ARTICLE

Synthesis of Pyrrole-Based PSiP Pincer Ligands and Their Palladium, Rhodium, and Platinum Complexes

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The synthesis and coordination chemistry of a new class of silyl pincer ligand featuring pyrrole-based linkers is reported. The steric and electronic properties of these bis(phosphinopyrrole)methylsilane ligands were interrogated using their palladium, rhodium, and platinum complexes. The pyrrole-based linker attenuates the donor ability of the ligand relative to its reported 1,2-phenylene congener while maintaining a similar steric profile. Additionally, the silyl donor connected to the *N*-pyrrolyl groups exhibits a weaker *trans* influence than the analogous ligand featuring 1,2-phenylene linkers.

Introduction

Pincer ligands have played an instrumental role in the development of new catalysts and modes of bond activation.[1,2] Within this broad class of ligands, the PSiP motif (flanking phosphine donors with a central silyl donor) has become ubiquitous[3,4] because of its applications in hydrogenation,[5] hydrofunctionalization,[6] cross-coupling,[7] borylation,[8,9] small molecule fixation,[10–12] and C–H bond activation reactions.[13] The majority of studies using PSiP ligands employ 1,2-phenylene linkers connecting the central Si site with the outer phosphines ($(^{R}P_{Ph})_2Si$) (Figure 1). The modular synthesis of these ligands and the facile variation of substituents on both the silyl and phosphino donors have made this ligand class ideal for finely tuning the steric and electronic properties of complexes to optimize challenging reactions.[8,10] Variation of the linkers in PSiP ligands has been less explored, particularly regarding 1,2-arylene groups, which encourage preorganization; to our knowledge, only indole-based linkers have been incorporated ($(^{iPr}P_{In})_2Si$).[12,14] Due to this dearth of alternative linkers, the steric and electronic effects of changing arylene linkers for PSiP complexes have not been systematically studied.

2-Phosphino pyrroles have emerged as a promising building block for the construction of polydentate ligands.[15–19] To date, the effect of these fragments on the structure of pincer ligands has not been examined in depth. The PSiP class of ligands represents fertile ground for comparison because of the abundance of $(^{R}P_{Ph})_2Si$-based complexes in the literature and their continued use in catalysis. Herein, we report the synthesis and metalation of pyrrole-based PSiP pincer ligands $(^{R}P_{Py})_2Si$ with a focus on understanding the steric and electronic properties that pyrrole-based linkers impart relative to 1,2-phenylene linkers.

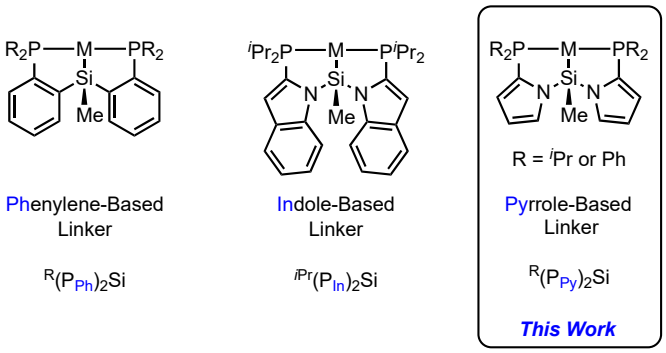

Fig. 1 PSiP ligands featuring arylene linkers.

Results and discussion

Both the ^{i}Pr- (**1**) and Ph-substituted (**2**) $(^{R}P_{Py})_2SiH$ proligands were prepared by treating dichloromethylsilane with the corresponding 2-phosphino lithium pyrrolide in diethyl ether (eq. 1). These compounds are easily purified by filtration (**1**) or crystallization from diethyl ether (**2**). The ^{1}H Si–H signals for ligands **1** and **2** are comparable to those of the analogous $(^{R}P_{Ph})_2SiH$ proligands[9,20] (δ = 6.0 to 6.7 ppm), and the ^{31}P resonances are shifted upfield approximately 20 ppm relative to their 1,2-phenylene congeners. Notably, both alkyl and aryl phosphine donors are tolerated, which demonstrates promise for the modular synthesis of related ligands.

Palladium, platinum, and rhodium chloride complexes of $(^{R}P_{Py})_2Si$ were prepared (Scheme 1) to facilitate comparisons between this new ligand and its 1,2-phenylene and indole-based analogs. Proligands **1** and **2** were both treated with $[Pd(allyl)Cl]_2$ in toluene to yield the desired products $[(^{R}P_{Py})_2Si]PdCl$ in 31% (R = ^{i}Pr, **3**) and 88% (R = Ph, **4**) yield. Ligand **2** was treated with $Pt(cod)Cl_2$ in the presence of *N*,*N*-

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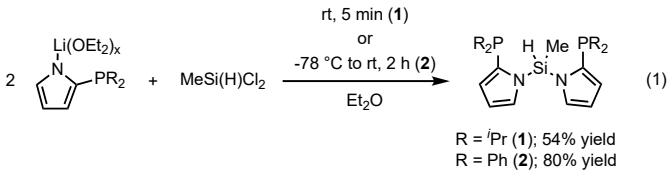
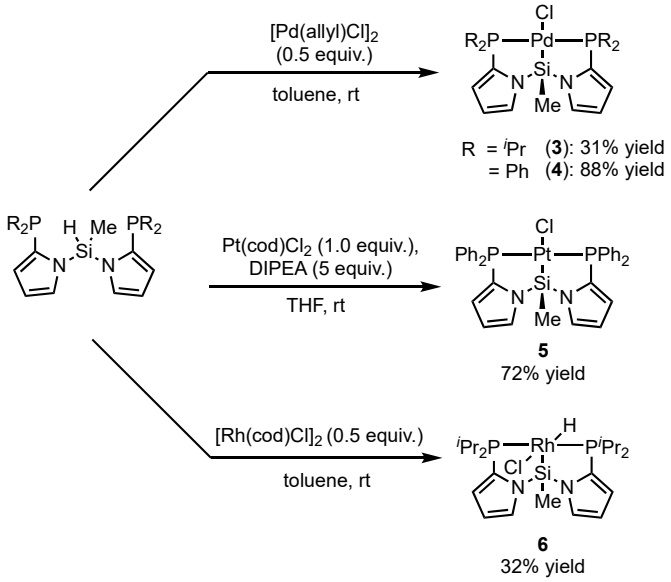


R = ^{i}Pr (**1**); 54% yield
R = Ph (**2**); 80% yield

diisopropylethylamine to yield [($^{Ph}P_{Py}$)$_2$Si]PtCl (**5**, 72% yield); the same route was not pursued with ligand **1** because the 1,2-phenylene congener [($^{iPr}P_{Ph}$)$_2$Si]PtCl is not reported in the literature. When treated with **1**, [Rh(cod)Cl]$_2$ is rapidly converted to the five-coordinate [($^{iPr}P_{Py}$)$_2$Si]Rh(H)Cl (**6**); however, the analogous reaction with **2** results in an intractable mixture of species, despite canvassing multiple rhodium-based starting materials. This result is unsurprising given the lack of structurally characterized [(^{Ph}P)$_2$X]Rh(H)Cl pincer complexes in the literature. Some of the challenges involved in the synthesis of five-coordinate Rh(III) hydrides with sterically modest pincers have been discussed.[21] All four complexes can be crystallized from dichloromethane/pentane mixtures, and the solid-state structures of **4** and **5** were obtained (Figure 2).

Complex **4** and [($^{Ph}P_{Ph}$)$_2$Si]PdCl[22] were selected to compare the structural properties of their respective ligands. There is greater pyramidalization at silicon for ^{Ph}(P_{Py})$_2$Si compared to ^{Ph}(P_{Ph})$_2$Si, both as indicated by the sum of angles at silicon (not including the Si–Me bond) as well as the distance that this atom resides above the X$_{ipso}$–M–X$_{ipso}$ (X = C or N) plane (Table 1). This distortion is also observed in complexes of ^{iPr}(P_{In})$_2$Si,[12] potentially due to the greater electronegativity of nitrogen than carbon as described by Bent's rule,[23] and in other silyl pyrrole complexes.[24] Notably, the dihedral angle defined by C–X–X–C (X = *ipso* C or N) deviates by less than a degree between the 1,2-phenylene and pyrrole-based systems; however, in the isopropyl indole-based system it is larger (14.2(2)°), potentially due to eclipsing interactions between the C7 hydrogens of the indoles. In comparing the palladium complexes, we found that the steric bulk, as determined by buried volume calculations,[25] differs by less than 1% between ^{Ph}(P_{Py})$_2$Si (**4**) and ^{Ph}(P_{Ph})$_2$Si.



Scheme 1 Synthesis of metal chlorides of $^{R}P_{Py}$Si.

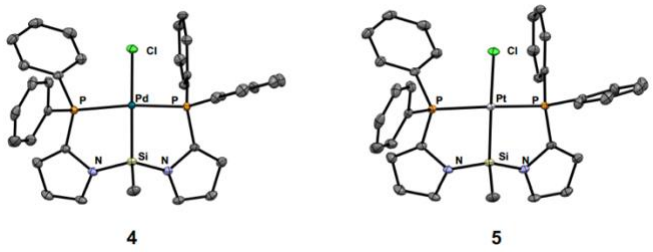


Fig. 2 Solid-state structures of **4** and **5** (50% thermal ellipsoids). All hydrogen atoms are omitted for clarity.

Taken together, these structural data suggest that the ^{R}(P_{Py})$_2$Si ligand maintains a similar steric profile to ^{R}(P_{Ph})$_2$Si but with more pyramidalization observed at silicon.

The electronic properties of our pyrrole-based ligands were examined electrochemically and by NMR spectroscopy (Table 2). The E_{red} of both the pyrrole- and 1,2-phenylene-based [^{Ph}(P_R)$_2$SiPd]Cl complexes was determined by cyclic voltammetry. The pyrrole-based analog **4** is more easily reduced (-2.5 V vs. -2.7 V), which is in agreement with our previous studies comparing pyrrole-based and 1,2-phenylene linkers in bidentate ligands[15] and is consistent with attenuated silyl donor ability due to replacement of carbon with more electronegative nitrogen.

The Pt–Si coupling as determined by ^{29}Si NMR spectroscopy indicates a stronger interaction between these two nuclei for the pyrrole-based complex (**5**, $J_{Pt–Si}$ = 1,499 Hz) than its 1,2-phenylene analog ($J_{Pt–Si}$ = 1,110 Hz) (Table 2), a phenomenon also observed in [^{iPr}(P_{In})$_2$Si]PtCl ($J_{Pt–Si}$ = 1,505 Hz).[12] This trend is corroborated by the slightly shorter Pt–Si bond length observed for **5** (2.2489(6) Å) versus with the phenylene-based ligand (2.278(2) Å)[26] (Table 1). The Pt–P coupling as observed by ^{31}P NMR spectroscopy is weaker in **5** ($J_{Pt–P}$ = 2,701 Hz) than in the 1,2-phenylene analog ($J_{Pt–P}$ = 3,074 Hz), which is consistent with the longer Pt–P bonds of the former (Table 1). It should be noted that the relative Pd–Si and Pd–P bond lengths of complex **4** and its 1,2-phenylene analog share the same pattern as their platinum congeners.

Table 1 Structural comparison of [($^{Ph}P_{Py}$)$_2$Si]MCl and [($^{Ph}P_{Ph}$)$_2$Si]MCl (M = Pd or Pt).

	[($^{Ph}P_{Py}$)$_2$Si]MCl	[($^{Ph}P_{Ph}$)$_2$Si]MCl
Σ∠Si[a]	ca. 327°	ca. 333°[b]
d Si–[X$_{ipso}$–M–X$_{ipso}$] plane (M = Pd)	0.651 Å	0.619 Å[b]
Dihedral ∠ C–X–X–C (M = Pd)	4.6(2)°	6.1(6)°[b]
%V_{Bur} (M = Pd)	71.4%	71.1%
$d_{Pd–Si}$ (M = Pd)	2.2483(5) Å	2.286(2) Å[b]
$d_{Pt–Si}$ (M = Pt)	2.2489(6) Å	2.278(2) Å[c]
$d_{Pd–P}$ (M = Pd)	2.2808(7) Å 2.2854(6) Å	2.275(2) Å[b] 2.279(2) Å[b]
$d_{Pt–P}$ (M = Pt)	2.2682(7) Å 2.2711(6) Å	2.261(2) Å[c] 2.261(2) Å[c]

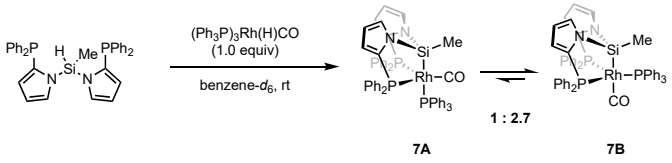
[a]Σ∠Si = sum of bond angles around silicon, excluding Me. [b]From reference 22. [c]From reference 26.

Table 2 Electronic comparison of $(^{Ph}P_{Py})_2Si$ and $(^{Ph}P_{Ph})_2Si$.

	$[(^{Ph}P_{Py})_2Si]ML_n$	$[(^{Ph}P_{Ph})_2Si]ML_n$
E_{red} (vs. $Fc^{+/0}$; PdCl)	-2.5 V	-2.7 V
J_{Pt-Si} (PtCl)	1,499 Hz	1,110 Hz [a]
J_{Pt-P} (PtCl)	2,701 Hz	3,074 Hz [a]
ν_{CO} ($Rh(CO)PPh_3$)	1,977 (**7B**), 1,932 (**7A**) cm^{-1}	1,897 cm^{-1} [b]
d_{Pd-Cl} (PdCl)	2.4119(4) Å	2.441(2) Å [c]
d_{Pt-Cl} (PtCl)	2.4156(5) Å	2.437(2) Å [d]

[a]From reference 20. [b]From reference 27. Value is for the isomer with CO in the equatorial position. [c]From reference 22. [d]From reference 26.

To complete our analysis of the electronic properties of $^{Ph}(P_{Py})_2Si$, we metalated **2** with $(Ph_3P)_3Rh(H)(CO)$ (Scheme 2) to compare $[(^{Ph}P_{Py})_2Si]Rh(CO)PPh_3$ (**7**) with the known 1,2-phenylene analog.[27] Upon mixing $(Ph_3P)_3Rh(H)(CO)$ and **2** in benzene-d_6, a pair of resonances in a 2:1 ratio consistent with the desired product (**7A**) forms by ^{31}P NMR spectroscopy. An additional pair of resonances emerges within minutes (**7B**). The relative ratio of these complexes changes over time and reaches an equilibrium in which **7B** is favored. Crystallization results in isolation of isomer **7B** and structural confirmation that CO is *trans* to the silyl donor with all phosphine donors occupying equatorial positions (Figure 3). Assignment of crystalline material as **7B** is based on analysis of both IR and ^{31}P NMR data in relation to analogous compounds reported in the literature (see ESI). For example, the $^2J_{P\text{-}PPh3}$ value in **7B** (88 Hz) is expected to be higher than in **7A** (38 Hz) since PPh_3 in **7B** is roughly in plane with the other two P donors, whereas in **7A**, it is *cis* to both. Dissolution of crystals of **7B** in benzene-d_6 leads to equilibration to a mixture of **7A** and **7B**. It appears that **7A** forms kinetically but isomerizes to **7B**, the thermodynamic product in benzene-d_6, albeit with a relative energy less than 1 kcal/mol lower than that of **7A**.[28] In contrast, Nakazawa and co-workers observed $[(^{Ph}P_{Ph})_2Si]Rh(CO)PPh_3$ where CO is exclusively in the equatorial position (Table S1).[27] This result suggests that the silyl donor of $(^{Ph}P_{Py})_2Si$ imparts a weaker *trans* influence than does that of $(^{Ph}P_{Ph})_2Si$. Decreased *trans* influence is further corroborated by the shorter M–Cl bonds for complexes **4** (2.4119(4) Å) and **5** (2.4156(5) Å) relative to their 1,2-phenylene analogs (2.441(2) Å[22] and 2.437(2) Å,[26] respectively). In fact, the Pd–Cl bond length of complex **4** indicates that the silyl donor imparts a weaker *trans* influence than does a triorganogermyl (2.4219(11) Å) or triorganostannyl donor (2.4270(8) Å) in a similar $(^{Ph}P_{Ph})_2X$ motif[22,29] or the silyl donor of $(^{iPr}P_{In})_2Si$ (2.4256(5) Å).[12] Additionally, **7A** evinces considerably weaker backbonding between rhodium and CO (ν_{CO} = 1,932 cm^{-1}) than in the analogous isomer of $[(^{Ph}P_{Ph})_2Si]Rh(CO)PPh_3$ (ν_{CO} = 1,897 cm^{-1}), which is consistent with the weaker donating ability of $(^{Ph}P_{Py})_2Si$.



Scheme 2 Synthesis and isomerization of **7A**/**7B**.

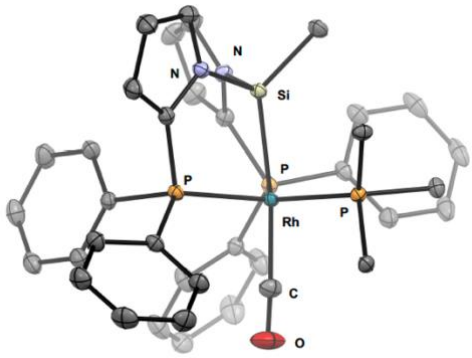


Fig. 3. Solid-state structure of **7B** (50% thermal ellipsoids). Hydrogens and the phenyl groups of PPh_3 (except for the *ipso* carbons) are omitted for clarity.

Conclusions

In conclusion, we have developed a new family of PSiP ligands featuring pyrrole-based linkers. Our structural, electrochemical, and spectroscopic analyses indicate that these ligands maintain a steric profile similar to that of their 1,2-phenylene-based analogs but are weaker donors. This attenuated donation is manifested in more facile reduction of $[(^{Ph}P_{Py})_2Si]PdCl$ compared to $[(^{Ph}P_{Ph})_2Si]PdCl$, decreased *trans* influence in multiple complexes compared to their 1,2-phenylene-based analogs, and decreased backbonding in a rhodium carbonyl complex. The $(^{R}P_{Py})_2Si$ motif fills an electronic niche in the ever-growing family of PSiP ligands that may be beneficial in future catalyst design.

Experimental

General considerations. Unless specified otherwise, all manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk line or glovebox techniques. All glassware was oven-dried overnight at greater than 110 °C and cooled under vacuum prior to use. For chemistry involving $(^{iPr}P_{Py})_2Si$: diethyl ether, dichloromethane, toluene, and pentane were dried and deoxygenated (by purging) using an Innovative Technologies MD-5 solvent purification system and stored over molecular sieves in an argon-filled glovebox. For chemistry involving $(^{Ph}P_{Py})_2Si$: reaction solvents were collected from a Glass Contour Solvent Purification System, degassed, and stored over 3 Å molecular sieves in a nitrogen-filled glovebox. For chemistry involving ligand $(^{iPr}P_{Py})_2Si$: $CDCl_3$ was dried over CaH_2 and C_6D_6 was dried over NaK/Ph_2CO/18-crown-6. Both solvents were distilled or vacuum transferred and stored over molecular sieves in an argon-filled glovebox. For chemistry involving $(^{Ph}P_{Py})_2Si$: CD_2Cl_2 and C_6D_6 were degassed and stored over 3Å molecular sieves in a nitrogen-filled glovebox. Lithium 2-(diisopropylphosphino)pyrrolide•diethyl ether,[30] lithium 2-

(diphenylphosphino)pyrrolide,[31] bis(2-diphenylphosphinophenyl)methylsilyl palladium chloride,[20] and $[Rh(cod)Cl]_2$[32] were prepared according to literature procedures. Tetrabutylammonium hexafluorophosphate ([*n*-$Bu_4N][PF_6$]) for electrochemical studies was recrystallized three times from ethanol. $[Pd(allyl)Cl]_2$ (Strem), dichloromethylsilane (Sigma), and $Pt(cod)Cl_2$ (Strem) were purchased from commercial suppliers and used as received. $RhH(CO)(PPh_3)_3$ was purchased from commercial suppliers and washed with diethyl ether to remove triphenylphosphine oxide prior to use. *N*,*N*-diisopropylamine (DIPEA, Oakwood) was distilled from CaH_2 prior to use.

Spectroscopy. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} spectra were collected on Avance 400, Avance 500, and Inova 500 NMR spectrometers at ambient temperature. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference (^{1}H NMR: δ 7.16 for C_6D_6, 7.26 for $CDCl_3$, and 5.32 for CD_2Cl_2; ^{13}C NMR: δ 128.06 for C_6D_6, 77.16 for $CDCl_3$, and 53.84 for CD_2Cl_2). ^{31}P{^{1}H} and ^{29}Si{^{1}H} spectra were referenced using the absolute reference function of the Mnova 9.0.1 NMR software package or 85% H_3PO_4 as an external standard. ^{13}C resonances for complexes **4** and **5** were identified based on ^{13}C-DEPT and ^{1}H-^{13}C HSQC data. Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer.

Electrochemistry. Electrochemical experiments were performed in a nitrogen-filled glovebox in tetrahydrofuran (THF) with 0.1 M [*n*-$Bu_4N][PF_6$] and 1 mM analyte. A CH Instruments 660E potentiostat was used with a 3 mm glassy carbon working electrode and a platinum wire auxiliary electrode. The silver wire reference electrode was referenced to the ferrocene-ferrocenium couple.[33]

Elemental Analysis. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ) or Midwest Microlab, LLC (Indianapolis, IN).

Synthesis

Bis(2-diisopropylphosphino-pyrrole)methylsilane (1). Dichloromethylsilane (64 µL, 0.61 mmol) was added as a single portion, via syringe, to a room temperature solution of lithium-diisopropylphosphinopyrrole•2.2diethyl ether (434 mg, 1.23 mmol) in ether (7 mL). Upon mixing, the solution becomes cloudy as a white precipitate formed. The solution was stirred for five minutes and was then filtered through Celite to remove lithium chloride. The volatiles were removed under reduced pressure to afford the title compound as an oil of ca. 90% purity (based on integration of the ^{31}P{^{1}H} NMR spectrum of the isolated crude) that was used without further purification (150 mg, 0.330 mmol based on 90% purity, 54% yield). **^{1}H NMR** (400 MHz, C_6D_6): δ 6.90 (m, 2H, pyrrole), 6.63 (m, 1H, Si*H*), 6.56 (dd, *J* = 3.2, 1.2 Hz, 2H, pyrrole), 6.46 (t, *J* = 3.2 Hz, 2H, pyrrole), 1.98 – 1.81 (m, 4H, C*H*Me$_2$), 1.06 – 0.93 (m, 24H, CH*Me*$_2$), 0.79 (dt, *J* = 2.9, 1.4 Hz, 3H, SiC*H*$_3$); **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 131.9 (d, *J* = 8.3 Hz, pyrrole), 128.9 (dd, *J* = 5.9, 2.4 Hz, pyrrole), 120.4 (d, *J* = 4.0 Hz, pyrrole), 112.4 (pyrrole), 25.2 (d, *J* = 8.4 Hz, *C*HMe$_2$), 24.9 (d, *J* = 7.6 Hz, *C*HMe$_2$), 20.3 (d, *J* = 2.2 Hz, CH*Me*$_2$), 20.1 (d, *J* = 2.5 Hz, CH*Me*$_2$), 19.7 (d, *J* = 10.0 Hz, CH*Me*$_2$), 19.3 (d, *J* = 8.2 Hz, CH*Me*$_2$), -0.3 (t, *J* = 8.3 Hz, SiCH$_3$); **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): δ -17.1 (s).

Bis(2-diphenylphosphino-pyrrole)methylsilane (2). A 50-mL Schlenk flask was charged with lithium-2-diphenylphosphinopyrrolide (309 mg, 1.20 mmol) and diethyl ether (15 mL). The reaction flask was cooled to -78 °C, at which time dichloromethylsilane (63 µL, 0.60 mmol) was added to the solution dropwise via syringe. The reaction mixture was stirred for 2 h at room temperature and became cloudy as it warmed to room temperature. Removal of volatiles under vacuum produced a colorless foam, which was then filtered through a syringe filter with diethyl ether to remove lithium chloride. Crystallization from a concentrated ether solution produced colorless crystals that were washed with pentane (*ca.* 1 mL) and exposed to vacuum to yield the title compound (264 mg, 0.49 mmol, 80% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.35 – 7.17 (overlapping resonances, 20H, C_6H_5), 6.96 (m, 2H, pyrrole), 6.30 (vt, *J* = 3.0 Hz, 2H, pyrrole), 6.17 (dd, *J* = 3.3, 1.3 Hz, 2H, pyrrole), 6.05 (m, 1H, Si*H*), 0.91 (dt, *J* = 3.0 Hz, 1.4 Hz, 3H, SiC*H*$_3$); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 137.8 (d, *J* = 5.5 Hz, aromatic), 133.5 (vt, *J* = 19.4 Hz, aromatic), 132.8 (aromatic), 129.0–128.5 (two overlapping resonances, aromatic), 123.2 (aromatic), 113.0 (aromatic), -0.6 (t, *J* = 7.7 Hz, Si*C*H$_3$); **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ -30.0 (s).

[(^{iPr}P$_{Py}$)$_2$Si]PdCl (3). $[Pd(allyl)Cl]_2$ (95 mg, 0.26 mmol) was added to a solution of proligand **1** (223 mg, 0.491 mmol based on 90% ligand purity) in toluene (2 mL) at room temperature and the reaction mixture was stirred for 5 min. Volatiles were removed from the solution under reduced pressure and the product was washed twice with pentane. The product can be further purified by recrystallization from DCM/pentane at -38 °C to yield light yellow crystals (80 mg, 0.15 mmol, 31%). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.06 (m, 2H, pyrrole), 6.66 (t, *J* = 2.9 Hz, 2H, pyrrole), 6.40 (d, *J* = 3.3 Hz, 2H, pyrrole), 2.98 (tsep, *J* = 7.0, 1.9 Hz, 2H, C*H*Me$_2$), 2.15 (m, 2H, C*H*Me$_2$,), 1.30 (m, 12H, CH*Me*$_2$,), 1.05 (dt, *J* = 7.2, 7.2 Hz, 6H, CH*Me*$_2$,), 0.89 (td, *J* = 8.8, 6.9 Hz, 6H, CH*Me*$_2$,), 0.53 (s, 3H, SiC*H*$_3$); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 128.1 (t, *J* = 29.2 Hz, pyrrole), 125.7 (t, *J* = 6.7 Hz, pyrrole), 118.5 (t, *J* = 2.7 Hz, pyrrole), 116.4 (t, *J* = 2.7 Hz, pyrrole), 27.5 (t, *J* = 14.4 Hz, *C*HMe$_2$), 26.0 (t, *J* = 14.0 Hz, *C*HMe$_2$), 19.9 (t, *J* = 2.0 Hz, CH*Me*$_2$), 19.3 (t, *J* = 1.8 Hz, CH*Me*$_2$), 19.25 (t, *J* = 3.1 Hz, CH*Me*$_2$), 17.7 (CH*Me*$_2$), 9.1 (SiCH$_3$); **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): 35.1 (s); **EA**: Anal. calcd. for $C_{21}H_{37}ClN_2P_2PdSi$, Found (Calculated): C, 45.81 (45.91); H, 6.62 (6.79); N, 4.96 (5.10).

[(^{Ph}P$_{Py}$)$_2$Si]PdCl (4). $[Pd(allyl)Cl]_2$ (18 mg, 0.050 mmol) was added to a solution of proligand **2** (55 mg, 0.10 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 16 h. The solution was concentrated and filtered through a syringe filter using DCM. Removal of volatiles produced a yellow solid. Crystallization by layering a DCM solution of the complex

with pentane at room temperature produced the desired product as yellow crystals (60 mg, 0.088 mmol, 88% yield). X-ray quality crystals were grown in the same manner. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.90 – 7.82 (m, 4H, C_6H_5), 7.69 – 7.61 (m, 4H, C_6H_5), 7.55 – 7.34 (overlapping resonances, 14H, C_6H_5 + pyrrole), 6.76 (vt, *J* = 3.0 Hz, 2H, pyrrole), 6.72 – 6.67 (m, 2H, pyrrole), 0.36 (m, 3H, SiCH_3); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 133.7 (vt, *J* = 6.9 Hz, aromatic), 133.7 (vt, *J* = 7.8 Hz, aromatic) 132.2 (vt, *J* = 27.5 Hz, *ipso* aromatic), 131.9 (vt, *J* = 26.0 Hz, *ipso* aromatic), 131.3 (s, aromatic), 131.0 (s, aromatic), 130.4 (vt, *J* = 37.1 Hz, *ipso* aromatic), 129.4 (vt, *J* = 5.5 Hz, aromatic), 128.7 (vt, *J* = 5.6 Hz, aromatic), 126.9 (vt, *J* = 7.4 Hz, aromatic), 119.4 (vt, 3.3 Hz, aromatic), 119.4 (vt, 3.1 Hz, aromatic), 7.5 (t, *J* = 2.6 Hz, CH_3); **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 10.4 (s); **EA**: Anal. calcd. for $C_{33}H_{29}ClN_2P_2PdSi$, Found (Calculated): C, 56.70 (57.82); H, 4.28 (4.26); N, 4.20 (4.09). Combustion analysis was consistently low in carbon despite multiple attempts.

[(^{Ph}P$_{Py}$)$_2$Si]PtCl (5). Diisopropylethylamine (87 µL, 0.50 mmol) was added to a solution of proligand **2** (55 mg, 0.10 mmol) in THF (2 mL). The solution was stirred for one minute at which time Pt(cod)Cl_2 (37 mg, 0.10 mmol) was transferred to the reaction mixture using THF (3 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting clear, pale yellow solution was then filtered through a plug of silica (4 cm high in a pipette) to remove the ammonium salt. Volatiles were removed under reduced pressure to afford an off-white residue, which was washed with pentane (3 × 1 mL) and exposed to vacuum again. The desired product was isolated as off-white crystals (56 mg, 0.072 mmol, 72% yield) by layering a DCM solution of the title compound with pentane at 25 °C twice. X-ray quality crystals were grown in the same manner. *Note*: It is critical that Pt(cod)Cl_2 is added to a solution of the proligand and amine. The proligand and Pt(cod)Cl_2 form an undesired product in the absence of base (see below). This byproduct can be suppressed to less than 5% using the above procedure. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.88 – 7.79 (m, 4H, C_6H_5), 7.65 – 7.57 (m, 4H, C_6H_5), 7.55 – 7.35 (overlapping resonances, 14H, C_6H_5 + pyrrole), 6.82 (dd, *J* = 3.4, 2.5 Hz, 2H, pyrrole), 6.62 (dd, *J* = 3.3, 1.0 Hz, 2H, pyrrole), 0.32 (s with Pt satellites, $J_{H\text{-}Pt}$ = 19.4 Hz, 3H, SiCH_3); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ 133.8 (vt, *J* = 6.6 Hz, aromatic), 133.7 (vt, *J* = 7.5 Hz, aromatic), 132.2 (vt, *J* = 29.3 Hz, *ipso* aromatic), 131.4 (s, aromatic), 131.2 (vt, *J* = 32.0 Hz, *ipso* aromatic), 131.2 (s, aromatic), 130.5 (vt, *J* = 43.3 Hz, *ipso* aromatic), 129.3 (vt, *J* = 5.7 Hz, aromatic), 128.6 (vt, *J* = 5.7 Hz, aromatic), 126.5 (vt, *J* = 6.3 Hz, aromatic), 119.1 (vt, *J* = 4.6 Hz, aromatic), 118.8 (vt, *J* = 3.7 Hz, aromatic), 6.37 (s with Pt satellites, J_{C-Pt} = 110.2 Hz, SiCH_3); **^{29}Si{^{1}H} NMR** (99 MHz, CD_2Cl_2): δ 34.8 (t with platinum satellites, *J* = 9.8 Hz, J_{Si-Pt} = 1,499 Hz); **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 16.1. (s with Pt satellites, J_{P-Pt} = 2,701 Hz); **EA**: Anal. calcd. for $C_{33}H_{29}ClN_2P_2PtSi$, Found (Calculated): C, 51.00 (51.20); H, 3.85 (3.78); N, 3.51 (3.62).

***cis*-Bis[(2-diphenylphosphino)pyrrole] platinum dichloride.** The crude material that resulted from initial attempts to synthesize complex 5 contained significant quantities of the title compound as an impurity. X-ray quality crystals of the compound were grown by layering a DCM solution of the crude material with pentane. Crude NMR spectra and X-ray data of these crystals are provided to aid in identifying this impurity. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 10.68 (br s, 2H, N–H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.21 (overlapping resonances, aromatic), 7.17 – 7.01 (overlapping resonances, aromatic), 6.24 (m, 2H, pyrrole), 5.86 (m, 2H, pyrrole); **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): -2.86 (s with Pt satellites, J_{P-Pt} = 3,697 Hz).

[(^{iPr}P$_{Py}$)$_2$Si]Rh(H)Cl (6). [Rh(cod)Cl]$_2$ (128 mg, 0.26 mmol) was added to a solution of proligand **1** (218 mg, 0.473 mmol based on 90% purity) in toluene (5 mL) at room temperature and stirred for 5 min. The title complex is formed in the time of mixing. Volatiles were removed from the solution under vacuum to afford an orange oil. Excess ligand was removed by washing the crude product with pentane to afford the product as a yellow solid. The product can be further purified by recrystallization from DCM/pentane at -38 °C (82 mg, 0.15 mmol, 32%). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.05 (m, 2H, pyrrole), 6.60 (t, *J* = 2.9 Hz, 2H, pyrrole), 6.42 (d, *J* = 3.2 Hz, 2H, pyrrole), 2.68 (sep, *J* = 7.0 Hz, 2H, C*H*Me$_2$), 2.15 (m, 2H, C*H*Me$_2$,), 1.27 – 1.17 (m, 12H, CH*Me*$_2$,), 1.02 (dvt, *J* = 6.9, 6.9 Hz, 6H, CH*Me*$_2$,), 0.95 (dt, *J* = 9.2, 7.2 Hz, 6H, CH*Me*$_2$,), 0.68 (s, 3H, SiCH_3,), -18.07 (dt, *J* = 22.6, 13.6 Hz, 1H, Rh*H*); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 129.4 (appt, *J* = 30.9 Hz, pyrrole), 125.5 (t, *J* = 5.2 Hz, pyrrole), 116.7 (pyrrole), 116.2 (t, *J* = 2.9 Hz, pyrrole), 26.8 (t, *J* = 14.9 Hz, *C*HMe$_2$), 24.7 (t, *J* = 13.2 Hz, *C*HMe$_2$), 20.5 (CH*Me*$_2$), 19.7 (CH*Me*$_2$), 19.1 (t, *J* = 3.6 Hz, CH*Me*$_2$), 17.1 (CH*Me*$_2$), 8.2 (Si*C*H$_3$); **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): δ 39.8 (dd, *J* = 107.5, 12.9 Hz); **EA**: Anal. calcd. for $C_{21}H_{38}ClN_2P_2RhSi$, Found (Calculated): C, 45.76 (46.12); H, 6.89 (7.00); N, 4.94 (5.12).

[(^{Ph}P$_{Py}$)$_2$Si]Rh(CO)PPh$_3$ (7A/7B). A scintillation vial was charged with $(Ph_3P)_3Rh(H)CO$ (46 mg, 0.050 mmol), toluene (3 mL), and proligand **2** (27 mg, 0.050 mmol). The reaction mixture was stirred for 22 h at rt, during which time the reaction mixture became pale yellow and homogeneous. The reaction mixture was concentrated, and the resulting residue was suspended in hexane (5 mL) with stirring. The vial was then stored at -35 °C to ensure precipitation of product. The supernatant was decanted to remove triphenylphosphine. The precipitate was washed with chilled hexane (1 mL) and residual solvent was removed under vacuum. The title compound was obtained by layering a concentrated DCM solution of **7A**/**7B** with pentane at room temperature (29 mg, 0.031 mmol, 62% yield). X-ray quality crystals of 7B were isolated by this crystallization method. The title compounds were allowed to equilibrate in CD_2Cl_2 for several days before spectral data were obtained. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.63 – 7.55 (m, 4H, C_6H_5 of **7B**), 7.32 – 6.95 (overlapping resonances, aromatic resonances of **7A** and **7B**), 6.94 – 6.79 (overlapping resonances, aromatic resonances of **7A** and **7B**), 6.74 – 6.63 (overlapping resonances, aromatic resonances of **7A** and **7B**), 6.62 – 6.59 (m, 2H, pyrrole of **7B**), 6.59 – 6.54 (m, 2H, pyrrole of **7A**), 6.47 – 6.45 (m, 2H, pyrrole of **7A**), 6.44 (dd, *J* = 3.3, 1.1 Hz, 2H, pyrrole of **7B**), 6.13 (d, *J* = 2.8 Hz, 3H, pyrrole of **7A**), 1.10 (d, *J* = 1.7 Hz, 3H, SiCH_3 of **7A**), -0.05 (d, *J* = 1.8 Hz, 3H, SiCH_3 of **7B**); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2):

δ 140.5 (t, *J* = 21.8 Hz, aromatic), 139.6 – 138.1 (overlapping resonances, aromatic), 134.5 (d, *J* = 12.8 Hz, aromatic), 133.6 (d, *J* = 13.8 Hz, aromatic), 133.4 (t, *J* = 8.1 Hz, aromatic), 132.9 (t, *J* = 7.8 Hz, aromatic), 132.7 (t, *J* = 6.5 Hz, aromatic), 131.1 (t, *J* = 6.4 Hz, aromatic), 129.5 (d, *J* = 1.9 Hz, aromatic), 129.2 (aromatic), 128.9 (aromatic), 128.6 (aromatic), 128.3 (t, *J* = 5.2 Hz, aromatic), 128.1 – 127.9 (overlapping resonances, aromatic), 127.8 (d, *J* = 9.4 Hz, aromatic), 125.5 (t, *J* = 8.0 Hz, aromatic), 124.5 (t, *J* = 6.8 Hz, aromatic), 117.0 –116.8 (m, aromatic), 116.57 (d, *J* = 38.6 Hz, aromatic), 114.7 (aromatic), 5.51 – 5.30 (m, Si*C*H$_3$), 5.17 – 5.01 (m, Si*C*H$_3$); **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ 37.5 – 34.4 (m, *P*Ph$_3$ of **7B**), 30.8 (dt, *J* = 91.6, 38.2 Hz, *P*Ph$_3$ of **7A**), 26.3 (dd, *J* = 138.4, 88.0 Hz, *P*Ph$_2$ of **7B**), 15.3 (dd, *J* = 134.2, 38.2 Hz, *P*Ph$_2$ of **7A**); **IR** (ATR, cm^{-1}): 1977 (ν_{CO}, **7B**), 1932 (ν_{CO}, **7A**). *Note:* Combustion analysis of **7A**/**7B** failed on multiple attempts despite repeated crystallization and filtration. NMR spectra (^{1}H, ^{13}C, ^{31}P) are provided as evidence of purity and identity of the bulk material. *Note:* The title compounds exhibit low solubility in common NMR solvents. The ^{13}C{^{1}H} NMR spectrum provided is of a saturated solution collected over a prolonged period.

Author Contributions

JFV, MNC, NKS, and MWJ conducted all experimental work. NB collected and analyzed all crystallographic data. MWJ and OVO supervised this work and wrote the original draft. All authors were involved in the revision and editing process.

Conflicts of interest

There are no conflicts to declare.

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