes, instead displaying a predisposition for the formation of bimetallic, κ^2-P,P-bridged compounds. In reactions with **1 a**, three rare examples of *cis*,-*trans*-dimers were isolated (**5**–**7**), all of which underwent metallation upon prolonged thermolysis to yield the desired plati-

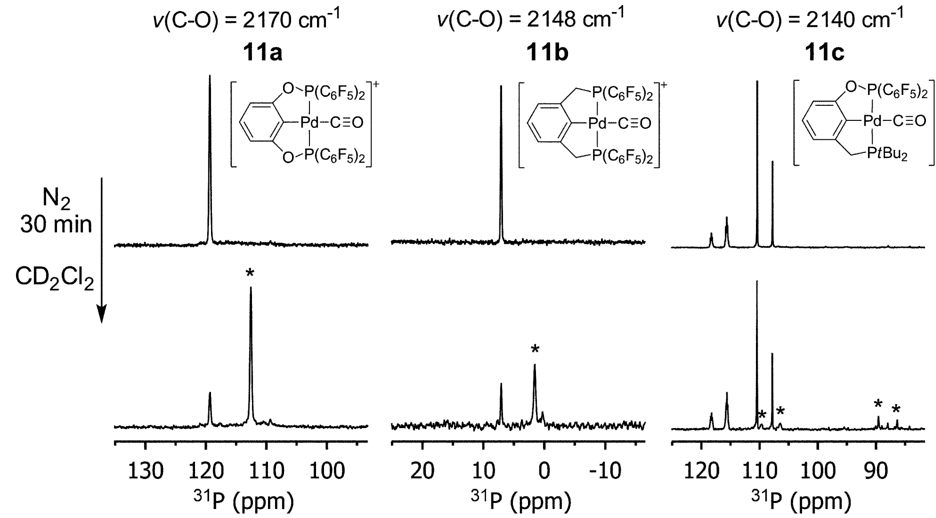


Figure 5. ^{31}P NMR spectra showing the decarbonylation of compounds **11 a**–**11 c** in CD_2Cl_2. Resonances arising from decarbonylated products are denoted with an asterisk.

num or palladium [(POCOP)MCl] pincer complexes. It was observed during these ligand metallation reactions that the reaction rate depended to some extent on the ancillary ligand of the [$PtCl_2(L)_n$] precursor; using more strongly binding ancillary ligands disfavoured the formation of the *cis*,*trans*-dimer **6**, and in doing so, improved the rate of ligand metallation.

Platinum and palladium carbonyl complexes of the metallated ligands **1a**–**1c** were synthesised, and CO stretching frequencies indicated that $[(POCOP)Pd(CO)]^+$ (**11a**) possessed one of the most electron-poor metal centres of a pincer compound reported to date. Consequently, the electron-poor palladium compounds **11a**–**11c** demonstrated the ability to reversibly bind carbon monoxide, with decarbonylation proceeding more rapidly for the compounds with larger CO stretching frequencies. A subsequent report will outline the performance of the palladium pincer compounds **9a**–**9c** as catalysts in cross-coupling reactions.

Experimental Section

General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Dichloromethane, diethyl ether, and THF were carefully dried and distilled prior to use. Other solvents were degassed and stored over molecular sieves. Unless otherwise stated, all other reagents were used as obtained from commercial suppliers. The compounds (3-hydroxybenzyl)di-*tert*-butyl phosphine,[12a] bis(pentafluorophenyl)bromophosphine,[38] [$PdCl_2(NCMe)_2$],[39] [$PtCl(N(SiMe_3)_2)(COD)$],[26] [$PtCl_2(COD)$],[40] [$PtCl_2(hex)$],[41] [$PtCl_2(SEt_2)_2$],[42] and [$Pt(nb)_3$][43] were synthesised according to literature procedures. NMR spectra were obtained using a Varian Unity Inova 300 (300 MHz for ^1H, 121 MHz for ^{31}P, and 282 MHz for ^{19}F), a Varian Unity Inova 500 (500 MHz for ^1H and 125 MHz for ^{13}C), or a Varian DirectDrive 600 (600 MHz for ^1H and 150 MHz for ^{13}C). Chemical shifts (δ) are given in ppm, referenced to the residual solvent peak (^1H and ^{13}C), or to H_3PO_4 or $CFCl_3$ (^{31}P and ^{19}F, respectively). NMR samples were prepared under an inert atmosphere unless otherwise stated. Infrared spectra were obtained with a PerkinElmer Spectrum One FT-IR spectrophotometer using pressed KBr discs. Microanalyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. Single-crystal X-ray diffraction data were obtained by the X-ray Crystallography Laboratory at the University of Canterbury. Electrospray ionisation mass spectra were obtained using an Agilent 6530 Series Q-TOF mass spectrometer. Carbon-13 NMR data, as well as infrared spectra for the decarbonylation of **11b** to form **12b** are located in the Supporting Information.

X-ray data measurements

Diffraction data were collected using Bruker CCD diffractometers with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) using Bruker SMART (Version 5.054), SAINT (Version 6.02 A), and SADABS (Version 2.03) software. The structures were solved using Patterson methods, and refined using a full-matrix least squares method, with anisotropic thermal motion parameters for all non-hydrogen atoms.[44] Hydrogen atoms were placed in calculated positions and allowed to refine freely using a riding model. OLEX2 (Version 1.1.5)[45] was used as a front-end for the SHELX97 executables during structure solution and refinement. All relevant bond distances and angles were calculated using Mercury (Version 2.4.5), and molecular drawings were generated using ORTEP3 (Version 1.0.3). CCDC-970819 (**2**) and -970820 (**10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and characterization

Synthesis of 1,3-[$(C_6F_5)_2PO]_2C_6H_4$ (POCOPH) (1a): Resorcinol (1.00 g, 9.1 mmol) was suspended in a solution of triethylamine (2.6 mL, 18.6 mmol) in diethyl ether (80 mL). The reaction mixture was cooled on ice and a solution of $BrP(C_6F_5)_2$ (4.1 mL, 18.2 mmol) in diethyl ether (10 mL) was added dropwise. The reaction mixture was stirred for 1 h on ice and 18 h at RT, and then filtered through Celite. Removal of volatiles in vacuo and recrystallisation from toluene/hexane at −15 °C gave **1a** as white needles (6.61 g, 87%). ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 7.24$ (t, $^3J_{H,H} = 7.8$ Hz, 1H; H5), 6.86 (dd, $^3J_{H,H} = 7.5$ Hz, $^4J_{H,H} = 1.6$ Hz, 2H; H4,H6), 6.85 ppm (s, 1H; H2); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 87.1$ ppm (quint, $^3J_{P,F} = 35.0$ Hz); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta = -133.1$ (m, 2F; *o*-C_6F_5), −148.6 (t, $^3J_{F,F} = 19.7$ Hz, 1F; *p*-C_6F_5), −160.6 ppm (m, 2F; *m*-C_6F_5); elemental analysis calcd (%) for $C_{30}H_4O_2F_{20}P_2$: C 42.98, H 0.48; found: C 42.86, H 0.63; HRMS calcd for ($C_{30}H_8NO_4F_{20}P_2$) $[M+2O+NH_4]^+$: *m/z* 887.9609, found 887.9618.

Synthesis of 1,3-[$(C_6F_5)_2PCH_2]_2C_6H_4$ (PCCCPH) (1b): Magnesium powder (0.10 g, 4.1 mmol) in THF (24 mL) was activated with 1,2-dibromoethane (0.1 mL) and heated with a heat gun until rapid bubbling was observed. After bubbling had ceased, anthracene (1.4 g, 9.0 mmol) was added, and the reaction mixture was stirred at RT for 4 days. The supernatant liquid was decanted, the solid [$Mg(anth)(THF)_3$] was resuspended in THF, and a solution of dichloro-*m*-xylene (350 mg, 2.0 mmol) in THF (6 mL) was added dropwise and stirred, overnight. The supernatant was decanted and cooled to −78 °C, and to it was added $BrP(C_6F_5)_2$ (0.84 mL, 3.68 mmol) dropwise. The reaction mixture was allowed to warm to RT, overnight, then the volatiles were removed in vacuo and the remaining solid was extracted with hexane (4×50 mL) and filtered through Celite. The solvent was removed under vacuum, and chromatography on silica in air (petroleum ether eluent, $R_f = 0.1$) afforded **1b** as a white solid (1.03 g, 67%). Spectroscopic data matched that previously reported for **1b**.[10]

1-[$(C_6F_5)_2PO$]-3-(tBu_2PCH_2)C_6H_4 (POCCPH) (1c): A solution of (3-hydroxybenzyl)di-*tert*-butyl phosphine (1.15 g, 4.56 mmol) and triethylamine (1.4 mL, 10 mmol) in THF (50 mL) was cooled on ice, and a solution of $BrP(C_6F_5)_2$ (1.04 mL, 4.56 mmol) in THF (15 mL) was added over 10 min. The solution was stirred on ice for a further 10 min, then at RT, overnight. The reaction mixture was filtered through Celite, and the filter cake was washed with THF. The crude material was dried in vacuo, and purified by extraction with hexane (3×12 mL) at −78 °C, followed by filtration through Celite. Removal of hexane in vacuo gave **1c** as a viscous, pale yellow oil (2.42 g, 86%). ^1H NMR (500 MHz, C_6D_6): $\delta = 7.47$ (s, 1H; H2), 7.02 (m, 3H; H4,H5,H6), 2.65 (d, $^2J_{P,H} = 2.6$ Hz, 2H; CH_2), 0.99 ppm (d, $^3J_{P,H} = 10.8$ Hz, 18H; $C(CH_3)_3$); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 82.9$ (quint, $^3J_{P,F} = 35.5$ Hz, 1P; $P(C_6F_5)_2$), 34.3 ppm (s, 1P; $PtBu_2$); ^{19}F NMR (282 MHz, C_6D_6): $\delta = -133.2$ (m, 4F; *o*-C_6F_5), −148.5 (t, $^3J_{F,F} = 21.3$ Hz, 2F; *p*-C_6F_5), −160.3 ppm (tm, $^3J_{F,F} = 21.5$ Hz, 4F; *m*-C_6F_5); HRMS calcd for ($C_{27}H_{24}OF_{10}P_2$) $[M+H]^+$: *m/z* 617.1215, found 617.1220; HRMS calcd for ($C_{15}H_{25}OP$) $[M-P(C_6F_5)_2+2H]^+$: *m/z* 253.1716, found 253.1756.

[(POCOPH)Pt(nb)]$_2$ (2): A solution of $Pt(nb)_3$ (117 mg, 0.25 mmol) and **1a** (204 mg, 0.24 mmol) in dichloromethane (7 mL) was heated at 40 °C for 36 h, at which point all volatiles were removed in vacuo. The oily solid was washed with ice-cold pentane, then redissolved in toluene (5 mL) and heated at 50 °C for 12 h. The volume was reduced in vacuo to approximately 2 mL, with the addition of hexane to the toluene solution causing the precipitation of **4** as a white solid, which was isolated by decantation of the supernatant and washing with pentane (107 mg, 39 %). Crystals suitable for single crystal X-ray diffraction were obtained by solvent diffusion at RT, with methanol layered above a dichloromethane solution of **2**. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 6.85$ (t, $^3J_{H,H} = 8.1$ Hz, 1H; H5), 6.69 (d, $^3J_{H,H} = 8.1$ Hz, 2H; H4,H6), 6.12 (s, 1H; H2), 2.75 (d, $^2J_{Pt,H} = 70.8$ Hz, ^3J-H = 10.7 Hz, 2H; nb C=CH), 2.20 (d, $^2J_{H,H} = 10.0$ Hz, 2H; nb C-CH), 1.44 (d, $^2J_{H,H} = 7.3$ Hz, 2H; nb H_2C-CH_2), 0.96 (d, $^2J_{H,H} = 7.6$ Hz, 2H; nb H_2C-CH_2), 0.42 (m, 1H; nb HC-C*H*$_2$-CH), 0.15 ppm (d, $^2J_{H,H} = 8.5$ Hz, 1H; nb HC-C*H*$_2$-CH); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 100.5$ ppm (s, $^1J_{Pt,P} = 4623$ Hz); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta = -131.5$ (m, 8F; o-C_6F_5), −149.3 (m, 4F; p-C_6F_5), −160.8 ppm (m, 8F; m-C_6F_5); elemental analysis calcd (%) for $C_{74}H_{28}O_4F_{40}P_4Pt_2{\cdot}CH_2Cl_2$: C 38.50, H 1.29; found C 38.80, H 1.40; HRMS calcd for ($C_{60}H_8O_4F_{40}NaP_4Pt_2$) $[M-2\,nb+Na]^+$: *m/z* 2086.7886, found 2086.7883.

***cis*-[(POCOPH)PtMe$_2$]$_2$ (3)**: A solution of ligand **1a** (200 mg, 0.24 mmol) and [PtMe$_2$(hex)] (73.3 mg, 0.24 mmol) in toluene (15 mL) was stirred at RT for 72 h. The solution was concentrated in vacuo to approximately 3 mL, and the oligomeric by-product **4** precipitated out by the addition of 3 mL hexane to the solution. Decantation and isolation of the supernatant, followed by removal of the solvent in vacuo and washing with hexane afforded **3** as a yellow, microcrystalline solid (199 mg, 78 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.05$ (t, $^3J_{H,H} = 8.3$ Hz, 2H; H5), 6.82 (d, $^3J_{H,H} = 7.7$ Hz, 4H; H4,H6), 6.42 (s, 2H; H2), 0.21 ppm (br s, $^2J_{Pt,H} = 71.0$ Hz, 12H; CH_3); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 89.9$ ppm (s, $^1J_{Pt,P} = 2202$ Hz); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -129.4$ (br s, 16F; o-C_6F_5), −145.7 (br s, 8F; p-C_6F_5), −159.1 ppm (br s, 18F; m-C_6F_5); HRMS calcd for ($C_{64}H_{20}O_4F_{40}NaP_4Pt_2$) $[M+Na]^+$: *m/z* 2146.8825, found 2146.8855.

***cis*-[(POCOPH)PtMe$_2$]$_x$ (4)**: The oligomeric species **4** could be isolated as a by-product during the synthesis of the dimer **3** as above, with shorter reaction times in dichloromethane observed to increase the yield of **4**. A solution of ligand **1a** (50 mg, 60 µmol) and [PtMe$_2$(hex)] (18.5 mg, 60 µmol) in dichloromethane (5 mL) was stirred at RT for 24 h. The solvent was reduced to about 0.5 mL in vacuo, and precipitation of the product with hexane followed be decantation of the supernatant and washing with pentane afforded **4** as a white solid (48 mg, 76 %). Samples of **4** were found to be contaminated with small quantities of the dimer **3**. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.14$ (t, $^3J_{H,H} = 8.2$ Hz, 1H; H5), 6.94 (s, 1H; H2), 6.77 (d, $^3J_{H,H} = 8.2$, 2H; H4,H6), 0.42 ppm (vt, $^2J_{Pt,H} = 70.6$ Hz, $^3J_{P-H} = 3.0$ Hz, 6H; CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 90.9$ ppm (s, $^1J_{Pt,P} = 2150$ Hz); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta = -129.0$ (dm, $^3J_{P,F} = 16.4$ Hz, 8F; o-C_6F_5), −146.5 (tm, $^3J_{F,F} = 20.8$ Hz, 4F; m-C_6F_5), −159.7 ppm (m, 8F; p-C_6F_5).

***cis,trans*-[(POCOPH)PtCl$_2$]$_2$ (5)**: A solution of ligand **1a** (30 mg, 36 µmol) and [PtCl$_2$(hex)] (12.5 mg, 36 µmol) in [D$_6$]benzene was heated at 90 °C for 3 min (to ensure dissolution of starting material), then left standing at RT for 12 h. The reaction mixture was heated for a further 80 min at 90 °C, at which point NMR spectroscopy revealed almost quantitative formation of **5**. Removal of volatiles in vacuo and repeated washing with hexane afforded the product **5** as a cream-coloured solid (8 mg, 20 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.38$ (s, 2H; H2), 6.68 (d, $^3J_{H,H} = 8.5$ Hz, 2H; H6), 6.61 (vt, $^3J_{H,H} = 8.2$ Hz, 2H; H5), 6.53 ppm (d, $^3J_{H,H} = 7.7$ Hz, 2H; H4); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 80.6$ (s, $^1J_{Pt,P} = 3357$ Hz, 2P; P-*trans*-P), 55.5 ppm (s, $^1J_{Pt-P} = 4582$ Hz, 2P; P-*trans*-Cl); ^{19}F NMR (282 MHz, C_6D_6): $\delta = -126.9$–130.5 (br m, 16F; o-C_6F_5), −141.0–142.3 (br m, 8F; p-C_6F_5), −158.2–158.6 ppm (br m, 16F; m-C_6F_5); HRMS calcd for ($C_{60}H_8O_4F_{40}NaCl_4P_4Pt_2$) $[M+Na]^+$: *m/z* 2230.6665, found 2230.6653. Samples of **7** were contaminated with small amounts of *cis*-[(POCOPH)$_2$PtCl$_2$], preventing satisfactory elemental analysis data from being obtained.

***cis,trans*-[(POCOPH)PtClMe]$_2$ (6)**: A solution of [PtClMe(hex)] (101 mg, 0.30 mmol) and **1a** (249 mg, 0.31 mmol) in toluene (5 mL) was heated at 40 °C for 24 h, then stirred at RT for a further 8 h. The solution was filtered through a short alumina column in air, washing the column with toluene (3×2 mL). Volatiles were removed in vacuo, and the crude product was purified by the precipitation of by-products from a toluene/hexane solution of **6** at −15 °C. The supernatant was decanted and collected; removal of the volatiles in vacuo followed by washing with pentane gave **6** as a white, microcrystalline solid (65 mg, 20 %). ^{1}H NMR (600 MHz, C_6D_6): $\delta = 7.54$ (s, 1H; H2), 7.34 (s, 1H; H2′), 6.68 (d, $^3J_{H,H} = 7.9$ Hz, 1H; H6), 6.62 (m, 3H; H5,H5′,H6′), 6.55 (d, $^3J_{H,H} = 8.2$ Hz, 1H; H4), 6.53 (d, $^3J_{H,H} = 7.0$ Hz, 1H; H4′), 1.27 (br m, 3H; CH_3-*trans*-P), 0.26 ppm (br t, $^3J_{P,H} = 6.6$ Hz, 3H; CH_3-*trans*-Cl); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 94.4$ (d, $^1J_{Pt,P} = 2066$ Hz, $^2J_{P,P} = 15.4$ Hz, 1P; P-*trans*-CH_3), 90.3 (s, $^1J_{Pt,P} = 4028$ Hz, 2P; P-*trans*-P), 62.1 ppm (d, $^1J_{Pt,P} = 5494$ Hz, $^2J_{P,P} = 15.4$ Hz, 1P; P-*trans*-Cl); ^{19}F NMR (282 MHz, C_6D_6): $\delta = -127.6$–129.5 (m, 16F; o-C_6F_5), −142.7–144.0 (m, 8F; p-C_6F_5), −158.2–159.6 ppm (m, 16F; m-C_6F_5); HRMS calcd for ($C_{64}H_{17}NO_4F_{40}P_4ClPt_2$) $[M-Cl+NCMe]^+$: *m/z* 2170.8430, found 2170.8496. Accurate elemental analysis data could not be obtained for **6**.

***cis,trans*-[(POCOPH)PdCl$_2$]$_2$ (7)**: A solution of **1** (101 mg, 0.12 mmol) and [PdCl$_2$(NCMe)$_2$] (32 mg, 0.12 mmol) in dichloromethane (15 mL) was heated in an oil bath at 45 °C for 12 h, then concentrated in vacuo to a volume of approximately 2 mL. The supernatant was decanted and retained; addition of hexane to the supernatant gave a pale yellow precipitate, which was isolated and washed with pentane, affording **7** as a pale yellow solid (101 mg, 83 %). Samples of **7** were observed to undergo a degree of rearrangement to higher oligomers on standing in polar solvents such as chloroform or acetone. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 7.17$ (s, 2H; H2), 7.16 (vt, $^3J_{H,H} = 8.3$ Hz, 2H; H5), 6.85 (dd, $^3J_{H,H} = 8.3$ Hz, $^4J_{H,H} = 2.0$ Hz, 2H; H4), 6.55 ppm (d, $^3J_{H,H} = 8.1$ Hz, 2H; H6); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 88.7$ (s, 2P; P-*trans*-P), 78.5 ppm (s, 2P; P-*trans*-Cl); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta = -126.4$ (s, 8F; o-C_6F_5), −126.8 (s, 8F; o-C_6F_5), −141.7 (s, 4F; p-C_6F_5), −143.1 (s, 4F; p-C_6F_5), −158.5 (t, $^3J_{F,F} = 19.3$ Hz, 8F; m-C_6F_5), −158.9 ppm (td, $^3J_{F,F} = 21.7$, 6.9 Hz, 8F; m-C_6F_5); elemental analysis calcd (%) for $C_{60}H_8O_4F_{40}P_4Cl_4Pd_2$: C 35.48, H 0.40; found C 35.64, H 0.38; HRMS calcd for ($C_{60}H_8O_4F_{40}P_4Cl_3Pd_2$) $[M-Cl]^+$: *m/z* 1994.5881, found 1994.5869.

General procedure for the synthesis of pincer chloride complexes 8a–8c, 9a–9c: A 1:1 mixture of metal precursor and pincer ligand were heated to reflux in toluene for a sustained period of time. At the conclusion of the reaction, all volatiles were removed in vacuo, and the oily residue triturated with hexane to afford the crude product. Any unmetallated, oligomeric species present precipitated from toluene/hexane solutions of the crude product by the addition of hexane. The desired pincer complexes were then purified by recrystallisation or precipitation from toluene/hexane or dichloromethane/hexane mixtures at −15 °C.

[(POCOP)PtCl] (8a): A solution of [PtClMe(hex)] (79 mg, 0.24 mmol) and **1a** (203 mg, 0.24 mmol) in toluene (6 mL) for 48 h gave **8a** as a pale yellow solid (121 mg, 47 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.87$ (t, $^3J_{H,H} = 8.0$ Hz, 1H; H5), 6.79 ppm (d, $^3J_{H,H} = 7.8$ Hz, 2H; H4,H6); ^{31}P NMR (121 MHz, C_6D_6): $\delta = 107.8$ ppm (s, $^1J_{Pt,P} = 3663$ Hz); ^{19}F NMR (282 MHz, C_6D_6): $\delta = -128.4$ (dm, $^3J_{P,F} = 22.2$ Hz, 8F; o-C_6F_5),

−141.8 (tt, $^{3}J_{F,F}=20.0$ Hz, $^{5}J_{F,F}=6.8$ Hz, 4F; p-C_6F_5), −157.6 ppm (m, 8F; m-C_6F_5); elemental analysis calcd for $C_{30}H_3O_2F_{20}P_2ClPt{\cdot}CH_2Cl_2$: C 32.30, H 0.44; found C 32.45, H 0.55; HRMS calcd for ($C_{30}H_3O_2F_{20}NaP_2ClPt$) $[M+Na]^+$: m/z 1088.8502, found 1088.8513.

[(PCCCP)PtCl] (8b): A solution of [PtClMe(hex)] (82 mg, 0.25 mmol) and **1b** (206 mg, 0.25 mmol) in toluene (5 mL) for 18 h afforded **8b** as an off-white solid (252 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.11$ (m, 3H; H4,H5,H6), 4.26 ppm (vt, $^{3}J_{Pt,H}=29.8$ Hz, $^{2}J_{P,H}=4.5$ Hz, 4H; CH_2); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta=11.5$ ppm (s, $^{1}J_{Pt,P}=3379$ Hz); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-126.7$ (m, 8F; o-C_6F_5), −144.6 (t, $^{3}J_{F,F}=20.7$ Hz, 4F; p-C_6F_5), −157.9 ppm (m, 8F; m-C_6F_5); elemental analysis calcd for $C_{32}H_7F_{20}P_2ClPt$: C 36.13, H 0.66; found C 36.13, H 0.88; HRMS calcd for ($C_{34}H_{10}NF_{20}P_2Pt$) $[M-Cl+CH_3CN]^+$: m/z 1063.9568, found 1063.9564.

[(POCCP)PtCl] (8c): A solution of $[PtCl_2(SEt_2)_2]$ (191 mg, 0.43 mmol) and **1c** (265 mg, 0.24 mmol) in toluene (15 mL) for 64 h yielded **8c** as a yellow microcrystalline solid (181 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.04$ (vt, $^{3}J_{H,H}=7.6$ Hz, 1H; H5), 6.95 (d, $^{3}J_{H,H}=7.3$ Hz, 1H; H4), 6.76 (d, $^{4}J_{Pt,H}=16.7$ Hz, $^{3}J_{H,H}=7.9$ Hz, 1H; H6), 3.42 (d, $^{3}J_{Pt,H}=22.8$ Hz, $^{2}J_{P,H}=10.3$ Hz, 2H; CH_2), 1.45 ppm (d, $^{3}J_{P,H}=14.3$ Hz, 18H; $C(CH_3)_3$); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta=107.8$ (d, $^{1}J_{Pt,P}=3294$ Hz, $^{2}J_{P,P}=469$ Hz, 1P; $P(C_6F_5)_2$), 72.1 ppm (d, $^{1}J_{Pt,P}=3088$ Hz, $^{2}J_{P,P}=468$ Hz, 1P; PtBu$_2$); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-128.1$ (m, 4F; o-C_6F_5), −144.6 (tm, $^{3}J_{F,F}=20.7$ Hz, 2F; p-C_6F_5), −158.4 ppm (m, 4F, m-C_6F_5); HRMS calcd for ($C_{27}H_{27}NOF_{10}P_2ClPt$) $[M+NH_4]^+$: m/z 864.0737, found 864.0720.

[(POCOP)PdCl] (9a): A solution of $[PdCl_2(NCMe)_2]$ (96.5 mg, 0.37 mmol) and **1a** (316 mg, 0.38 mmol) in toluene (15 mL) for 80 h gave **9a** as a pale yellow solid (291 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.20$ (t, $^{3}J_{H,H}=8.3$ Hz, 1H; H5), 6.78 ppm (d, $^{3}J_{H,H}=7.9$ Hz, 2H; H4,H6); ^{31}P NMR (121 MHz, CDCl3): $\delta=114.4$ ppm (s); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-127.0$ (m, 8F; o-C_6F_5), −141.9 (tt, $^{3}J_{F,F}=20.9$ Hz, $^{4}J_{F,F}=6.4$ Hz, 4F; p-C_6F_5), −157.0 ppm (m, 8F; m-C_6F_5); HRMS calcd for ($C_{30}H_4O_2F_{20}P_2ClPt$) $[M+H]^+$: m/z 976.8501, found 976.8498.

[(PCCCP)PdCl] (9b): A solution of $[PdCl_2(NCMe)_2]$ (59 mg, 0.23 mmol) and **1b** (189 mg, 0.23 mmol) in toluene (6 mL) for 48 h gave **9b** as a yellow, microcrystalline solid (142 mg, 64%). Spectroscopic data matched that previously reported for **9b**.[10]

[(POCCP)PdCl] (9c): A solution of $[PdCl_2(NCMe)_2]$ (71.9 mg, 0.28 mmol) and **1c** (172 mg, 0.28 mmol) in toluene (6 mL) for 20 h afforded **9c** as a bright yellow solid (115 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.04$ (vt, $^{3}J_{H,H}=7.7$ Hz, 1H; H5), 6.95 (d, $^{3}J_{H,H}=7.6$ Hz, 1H; H4), 6.76 (d, $^{3}J_{H,H}=7.8$ Hz, 1H; H6), 3.47 (d, $^{2}J_{P,H}=9.5$ Hz, 2H; CH_2), 1.45 ppm (d, $^{3}J_{P,H}=14.4$ Hz, 18H; $C(CH_3)_3$); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta=111.5$ (d, $^{2}J_{P,P}=460$ Hz, 1P; $P(C_6F_5)_2$), 83.5 ppm (d, $^{2}J_{P,P}=460$ Hz, 1P; PtBu$_2$); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta=-127.8$ (dm, $^{3}J_{P,F}=21.3$ Hz, 4F; o-C_6F_5), −144.4 (t, $^{3}J_{F,F}=20.6$ Hz, 2F; p-C_6F_5), −158.3 ppm (m, 4F; m-C_6F_5); elemental analysis calcd (%) for $C_{27}H_{23}OF_{10}P_2ClPd{\cdot}{}^{1}\!/_{2}\,CH_2Cl_2$: C 41.38, H 3.03; found C 41.28, H 3.08; HRMS calcd for ($C_{29}H_{26}NOF_{10}P_2Pd$) $[M-Cl+CH_3CN]^+$: m/z 758.0386, found 758.0357.

General procedure for the synthesis of pincer carbonyl complexes 10a–10c, 11a–11c: A foil-wrapped flask containing the pincer chloride complex and $AgSbF_6$ was cooled to −78 °C and dichloromethane was added. The solution was stirred at −78 °C for 10 min, then carbon monoxide was bubbled through the solution as the reaction mixture was allowed to warm to RT. After a further 60 min the reaction mixture was filtered through Celite, reduced in volume to approximately 1 mL in vacuo, and the crude product precipitated out by the addition of hexane or diethyl ether to the dichloromethane solution saturated with carbon monoxide. Decantation of the supernatant and washing the precipitate with hexane furnished the desired carbonyl complex. Where further purification was required, recrystallisation from dichloromethane/diethyl ether mixtures was performed.

[(POCOP)Pt(CO)][SbF$_6$] (10a): Compound **8a** (50 mg, 0.047 mmol) and $AgSbF_6$ (18 mg, 0.052 mmol) in dichloromethane (10 mL) gave colourless rods of **10a** (17.9 mg, 30%). Crystals of **10a** suitable for single crystal X-ray diffraction were grown from the slow evaporation of a dichloromethane solution at RT. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.51$ (t, $^{3}J_{H,H}=8.2$ Hz, 1H; H5), 7.10 ppm (m, 2H; H4,H6); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=104.4$ ppm (s, $^{1}J_{Pt,P}=3345$ Hz); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta=-129.1$ (m, 8F; o-C_6F_5), −139.3 (m, 4F; p-C_6F_5), −156.6 ppm (m, 8F; m-C_6F_5); IR (KBr): $\tilde{\nu}=2145$ cm^{-1} (C≡O), elemental analysis calcd (%) for $C_{31}H_3O_3F_{26}P_2SbPt$: C 28.67, H 0.38; found C 28.73, H 0.23; HRMS calcd for ($C_{32}H_8NO_3F_{20}P_2Pt$) $[M-CO+CH_3CN+H_2O]^+$: m/z 1090.9305, found 1090.9317.

[(PCCCP)Pt(CO)][SbF$_6$] (10b): Compound **8b** (50 mg, 0.047 mmol) and $AgSbF_6$ (17 mg, 0.049 mmol) in dichloromethane (10 mL) gave **10b** as an off-white, microcrystalline solid (20.0 mg, 33%). ^{1}H NMR: (300 MHz, [D$_6$]acetone) $\delta=7.59$ (m, 2H; H4,H6), 7.44 (m, 1H; H5), 5.06 ppm (t, $^{3}J_{Pt,H}=36.6$ Hz, $^{2}J_{P,H}=5.3$ Hz, 4H; CH_2); ^{31}P NMR (121 MHz, [D$_6$]acetone): $\delta=6.2$ ppm (s, $^{1}J_{Pt,P}=3056$ Hz); ^{19}F NMR (282 MHz, [D$_6$]acetone): $\delta=-123.7$ (m, 8F; o-C_6F_5), −140.0 (tt, $^{3}J_{F,F}=20.6$ Hz, $^{4}J_{F,F}=6.7$ Hz, 4F; p-C_6F_5), −154.5 ppm (m, 8F; m-C_6F_5); IR (KBr): $\tilde{\nu}=2127$ cm^{-1} (C≡O); HRMS calcd for ($C_{33}H_7OF_{20}P_2Pt$) $[M]^+$: m/z 1055.9298, found 1055.9038.

[(POCCP)Pt(CO)][SbF$_6$] (10c): Compound **8c** (50 mg, 0.059 mmol) and $AgSbF_6$ (22 mg, 0.064 mmol) in dichloromethane (10 mL) afforded **10c** as a pale yellow solid (36.1 mg, 57%). ^{1}H NMR (300 MHz, CD_2Cl_2) $\delta=7.38$ (vt, $^{3}J_{H,H}=7.9$ Hz, 1H; H5), 7.29 (d, $^{3}J_{H,H}=7.5$ Hz, 1H; H4), 7.13 (d, $^{4}J_{Pt,H}=11.6$ Hz, $^{3}J_{H,H}=7.8$ Hz, 1H; H6), 3.96 (d, $^{3}J_{Pt,H}=24.0$ Hz, $^{2}J_{P,H}=10.1$ Hz, 2H; CH_2), 1.47 ppm (d, $^{3}J_{P,H}=15.4$ Hz, 18H; $C(CH_3)_3$); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=108.3$ (d, $^{1}J_{Pt,P}=2800$ Hz, $^{2}J_{P,P}=326$ Hz, 1P; $P(C_6F_5)_2$), 91.4 ppm (d, $^{1}J_{Pt,P}=2616$ Hz, $^{2}J_{P,P}=324$ Hz, 1P; PtBu$_2$); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta=-129.7$ (m, 4F; o-C_6F_5), −140.2 (ttd, $^{3}J_{F,F}=20.7$ Hz, $^{3}J_{F,F}=7.7$ Hz, $^{5}J_{P,F}=1.9$ Hz, 2F; p-C_6F_5), −156.7 ppm (tm, $^{3}J_{F,F}=20.1$ Hz, 4F; m-C_6F_5); IR (KBr): $\tilde{\nu}=2111$ cm^{-1} (C≡O).

[(POCOP)Pd(CO)][SbF$_6$] (11a): Compound **9a** (64.1 mg, 66 μmol) and $AgSbF_6$ (23.0 mg, 67 μmol) in dichloromethane (9 mL) afforded **11a** as an off-white solid (61.5 mg, 78%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.46$ (t, $^{3}J_{H,H}=8.1$ Hz, 1H; H5), 7.03 ppm (d, $^{3}J_{H,H}=8.3$ Hz, 1H; H4,H6); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=119.4$ ppm (s); ^{19}F NMR (282 MHz, CD_2Cl_2): $\delta=-129.5$ (m, 8F; o-C_6F_5), −140.0 (tt, $^{3}J_{F,F}=20.6$ Hz, $^{5}J_{F,F}=7.8$ Hz, 4F; p-C_6F_5), −156.9 ppm (m, 8F; m-C_6F_5); IR (KBr): $\tilde{\nu}=2170$ cm^{-1} (C≡O).

[(PCCCP)Pd(CO)][SbF$_6$] (11b): Compound **9b** (75 mg, 77 μmol) and $AgSbF_6$ (28 mg, 81 μmol) in dichloromethane (10 mL) gave **11b** as a white microcrystalline solid (35 mg, 38%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.34$ (m, 3H; H4,H5,H6), 4.63 ppm (t, $^{2}J_{P,H}=5.6$ Hz, 4H; CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=7.1$ ppm (s); ^{19}F NMR (282 MHz, CD_2Cl_2) $\delta=-128.7$ (m, 8F; o-C_6F_5), −142.5 (tt, $^{3}J_{F,F}=20.9$ Hz, $^{5}J_{F,F}=6.3$ Hz, 4F; p-C_6F_5), −157.1 ppm (m, 8F; m-C_6F_5); IR (KBr): $\tilde{\nu}=2148$ cm^{-1} (C≡O).

[(POCCP)Pd(CO)][SbF$_6$] (11c): Compound **9c** (51.2 mg, 67 μmol) and $AgSbF_6$ (24.1 mg, 70 μmol) in dichloromethane (6 mL) yielded **11c** as a yellow solid (41.0 mg, 62%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.33$ (t, $^{3}J_{H,H}=7.7$ Hz, 1H; H5), 7.19 (d, $^{3}J_{H,H}=7.6$ Hz, 1H; H4), 7.06 (d, $^{3}J_{H,H}=7.9$ Hz, 1H; H6), 3.85 (d, $^{2}J_{P,H}=10.0$ Hz, 2H; CH_2), 1.47 ppm (d, $^{3}J_{P,H}=15.3$ Hz, 18H; $C(CH_3)_3$); ^{31}P NMR: (121 MHz, CD_2Cl_2): $\delta=117.0$ (br dq, $^{2}J_{P,P}=320$ Hz, $^{3}J_{P,F}=16.7$ Hz, 1P; $P(C_6F_5)_2$), 109.1 ppm (d, $^2J_{P,P}=320$ Hz, 1P; P*t*Bu$_2$); ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): $\delta=-130.0$ (m, 4F; *o*-C$_6$F$_5$), -141.0 (tt, $^3J_{F,F}=20.6$ Hz, $^5J_{F,F}=7.5$ Hz, 2F; *p*-C$_6$F$_5$), -156.7 ppm (m, 4F; *m*-C$_6$F$_5$); IR (ATR film from CH$_2$Cl$_2$): $\tilde{\nu}=2140$ cm^{-1} (C≡O).

Observation of [(PCP)Pd(CO)][SbF$_6$] decarbonylation products [(PCP)Pd][SbF$_6$] (12a–12c): Compounds **12a**, **12b**, and **12c** were observed in solution arising from the decarbonylation of the parent palladium carbonyl compounds **11a**, **11b**, and **11c**, respectively, either by passage of inert gas through dichloromethane solutions, or upon prolonged standing under ambient conditions.

[(POCOP)Pd][SbF$_6$] (12a): ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta=7.30$ (t, $^3J_{H,H}=7.8$ Hz, 1H; H5), 8.85 ppm (d, $^3J_{H,H}=8.0$ Hz, 2H; H4,H6); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): $\delta=112.6$ ppm (s); ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): $\delta=-129.9$ (brs, 8F; *o*-C$_6$F$_5$), -141.0 (tm, $^3J_{F,F}=20.5$ Hz, 4F; *p*-C$_6$F$_5$), -157.5 ppm (tm, $^3J_{F,F}=18.9$ Hz, 8F; *m*-C$_6$F$_5$).

[(PCCCP)Pd][SbF$_6$] (12b): ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta=7.15$ (brs, 3H; H4,H5,H6), 4.38 ppm (t, $^2J_{P,H}=4.7$ Hz, 4H; CH$_2$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): $\delta=1.7$ ppm (s); ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): $\delta=-129.7$ (m, 8F; *o*-C$_6$F$_5$), -143.6 (tm, $^3J_{F,F}=20.4$ Hz, 4F; *p*-C$_6$F$_5$), -157.8 ppm (tm, $^3J_{F,F}=20.2$ Hz, 8F; *m*-C$_6$F$_5$).

[(POCCP)Pd][SbF$_6$] (12c): ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta=7.13$ (t, $^3J_{H,H}=7.6$ Hz, 1H; H5), 7.03 (d, $^3J_{H,H}=7.3$ Hz, 1H; H4), 6.81 (d, $^3J_{H,H}=8.0$ Hz, 1H; H6), 3.47 (d, $^2J_{P,H}=9.9$ Hz, 2H; CH$_2$), 1.44 ppm (d, $^3J_{P,H}=14.5$ Hz, 18H; C(CH$_3$)$_3$); ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): $\delta=107.9$ (brdq, $^2J_{P,P}=392$ Hz, $^3J_{P,F}=16.5$ Hz, 1P; P(C$_6$F$_5$)$_2$), 87.7 ppm (d, $^2J_{P,P}=392$ Hz, 1P; P*t*Bu$_2$); ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): $\delta=-130.5$ (m, 4F; *o*-C$_6$F$_5$), -142.8 (t, $^3J_{F,F}=20.2$ Hz, 2F; *p*-C$_6$F$_5$), -158.3 ppm (t, $^3J_{F,F}=18.9$ Hz, 4F, *m*-C$_6$F$_5$).

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Keywords: decarbonylation · metalation · palladium · pincer complexes · platinum

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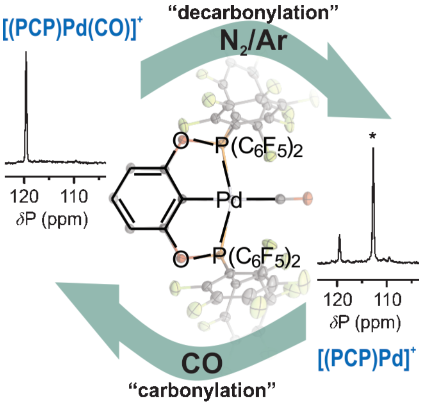
FULL PAPER

Back and forth: The electron-poor $P(C_6F_5)_2$ donor group was incorporated into the PCP pincer ligand motif to generate a range of poorly donating ligands. Palladium carbonyl complexes of these ligands demonstrated the ability to reversibly bind CO, with the ease of CO displacement increasing with increasing ν(CO) values (see figure). These ligands also displayed a reluctance to undergo metallation on Pt or Pd, which led to the formation of rare examples of *cis*,*trans*-dimers.



CO Binding

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■■ – ■■

The Coordination Chemistry of Pentafluorophenylphosphino Pincer Ligands to Platinum and Palladium