Inorganic Chemistry
Article
Cite This: *Inorg. Chem.* XXXX, XXX, XXX−XXX
pubs.acs.org/IC

Synthesis, Characterization, and Catalytic Studies of Dinuclear d^8 Metal−Phosphazane Complexes

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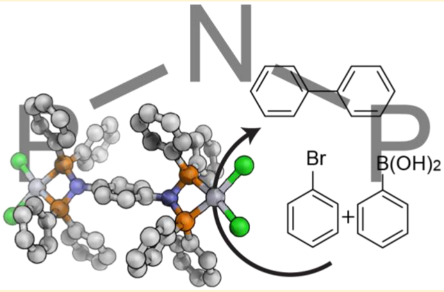
Supporting Information

ABSTRACT: Herein we report the synthesis and characterization of two diphosphazane (P−N−P) ligands, along with their corresponding novel palladium and platinum complexes. Compounds were characterized by FTIR and NMR spectroscopy, single crystal X-ray diffraction (SC-XRD), and powder X-ray diffraction (PXRD)), as well as mass spectrometry. The Pd(II) complex of the *p*-phenyldiphosphazane was shown to effectively and efficiently catalyze Suzuki-Miyaura cross-coupling reactions between a variety of substrates. Yields were as high as 96%, with reaction times as short as 15 min at room temperature and open to air. No additional supporting ligands, such as triphenylphosphine, were needed. The work reported here expands the use of phosphazane ligands to support catalytic centers and provides an understanding of phosphazane metal−ligand bonding interactions (specifically diphosphazanes).



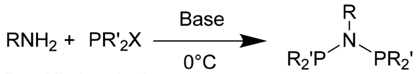
1. INTRODUCTION

Phosphazane compounds are an underexplored class of phosphorus−nitrogen compounds of interest to organic and inorganic chemists, the latter drawn to the interesting transition metal complexes thereof. Interest in phosphorus—nitrogen bonding prompted early explorations of phosphazanes and related species.[1] Since then, bis(diphenylphosphino)amine (dppa) emerged as one of the most popular and well-studied phosphazanes. First reported in 1965 by Clemens et al., it was used to study the mechanism of chloroamination reactions. Initial thrusts into the coordination behavior of phosphazane ligands focused on the nature of the electronic properties of the P−N bond along with its influence on the interaction of the donor phosphorus atom with a metal center.[2−4] Natural comparisons were made between phosphazane cores and their corresponding bisphosphine analogues, for example dppa versus bis(diphenylphosphino)methane (dppm). A suite of $Mo(CO)_4(L−L)$ (L−L = bidentate P−N−P or P−C−P, or two PR_3 ligands) complexes provided a platform to investigate the σ-donating and π-accepting abilities of the phosphorus-based ligand library. Findings revealed that changing the bridging atom from carbon to nitrogen did not have profound effects on the carbonyl stretching mode, and therefore the nature of the metal−phosphorus bond.[4] Although both P−N−P and P−C−P ligands possess small bite angles, the former will not always form the same architectures as the latter. For example, Mague et al. found that so-called dinuclear "A-frame" complexes formed when P−C−P ligands were used. In contrast, a series of mononuclear rhodium and iridium complexes were isolated when phosphazanes were employed.[5] That said, it is possible to isolate A-frame type complexes bearing phosphazane ligands that are structurally similar to their corresponding phosphine analogues.[6−8]

Whereas the chemistry of bidentate P−C−P ligands has been well-studied by many groups including those of Shaw,[9−30] Puddephatt,[31−33] Kubiak,[34−55] and White,[56−58] phosphazane ligands have received far less attention. From a synthetic standpoint, phosphazanes offer a higher degree of tunability owing to the wide availability of primary amines that are used in their formation. The amine building blocks enable both steric and electronic tuning depending on the specific R groups that are selected. Phosphazanes are significantly more cost-effective to synthesize; they are not formed from expensive or commercially unavailable bis-halogenated alkyl or benzyl precursors like their P−C−P analogues.

Scheme 1 illustrates a typical bis(diphenyl)phosphazane ligand synthesis. Preparations are mild and circumvent the use of aggressive organometallic reagents, strong bases, and the need for low temperature reaction conditions.[59] Figure 1 illustrates a substantial cost difference between the synthesis of a simple bis-P−N−P (**1**) versus its bis-P−C−P counterpart. Summing the reagent costs associated with treating $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*p*-xylene with lithium diphenylphosphide reveals an

Scheme 1. Typical Bis(diphenyl)phosphazane Ligand Synthesis



R = Alkyl or Aryl
R' = Alkyl or Aryl
X = Halide
Base = Triethylamine or Pyridine

Received: March 24, 2018

DOI: 10.1021/acs.inorgchem.8b00787

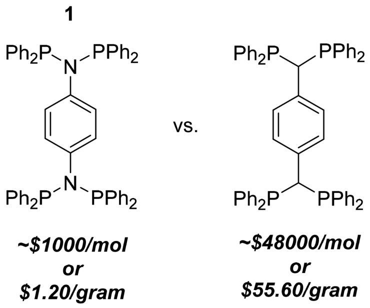


Figure 1. Comparing the cost of synthesis of a P−N−P ligand in comparison to the analogous P−C−P ligand.

~48-fold greater expense relative to synthesis of **1** reported herein.[60]

The central nitrogen atom of a phosphazane ligand typically deviates only slightly from an idealized *sp*^{2} geometry. Caution is necessary when strong nucleophilic reagents (i.e., strong bases and organometallic reagents) and/or electron-withdrawing R-groups, especially those on the nitrogen atom, are used. The P−N bond is susceptible to nucleophilic attack, resulting in bond cleavage that will ultimately reduce yields of a target phosphazane and necessitate further separation techniques.[1] To the same end, electron withdrawing R-groups can labilize the P−N bond, promoting isomerization to an N−P−P species.[61,62] As such, any reaction involving the outlined reagents should be performed prior to the P−N bond formation.

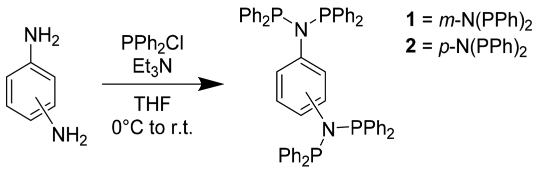
In this work, we report the modified synthesis and characterization of N1,N1,N4,N4-tetrakis(diphenylphosphino)-benzene-1,3-diamine (*m*-tdpb, **1**) and N1,N1,N4,N4-tetrakis-(diphenylphosphino)benzene-1,4-diamine (*p*-tdpb, **2**), as well as their corresponding dinuclear metal complexes: $(PtCl_2)_2$(*m*-tdpb) (**3**), $(PtCl_2)_2$(*p*-tdpb) (**4**), and $(PdCl_2)_2$(*p*-tdpb) (**5**). Group 10 metals in conjunction with phosphorus-based ligands are classic cross-coupling catalysts. Additionally, palladium phosphazane complexes have been shown to catalyze Suzuki-Miyaura cross-coupling reactions.[63] As such, we demonstrate that complex **5** is capable of effectively catalyzing Suzuki-Miyaura coupling reactions with short reaction times, in air, at room temperature, even when the substrate is an aryl chloride in place of the more reactive aryl bromide typically employed in cross-coupling reactions.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization.

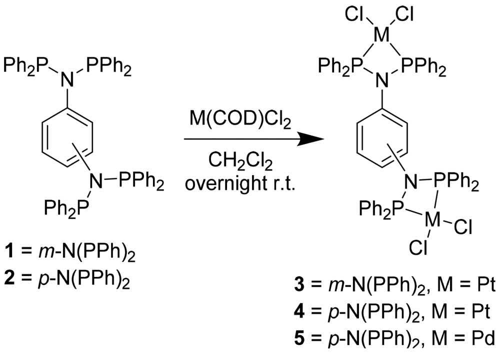
Ligands **1** and **2** were synthesized according to a modified literature procedure (Scheme 2).[64] We have improved upon the isolation method to provide excellent yields and purity in one step that avoids dissolution into diethyl ether, a solvent in which **1** and **2** are only sparingly soluble. The triethylammonium chloride was filtered from the crude reaction mixture and the filtrate added to a beaker filled with acetonitrile (4x the volume of the filtrate). During addition, the acetonitrile was stirred and upon completion the solution was allowed to stand for 5 min at room temperature. Compounds **1** and **2** crystallized out of solution and were collected by simple filtration. The crystals were washed with acetonitrile and dried *in vacuo*. The filtrate was allowed to evaporate slowly overnight in air to afford a second crop of crystals. The combined yields approached 91% with no further purification necessary based on both ^1H and $^{31}P\{^1H\}$ NMR. Ligands **1** and **2** are readily soluble in halogenated solvents and THF, insoluble in alcohols and paraffins, and sparingly soluble in aromatic solvents.

Scheme 2. Synthesis of Phosphazane Ligands 1 and 2



Complexes **3**−**5** were synthesized through a simple ligand exchange reaction in which the 1,5-cyclooctadiene (COD) ligand was replaced by the bidentate P−N−P moiety of a given diphosphazane ligand (Scheme 3). Complexes **4** and **5** precipitated from CH_2Cl_2 during the synthesis as a white and light yellow crystalline solids, respectively. Complex **3** remained in solution and was isolated as a colorless crystalline solid by slow evaporation of the reaction solvent. Complexes **3**-**5** were characterized by proton NMR, **3** and **4** with $^{31}P\{^1H\}$ NMR (due to poor solubility, a $^{31}P\{^1H\}$ of **5** was not acquired), along with ESI-mass spectrometry, and single crystal (**3** and **4**) and powder (**4** and **5**) X-ray diffraction studies.

Scheme 3. Synthesis of Dinuclear Complexes 3−5



All three reported metal complexes were insoluble or sparingly soluble in most common laboratory solvents with the following exceptions: complex **3** was initially soluble in CH_2Cl_2 during its synthesis. Once isolated from the reaction mixture its solubility in CH_2Cl_2 dropped significantly. This marked difference in solubility is typically due to solvent molecules cocrystallizing with a given complex, which alters the solubility of the resulting material. Solvents of crystallization were observed in diffraction studies, consistent with this explanation. To resolvate **3** 1,1,2,2-tetrachloroethane-d_2 was used with sonication, enabling characterization by ^1H NMR. Furthermore, **3** showed solubility in hot DMSO. Complexes **4** and **5** show an even lower degree of solubility, NMR characterization was only possible through solvation in 1,1,2,2-tetrachloroethane-d_2 (**4**) or hot DMSO-d_6 (**5**). In terms of air and water stability, the complexes are stable in air and water on the time scale of days and weeks at room temperature. In refluxing DMF, complex **5** undergoes a P−N isomerization resulting in decomposition of the dinuclear species.

The ^1H NMR of all three complexes show the expected splitting patterns, integrations, and chemical shifts consistent with dinuclear Pt_2 and Pd_2 species. The spectrum of complex **3** contained a singlet, a doublet, and a triplet in the 6−7 ppm range, representative of the four protons on the central

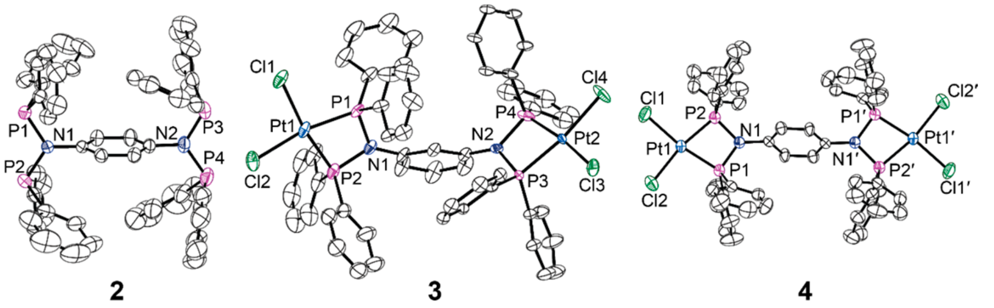


Figure 2. Oakridge Thermal Ellipsoid Plot (ORTEP) of compounds **2**−**4** drawn at the 50% probability level, hydrogen atoms and solvent molecules omitted for clarity. In the case of complex **4**, Z' = 0.5 and half the formula unit is symmetry generated by an inversion symmetry element, indicated by the primed labels.

phenylene moiety along with a series of three multiplets in the 7.3 to 7.7 ppm range that were assigned to the protons of the phenyl groups on phosphorus atoms. The ^{31}P{^{1}H} NMR spectrum featured a singlet at 23.09 ppm with platinum satellites ($J^{31}{}_{\mathrm{P}-}{}^{195}{}_{\mathrm{Pt}}$ = 3320 Hz), which is fully consistent with *cis* phosphazane coordination to a square planar platinum ion. The magnitude of the coupling constant gives insight into the coordination environment about each platinum atom, a $J^{31}{}_{\mathrm{P}\text{-}}{}^{195}{}_{\mathrm{Pt}}$ ∼ 3300 Hz indicates *cis* coordinated phosphorus donors, whereas $J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}}$ ∼ 2300 Hz indicates *trans* coordination.[65] In the case of complex **4**, the ^{1}H NMR contained a singlet at 6.21 ppm, assigned to the four phenylene protons, indicative of the higher symmetry of **4** as compared to **3**. Also present were two multiplets, a result of the protons of the phenyl rings. Due to poor solubility, the platinum satellites were not observed in the ^{31}P{^{1}H} spectrum; however, a singlet was observed at 21.33 ppm, a similar shift to that of **3**, further supporting that the desired complex was successfully synthesized. Due to its poor solubility, even in hot DMSO, only a ^{1}H NMR was acquirable for **5**, which contained similar splitting pattern and shifts to that of **4**.

ESI-mass spectrometry further corroborates that the desired complexes and ligands were successfully synthesized.[66,67] Compounds **2**−**5** were sonicated in CH_2Cl_2 and filtered prior to MS analysis (a small amount of acetonitrile was found to improve the solubility of **5** slightly). The mass spectrum of **2** (Figure S10) showed peaks corresponding to [**2** + H]$^{+}$ along with [**2** − PPh_2^{+} + 2H^{+}]$^{+}$ and [**2** + PPh_2^{+}]$^{+}$, all of which are in good agreement with simulated spectra for each species and are reasonable fragments of the parent compound (Figure S11). Complexes **3** and **4** show similar mass spectra (Figures S12 and S14, respectively); this is to be expected since they are isomers. Both show a peak corresponding to the parent complex with a Li^{+} cation [**M** + Li^{+}]$^{+}$, matching simulated isotopic distribution and mass to charge ratio (Figure S13). In the spectrum of complex **5**, a peak consistent with the loss of a chloride ligand and addition of acetonitrile was observed (Figure S15), in good agreement with the theoretical spectrum (Figure S16). A similar peak without an additional acetonitrile was also observed at an m/z of 1162.98 (predicted 1162.96).

The infrared spectra of all compounds presented were acquired. Compounds **1**−**3** showed a weak band around 3040−3050 cm^{-1}, assigned to aromatic C−H stretches. These peaks were less intense in compounds **4** and **5**. All five compounds had a series of three to four peaks in the range of 1586−1432 cm^{-1}, attributed to aromatic ring stretching.[68] The higher degree of symmetry present in compound **2** (idealized D_{2h}) compared to compound **1** (idealized C_{2v}) was apparent based on the P−N−C asymmetric stretching region (1110 to 930 cm^{-1}). Symmetry analysis predicts four IR active P−N stretches for **1**, but only two for **2**. In the spectra of **1**, there were four major peaks at 1091, 982, 930, and ∼929 cm^{-1}, with a strong shoulder on the peak at 930 cm^{-1} but only two major peaks (1091 and 923 cm^{-1}) in the spectrum of **2**. The spectra of **4** and **5** are similar since these species differ only in their metal ions and are otherwise expected to be largely isostructural. Since complex **5** was difficult to characterize by other methods due to its poor solubility, confirming that it had a similar IR to that of **4**, which was readily characterized, supports the formation of the Pd_2 species (Figure S9).

2.2. X-ray Diffraction Studies. Single crystals of **2** were grown by layering pentanes onto a saturated solution of the ligand in CH_2Cl_2. After standing at 0 °C for 1 day, colorless clear blocks were obtained. Complex **3** was crystallized by slow solvent evaporation of the reaction mixture filtrate (CH_2Cl_2), producing large clear and colorless block-like crystals that were prone to twinning. Crystals of **3** desolvated and fractured rapidly upon removal from the mother liquor, regardless of the solvents used during crystallization. Nonetheless, a tractable data set was obtained by minimizing exposure times to limit the duration of the diffraction experiment. Complex **4** was dissolved in 1,1,2,2-tetrachloroethane and the solvent was slowly evaporated over the course of 3 weeks at room temperature without agitation, resulting in the formation of small block-like crystals suitable for X-ray diffraction.

All structures were solved and refined using the Olex2 software package.[69] The structure of **2** was solved using SHELXS[70] via Direct Methods. Complex **4** was solved using SHELXS[70] using the Patterson Method. Complex **3** was solved using SHELXT[71] with Intrinsic Phasing. All structures were then refined using SHELXL using a least-squares minimization.[72] Ligand **2** refined quite well and did not require the use of any constraints or restrains in the refinement. Complex **4** contained four 1,1,2,2-tetrachloroethane units which required the use of SADI commands to restrain bond lengths to values which are chemically equivalent to similar lengths. The rigid bond restraint DELU was used to restrain anisotropic displacement parameters of bonded atoms. SIMU commands were also applied to the misbehaved solvent molecules. DFIX restraints were used to restrain the bond lengths and ISOR restraints were used to allow for isotropic refinement of anisotropic atom. Additionally, a SADI restraint was used on one of the phenyl rings of the phosphazane ligand to give more homogeneous C−C bond lengths (it is chemically reasonable to expect that the C−C bond in a phenyl ring should be approximately the same). Several CH_2Cl_2 molecules were

Table 1. Select Bond Lengths and Angles from 2, 3, and 4

2		3		4	
P1−N1 (Å)	1.729(1)	P1−N1 (Å)	1.71(1)	P1−N1 (Å)	1.708(6)
P2−N1 (Å)	1.726(1)	P2−N1 (Å)	1.71(1)	P2−N1 (Å)	1.704(6)
P3−N2 (Å)	1.726(1)	P3−N2 (Å)	1.70(1)	–	
P4−N2 (Å)	1.725(1)	P4−N2 (Å)	1.72(1)	–	
–		P1−Pt1−P2 (deg)	73.0(1)	P1−Pt1−P2 (deg)	73.02(8)
–		P3−Pt2−P4 (deg)	73.0(1)	–	

located and modeled, their occupancies allowed to freely refine in the crystal structure of **3**; however, this did not account for all the residual electron density and required the use of a solvent mask, applied with Olex2. The electron density was not localized around the desired molecule, but rather in the void space between, suggesting disordered solvent. Again SIMU and DELU restraints were applied when necessary and reasonable. Two on the phenyl ring of the phosphazane ligands were disordered; however, the disorder was modeled and SADI restrains were used to maintain P−C bond homogeneity.

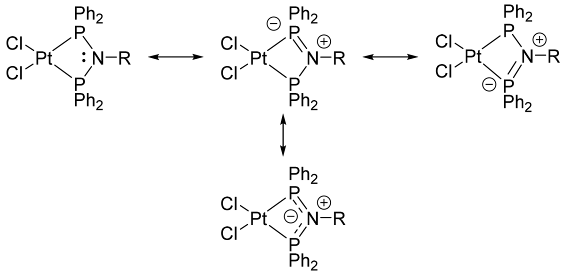
We are the first to report the solid state crystal structures of **2** (CCDC number: 1565704), **3** (CCDC number: 1565706), and **4** (CCDC number: 1565705). Each model refined well against the empirical data. The model of **4** shows a considerable amount of residual electron density near Pt1, this is not unexpected given the size and amount of electron density associated with a platinum.

Figure 2 illustrates the formula units of each compound. The thermal ellipsoids of **2** are considerably larger than those of **3** and **4**, despite the same probability level, a result of the room temperature data collection; however, this does not detract from the structure. Solvent molecules of crystallization are found in both **3** and **4**, 1.44 CH_2Cl_2 and 8 1,1,2,2-tetrachloroethane units, respectively. A noninteger number of CH_2Cl_2 was found in the case of complex **3** as a result of permitting the occupancy to freely refine.

Bond lengths are all within expected tolerances. Bonds of special interest are the P−N bonds along with the bite angle (defined as the P—M—P angle). Bond lengths and angles of interest have been compiled in Table 1. The free ligand possessed a P−N bond length of ∼1.73 Å in contrast to the platinum(II) complex, in which it was ∼1.71 Å. Moreover, the bite angles of **3** and **4** were shown to be ∼73.0°. To ensure that the experimentally determined bond lengths and bite angles make chemical sense, a survey of the CCDC was performed using ConQuest (version 1.19) and the results analyzed using Mercury (version 3.9).[73,74] A search for complexes containing the P−N−P motif chelating to any transition metal identified 284 structures. Of these matches, the average P−N bond length was found to be 1.70(2) Å and the average bite angle was 70(3)°.

An examination of the bond lengths in Table 1 reveals an interesting result of complexation: the P−N bond lengths decrease when complexed with platinum. Additionally, the four-membered Pt−P−N−P ring is almost perfectly planar in both **3** and **4**. This observation in conjunction with the P−N bond length contraction is evidence that the nitrogen atom lone pair is delocalized, leading to the formation of a conjugated ring system (see Scheme 4). Further support is offered by the work of Eady et al., who also observed a near perfectly planar iron-phosphazane ring structure.[75] The $^{31}P\{^1H\}$ NMR also support the delocalization as both **3** and **4** showed upfield shifts in their phosphorus resonances relative to the free ligand. The resonance localizes additional negative charge on the phosphorus atoms, further shielding the nuclei and causing an upfield shift with respect to the free ligand.

Scheme 4. Resonance Structures Which Aid to Explain the Observed Planarity and P−N Bond Contraction



The poor solubility of **5** prevented the growth of high quality crystals suitable for single crystal X-ray diffraction. Although a single crystal was obtained after refluxing **5** in DMF for 3 h in air and allowing the resulting solution to stand for several weeks, it was revealed to be hydrolysis decomposition products $Pd(PPh_2OH)_2Cl_2$ and $Pd[(PPh_2)_2N(C_6H_4NH_2)]Cl_2$, which cocrystallized with nonmerohedral twinning. No hydrolysis had been previously observed for these complexes and thus it appears only to occur at elevated temperatures, such as those reached in refluxing DMF. Examination of the ESI-MS of **5** that was not subjected to refluxing DMF conditions did not show any evidence of the two hydrolysis products, and thus, the bulk material was stable.

In order to gain insight into the atomic arrangement and molecular packing of **5** in the solid state, powder X-ray diffraction (PXRD) data was acquired (see Figure 3). A comparison of the powder patterns of **4** and **5** revealed a striking similarity in peak position, suggesting that the two materials have similar symmetries; however, the intensities of each peak varied due to the compositional differences (i.e., Pd vs Pt). As with the similarities in IR, these results support that **5** is isostructural to **4**. Using the FOX software package (Version

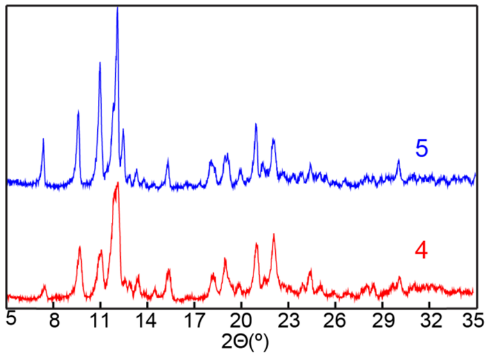
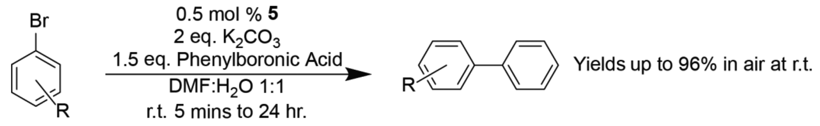
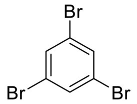
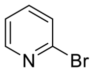
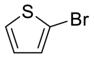
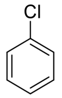


Figure 3. PXRD pattern for complexes **5** (top) and **4** (bottom).

Table 2. Substrate Scope for Catalytic Activity Screening of **5**



Entry	Aryl Halide	Time	Yield (%)	TON[d]
1	R = H	15 mins.	96	92[a]
2	R = 4-amino	12 hr.	90	191
3	R = 2-benylbromide	12 hr.	22	42
4	R = 2-C(O)H	12 hr.	72	142
5	R = 3-C(O)H	12 hr.	42	75[b]
6		24 hr.	65	100[b]
7		24 hr.	26	40
8		24 hr.	56	107
9		24 hr.	31	61

[a] Catalyst loading of 1 mol % used. [b] Catalyst loading of 0.6 mol % used. [d] Turnover number.

1.9.7-#1313), a Le Bail fit of the pattern of **5** was performed using the space group ($P2_1/n$) and starting unit cell dimensions of **4** determined from its SC-XRD parameters (Figure S19). After allowing a free fit to these parameters, the pattern fit quite well with a final Rwp of 14.6% and a goodness of fit (GooF) of 2.293. The unit cell converged to 15.6234 × 19.8425 × 17.0690 $Å^3$ and β of 114.911° (calculated volume 4799.28 $Å^3$). This is consistent with $Z = 4$ (reasonable for $P2_1/n$) based on the approximation that all nonhydrogen atoms occupy ~18 $Å^3$, further supporting that the Le Bail fit was able to fit an appropriate unit cell and that the desired material was synthesized.

2.3. Suzuki-Miyaura Coupling Screening. Complex **5** was hypothesized to catalyze Suzuki-Miyuara cross-coupling reactions given the propensity for palladium-based complexes to effect these transformations.[76] We found that **5** is able to efficiently catalyze the aforementioned cross-coupling reaction with yields spanning 22% up to 96% under mild, aerobic conditions in 1:1 DMF/H_2O. The catalyst did not require the addition of a supporting ligand such triphenylphosphine, often used in cross-coupling reactions to stabilize Pd(0) species. Eliminating the need for supporting ligands improves atom economy and reduces the amount of waste produced. Table 2 illustrates the substrate scope of the reaction.

A range of halides with varying steric bulk and electronic properties were employed to study the generality of the catalyst as well as its tolerance to various functionalities. Excellent yields (96%) with short reaction times (15 min) were achieved when coupling phenylboronic acid with bromobenzene. Colorless crystals of biphenyl were observed almost immediately and the reaction was quenched after 15 min by extracting the reaction mixture with diethyl ether. Conversion was confirmed by both ^1H NMR and GC-MS for all samples and yields were determined via quantitative ^1H NMR. A standard of 1,1,2,2-tetrachloroethane was used, with a chemical shift of 6.00, it did not interfere nor overlap with any of the peaks of any of the substrates or products studied.

The performance of **5** exceeds that of other bidentate bis(diphenylphosphino)methane-type catalyst based on reaction time, the use of milder conditions, and high yields.[77] Furthermore, the reported catalyst shows enhanced tolerance toward aerobic conditions when compared to other phosphazane-based catalyst used for cross-coupling catalysis which have, to date, only been reported under inert conditions.[63]

All product mixtures, regardless of the aryl halide used, also contained biphenyl and triphenylboroxine. The biphenyl can be attributed to the homocoupling of the phenylboronic acid. The homocoupling of boronic acids has been studied in great detail and it has been found that the reaction, under an O_2 containing atmosphere, proceeds through an η^2-O_2 peroxo complex, as reported by Adamo et al.[78] As for the triphenylboroxine, it is a product of the dehydration of phenylboronic acid. The presence of both compounds is not unexpected given that 1.5 equiv of phenylboronic acid with respect to aryl halide was present in solution and thus there would be half an equivalent remaining after the heterocoupling.

3. EXPERIMENTAL SECTION

3.1. General Information. Unless otherwise noted, all manipulations were carried out under an inert dinitrogen atmosphere either in a Vigor glovebox or using standard Schlenk techniques. All reagents were used as received unless otherwise indicated. Solvents were purified using a Grubbs style solvent system purchased from Pure Process Technology. ^1H NMR spectra and were acquired on a Varian 300 or 400 MHz spectrometer; $^{31}P\{^1H\}$ spectra were acquired on a 300 MHz NMR operating at 121 MHz. Chemical shift (δ) are reported in parts per million (ppm) and referenced against the residual protio-solvent peak in ^1H experiments and 85% H_3PO_4 in $^{31}P\{^1H\}$ experiments. For mass spectrometry samples were infused directly using an ESI (positive mode) linear ion trap (LTQ)-Orbitrap XL mass spectrometer (Thermo Fisher Scientific). For gas chromatography−mass spectrometry analysis an HP 5890 Series II GC in tandem with an HP 5972 Series Mass Selective Detector was used. FTIR spectra were acquired on a PerkinElmer 1760 FTIR spectrometer. Powder X-ray diffraction data was acquired on a Rigaku Ultima IV diffractometer equipped with a monochromated copper X-ray source (Cu Kα 1.5406 Å).

3.2. X-ray Crystallography. Single-crystal X-ray diffraction of **2** and **3** was performed on a Bruker D8 Venture diffractometer equipped with a fixed-chi goniometer, an Oxford cryostat, a molybdenum X-ray source (Mo Kα 0.7107 Å) with a graphite monochromator, and a Photon-100 area detector. The data set for **4** was collected at Cornell University by Dr. Samantha MacMillan using a Bruker X8 diffractometer equipped with an APEX-II CCD detector, a molybdenum X-ray tube (Mo Kα 0.7107 Å), and Oxford cryostat.

Crystals of **2** and **3** were mounted on MiTeGen MicroLoops with a drop of N-Paratone oil. Data for **2** was collected at room temperature, while **3** was held at 100 K and **4** at 223 K for the entirety of data collection. A series of φ and ω scans were used to cover reciprocal space. For a complete outline of all the crystallographic metrics see Table S1.

3.3. Synthesis of N1,N1,N4,N4-tetrakis(diphenylphosphino)-benzene-1,3-diamine (m-tdpb) 1. Compound **1** was synthesized using a slightly modified protocol found in the literature.[79] A three-neck flask was equipped with a gas inlet adapter, a pressure equalized addition funnel, a Teflon-coated magnetic stir bar, and a rubber septum. *m*-Phenylenediamine (2.930 g, 27.09 mmol) was added to the pressure equalized addition funnel, sealed with a rubber septum, and the apparatus put under an inert atmosphere. Via cannula, 200 mL of THF was added to the addition funnel and 150 mL to the three-neck flask. Freshly distilled chlorodiphenylphosphine (21.0 mL, 25.8 g, 116 mmol) and triethylamine (17.0 mL, 12.3 g, 122 mmol) were added to the three-neck flask by cannula and stirred to form a colorless, clear solution (note: if triethylamine has not been thoroughly dried and degassed a white precipitate will form immediately). The three-neck flask and its contents were cooled to 0 °C, the *m*-phenylenediamine solution was then slowly added dropwise. After completion of addition, the reaction mixture was a thick white suspension (NEt_3HCl), the reaction mixture was warmed to room temperature, and the mixture was stirred for an additional 2 h. In air the white suspension was filtered through a frit and the filtrate was added to 600 mL of acetonitrile and stirred for 45 min, followed by standing for 15 min. The white crystalline solid was collected by filtration. The filtrate solvent removed by rotary evaporation, and the residue redissolved in 100 mL of THF and added to 300 mL acetonitrile for afford a second crop of crystals. Yield of **1** was 90.4% (20.699 g, 24.500 mmol) as a white crystalline solid. The ^1H and $^{31}P\{^1H\}$ match literature values.[77] ^1H NMR ($CDCl_3$, 300 MHz): δ 7.31−7.15 (43H (overlaps with residual $CHCl_3$), m, Ph), 6.66 (1H, s), 6.49 (1H, t, J = 6.0 Hz), 6.26 (2H, d, J = 6.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) δ 67.49. FT-IR (neat, cm^{-1}) 3046, 1579, 1475, 1431, 1247, 1179, 1149, 1091, 1024, 981, 930, 854, 771, 742, 691, 670, 515, 500, 492, 480, 4623, 442, 424.

3.4. Synthesis of N1,N1,N4,N4-tetrakis(diphenylphosphino)-benzene-1,4-diamine (p-tdpb) 2. Synthesis and isolation of **2** follows the same procedure as **1**. *p*-Phenylenediamine (4.400 g, 40.688 mmol), triethylamine (25.0 mL, 18.1 g, 179 mmol), chlorodiphenylphosphine (34.0 mL, 41.8 g, 189 mmol), and 400 mL of THF total. X-ray quality crystals were grown by layering pentanes onto a saturation solution of **2** in CH_2Cl_2. Yield of **2** was 79% (27.096 g, 32.072 mmol). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.35−7.10 (45H (overlaps with residual $CHCl_3$), m, Ph), 6.00 (4H, s). $^{31}P\{^1H\}$ ($CDCl_3$, 121 MHz) δ 70.23. MS (ESI): m/z 845.27 (calcd for $C_{54}H_{45}N_2P_4^+$ $[M + H]^+$, 845.25). FT-IR (neat, cm^{-1}) 3042, 1585, 1516, 1493, 1478, 1430, 1310, 1203, 1184, 1091, 1069, 1026, 1016, 996, 923, 901, 793, 751, 739, 694, 617, 564, 519, 500, 477, 461, 425.

3.5. Synthesis of $(PtCl_2)_2$(m-tdpb) 3. $Pt(COD)Cl_2$ (102.46 mg, 0.27384 mmol) and **1** (102.50 mg, 0.12132 mmol) were weighed in air, and the solids moved to dinitrogen atmosphere glovebox. Each was dissolved in 2 mL of CH_2Cl_2 and the solution of **1** was added dropwise to the solution of $Pt(COD)Cl_2$. The faint yellow solution was then stirred overnight at room temperature. Overnight, the reaction mixture became colorless, it was then removed from the glovebox and allowed to slowly evaporate which afforded large, clear, colorless block-like crystals suitable for X-ray diffraction studies. The crystals were then ground to a powder, washed with hexanes, and dried in vacuo. Yield of **3** was 89% (0.14942 g, 0.10853 mmol). ^1H NMR (1,1,2,2-tetrachloroethane-d_2, 300 MHz) δ 7.63−7.60 (8H, m, Ph), 7.54−7.49 (16H, m, Ph), 7.35−7.31 (16H, m, Ph), 6.86 (1H, t, J = 8.0 Hz), 6.30 (2H, d, J = 8.0 Hz), 6.22 (s, 1H). $^{31}P\{^1H\}$ (CH_2Cl_2, 121 MHz) δ 23.09 (J_{Pt-P} = 3300 Hz). MS (ESI): m/z 1382.13 (calcd for $C_{54}H_{44}Cl_4N_2P_4Pt_2Li$ $[M + Li^+]^+$, 1382.06). FT-IR (neat, cm^{-1}) 3046, 1579, 1475, 1432, 1247, 1179, 1149, 1091, 1025, 982, 930, 854, 771, 742, 691, 671, 515, 500, 492, 480, 463, 442, 424.

3.6. Synthesis of $(PtCl_2)_2$(p-tdpb) 4. Complex **4** was synthesized in a manner analogous to that of **3** ($Pt(COD)Cl_2$, 104.27 mg, 0.27868 mmol; **2**, 104.43 mg, 0.12361 mmol), the deviations being the use of **2** in place of **1** as the phosphazane ligand and **4** crashed out of solution during the overnight stirring. In this case, the white solid was collected via vacuum filtration, washed with hexanes, and dried in vacuo. Yield of **4** was 86% (0.14722 g, 0.10693 mmol). ^1H NMR (1,1,2,2-tetrachloroethane-d_2, 300 MHz) δ 7.75−7.42 (40H, m, Ph), 6.21 (4H, s). $^{31}P\{^1H\}$ (1,1,2,2-tetrachloroethane-d_2, 121 MHz) δ 21.33. MS (ESI): m/z 1382.13 (calcd for $C_{54}H_{44}Cl_4N_2P_4Pt_2Li$ $[M + Li^+]^+$, 1382.06). FT-IR (neat, cm^{-1}) 1586, 1501, 1480, 1435, 1312, 1247, 1184, 1139, 1107, 998, 958, 887, 818, 748, 723, 700, 687, 617, 557, 556, 539, 519, 498, 489, 460, 440.

3.7. Synthesis of $(PdCl_2)_2$(p-tdpb) 5. Compound **5** was synthesized in a manner analogous to that of **4**, the only deviation being that $Pd(COD)Cl_2$ was used in place of $Pt(COD)Cl_2$ ($Pd(COD)Cl_2$, 100.01 mg, 0.35029 mmol; **2**, 140.81 mg, 0.16667 mmol). The yield of **5** was 82% (0.16410 g, 0.13681 mmol). ^1H NMR (DMSO-d_6, 300 MHz) δ 7.90−7.27 (m, Ph), 6.39 (4H, s). MS (ESI): m/z 1204.01 (calcd for $C_{56}H_{47}Cl_3N_3P_4Pd_2$ $[M + ACN\text{-}Cl^-]^+$, 1203.99). FT-IR (neat, cm^{-1}) 1504, 1479, 1435, 1312, 1233, 1140, 1103, 999, 954, 894, 820, 746, 722, 686, 565, 548, 511, 495, 482, 433.

3.8. General Procedure for Suzuki-Coupling Reaction. A scintillation vial, in air, was charge with 0.50 mmol arylhalide, 0.75 mmol arylboronic acid, 0.0025 mmol (unless otherwise noted, see Table 2) **5**, 1.0 mmol K_2CO_3, 2.0 mL of distilled water, and 2.0 mL of DMF. The reaction mixture was then stirred at room temperature for the indicated amount of time. The reaction mixture was then added to 15 mL of brine and extracted with diethyl ether (3 × 15 mL). The organic layer was dried over magnesium sulfate, filtered, and the volatiles were removed by rotary evaporation. The residue was then dissolved in $CDCl_3$ and subjected to ^1H NMR and GC-MS analysis. Yields were determined by NMR using an internal standard (1,1,2,2-tetrachloroethane).

4. CONCLUSIONS

The modified synthesis of two phosphazane ligands has been developed wherein purification consists of a single crystallization followed by direct isolation. Two isomeric ligands were used to form Pd_2 and Pt_2 dinuclear complexes via their straightforward combination with $M(COD)Cl_2$ (M = Pt(II) or Pd(II)). The ligands and resulting complexes were fully characterized by a suite of techniques, including FTIR and NMR (both ^1H and $^{31}P\{^1H\}$, for all except **5**, which was too insoluble to $^{31}P\{^1H\}$), ESI-mass spectrometry, SC-XRD (**2**, **3**, and **4**), and PXRD (**4** and **5**). Although the Pd_2 complex was insoluble to an extent that hindered some characterization methods, comparisons of the IR and powder X-ray diffraction patterns of the Pt_2 and Pd_2 complexes strongly supports the isostructural relationship between the two species. The activity of **5** toward Suzuki-Miyaura couplings was investigated. Yields ranged from 22% to 96%, depending on the substrates used. Regardless of substrate, all coupling reactions proceeded at room temperature, in air, in a water/DMF solvent mixture, without the addition any supporting ligands. This work contributes to the fields of cross-coupling catalysis as well as the growing field of phosphazane ligands and their applications. Furthermore, the modularity of the phosphazane platform opens the door to a rich field of chemistry and allows for enhanced tunability for targeted properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00787.

Crystallographic details, NMR, FT-IR, and MS (PDF).

Accession Codes

CCDC 1565704−1565706 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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M.R.C. designed and carried out the work and prepared the manuscript. A.E.F. collected ESI-MS characterization data. T.R.C. designed the work and prepared the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank SUNY Fredonia for use of their diffractometer. M.R.C. thanks the ACA Summer Course on Chemical Crystallography, especially Dr. Robert Papoular for helpful conversation regarding powder X-ray diffraction. We thank Cressa R. P. Fulong for acquiring the PXRD data and Dr. Sam MacMillan for collecting the data set for **4**. T.R.C. thanks the University at Buffalo and State University of New York Research Foundation for startup support funding.

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DOI: 10.1021/acs.inorgchem.8b00787
Inorg. Chem. XXXX, XXX, XXX−XXX