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Nickel(II) Complexes Containing a Pyrrole−Diphosphine Pincer Ligand

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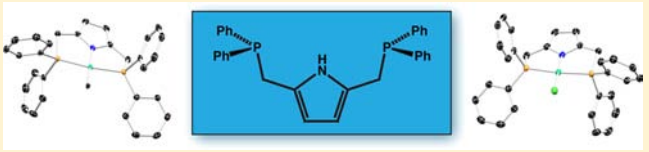
Supporting Information

ABSTRACT: A new pincer ligand, $(P_2^{Ph}Pyr)^-$, based on the anion of 2,5-bis[(diphenylphosphino)methyl]pyrrole has been prepared in four steps from pyrrole. The ligand undergoes oxidation to diphosphine oxide under ambient conditions and was therefore isolated as its borane adduct, $H(P_2^{Ph}Pyr)\cdot 2BH_3$ (**2**). Delivery of the ligand to nickel(II) was accomplished by the direct reaction of $NiCl_2$ with **2** in the presence of Et_2NH to afford $[NiCl(P_2^{Ph}Pyr)]$. Salt metathesis reactions of the chloro complex afford new compounds including $[Ni(CH_3)(P_2^{Ph}Pyr)]$ and $[Ni(NCCH_3)(P_2^{Ph}Pyr)](OTf)$. In all cases, the ligand gives rise to diamagnetic square-planar complexes, which have been fully characterized in solution and the solid state. All complexes examined display an irreversible oxidation to nickel(III) according to cyclic voltammetry. Reduction of the chloro complex in dichloromethane results in an electrocatalytic process, whereas reduction in tetrahydrofuran leads to the irreversible formation of a nickel(I) species.



INTRODUCTION

Pincer ligands are used to great effect in modern coordination chemistry to realize new forms of reactivity and to design better catalysts.[1−4] In particular, pincer ligands featuring a PNP ligating motif have been demonstrated to support a variety of interesting transition-metal complexes displaying unique geometries and small-molecule reactivity.[5−21] In many instances, the enhanced reactivity of these metal complexes results from the rigid meridional geometry imposed by the pincer ligand.[22] Despite the large diversity of pincer ligands reported to date, those based on a central pyrrole moiety have received less attention than those containing a pyridine, aryl, or amine unit.[23−38] Pyrrole is a versatile ligand that finds widespread use in coordination chemistry with both high- and low-oxidation-state metals.[39,40] The attenuated π basicity of the pyrrolic lone pair is significant in this respect, allowing for binding to metal ions with filled or partially filled d_π orbitals. In addition, the potential for pyrrole-centered redox events[41,42] makes pincer ligands containing these units especially intriguing given the beneficial ligand-centered redox and tautomerization demonstrated by pincer ligands reported by the groups of Chirik and Milstein.[43,44]

Nonmacrocyclic chelates based on pyrrole have been shown to be effective ligands for a variety of transition-metal ions. Bidentate ligands featuring phosphinopyrroles find precedent in nickel chemistry, suggesting that an analogous pincer-type ligand would be successful in supporting various metal complexes.[45] Furthermore, related diphosphinocarbazole ligands have found use in lanthanide chemistry (scandium, yttrium, and erbium), although the larger bite angle of these systems is likely incompatible with coordination to smaller 3d metals.[46] We therefore sought to prepare a new pincer ligand containing ligating phosphine atoms and a central pyrrole linked by a methylene group, reasoning that the resulting chelate angle would be ideal for transition-metal ions. We report here our findings concerning a new class of PNP ligand, $(P_2^{Ph}Pyr)^-$ ($P_2^{Ph}Pyr$ = anion of 2,5-bis[(diphenylphosphino)-methyl]pyrrole; Scheme 1), and its coordination chemistry with nickel(II).

RESULTS AND DISCUSSION

The preparation of $H(P_2^{Ph}Pyr)$ (**3**) proceeded by the addition of 2 equiv of diphenylphosphine to the previously reported pyrrole-2,5-dicarboxaldehyde[47] (Scheme 1) following a procedure adapted from the synthesis of phosphinopyrrole reported by Bochmann et al.[45] The resulting phosphine oxide (**1**) could be prepared on gram scales in satisfactory yield without chromatographic purification. The ^{31}P NMR spectrum of **1** displays a single resonance at 27.5 ppm in chloroform-*d* with a J_{PH} = 12 Hz coupling to the protons of the methylene linker. The reduction of **1** in tetrahydrofuran (THF) with $LiAlH_4$/$CeCl_3$ produced the desired diphosphine without requiring protection of the pyrrolic nitrogen atom. Reactions carried out in the absence of $CeCl_3$ resulted in incomplete reduction, likely because of inactivation of $LiAlH_4$ by coordination of **1**.[48,49]

The colorless diphosphinopyrrole, **3**, is not air-stable as judged by the reappearance of resonances for **1** in the ^1H and ^{31}P NMR spectra of solutions exposed to ambient conditions. Furthermore, attempted chromatographic purification of **3** on silica resulted in the isolation of diphosphine oxide. As a result, purification and complete characterization of this species was not pursued. As an alternative, the borane adduct, $H(P_2^{Ph}Pyr)\cdot 2BH_3$ (**2**), was prepared by the addition of $NaBH_4$

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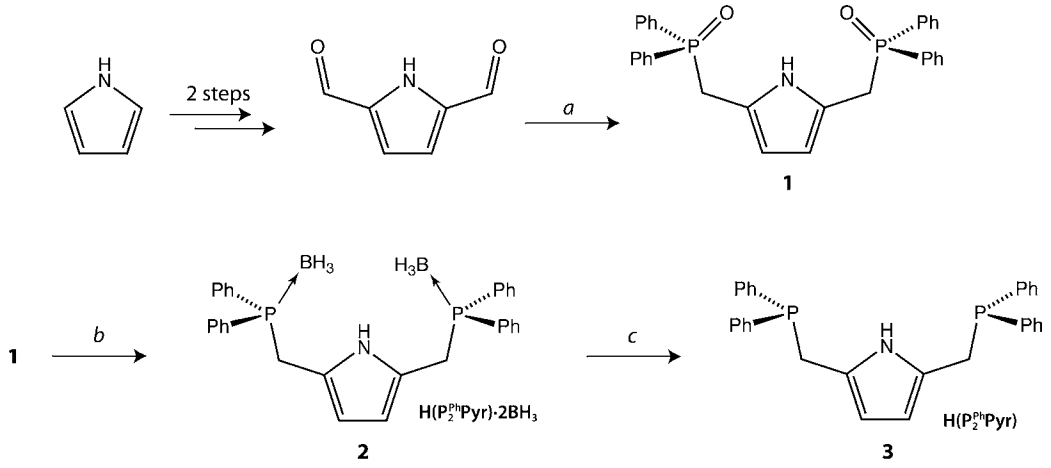
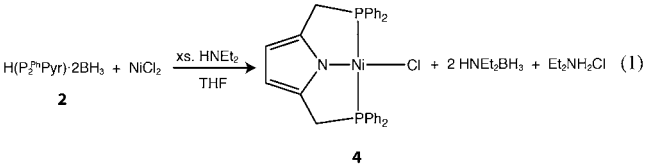
Scheme 1. Synthesis of 3



(*a*) 2 equiv. $PHPh_2$, HCl/CH_3OH; (*b*) $LiAlH_4/CeCl_3/NaBH_4$, THF; (*c*) MeOH/toluene

to the reduction conditions (Scheme 1). Compound **2** proved to be indefinitely stable and could be purified by alumina chromatography. The spectroscopic features of **2** are in line with the structure displayed in Scheme 1 and consistent with other phosphinoboranes[50,51] including those that have been subjected to structural characterization.[52−54] The ^{31}P NMR spectrum of **2** displays a broad resonance at 16.1 ppm in benzene-d_6 consistent with reduction of the two phosphorus atoms and coordination of the BH_3 group. The free diphosphine **3** could be easily accessed from **2** by refluxing the compound in methanol under nitrogen. The spectroscopic features of **2** are in line with that expected for a diphosphine, displaying a ^{31}P chemical shift of −16.2 ppm for the phosphorus atoms.

In order to deliver $(P_2^{Ph}Pyr)^-$ to nickel(II), we attempted the reaction of **2** with anhydrous $NiCl_2$ in the presence of several equivalents of $HNEt_2$. It was our hope that the diethylamine would serve to both deprotect the phosphinoborane groups and remove the pyrrolic NH proton. Gratifyingly, heating a mixture of anhydrous $NiCl_2$ in the presence of 1 equiv of **2** and an excess of $HNEt_2$ in THF afforded the desired nickel(II) complex, $[NiCl(P_2^{Ph}Pyr)]$ (**4**), as an orange solid in 62% yield (eq 1). The reaction of compound **2** with excess Et_2NH in the



2 **4**

absence of $NiCl_2$ produced free diphosphine **3**, as judged by ^1H NMR spectroscopy, confirming initial deprotection prior to metalation. As an alternative delivery route, the reaction of $NiCl_2$ with $Li(P_2^{Ph}Pyr)$, generated in situ from the reduction of **1** with $LiAlH_4/CeCl_3$, was examined. This route led to the same nickel(II) chloride complex, albeit in lower yields. Additionally, complex **4** could also be prepared by the direct reaction of **3** with $NiCl_2$ in the presence of Et_3N.

Complex **4** is an orange, air-stable crystalline solid that is soluble in THF, CH_2Cl_2, and aromatic solvents. ^1H NMR spectra in benzene-d_6 indicate a diamagnetic compound, displaying a virtual triplet for the methylene protons of the $P_2^{Ph}Pyr$ ligand, as has been observed in other $Ni^{II}PNP$ systems.[55] The ^{31}P NMR resonance for complex **4** appears at 30.3 ppm, substantially downfield of that observed for **3**.

Crystallization of **4** from benzene/pentane afforded material suitable for X-ray diffraction. The solid-state structure of the complex is depicted in Figure 1 (crystallographic and metric

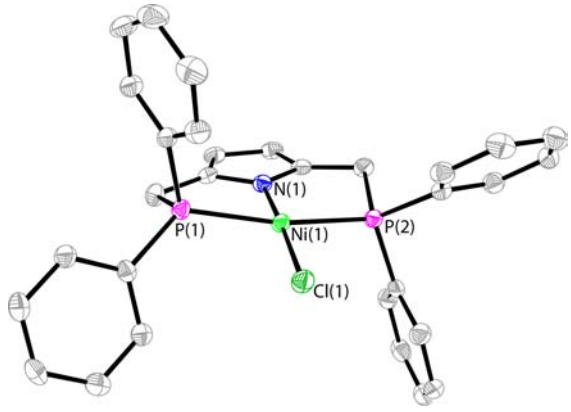


Figure 1. Thermal ellipsoid drawing (50%) of **4**. Hydrogen atoms are omitted for clarity. See Table 2 for selected bond lengths and angles.

parameters can be found in Tables 1 and 2, respectively). The geometry about nickel(II) is planar [sum of the angels about Ni = 360.3(1)°] with a slight contraction of the P−Ni−N bond angles [avg = 83.4(1)°] away from 90°. The pyrrole group is canted at an angle of 13.3° with respect to the coordination plane but remains planar. The Ni−Cl distance of 2.1768(9) Å is in the range encountered for similar square-planar nickel(II) complexes, as is the average Ni−P distance of 2.20 Å.[45] By contrast, the Ni−N distance of 1.856(2) Å is somewhat shorter than other reported nickel pyrrolide compounds.[45,56] In summary, the bond metrics indicate that $(P_2^{Ph}Pyr)^-$ is capable of supporting square-planar complexes of nickel(II) with minimal geometric distortion.

The chloride ligand in **4** can be replaced in straightforward fashion via salt metathesis reactions (Scheme 2). Alkylation of complex **4** with MeMgCl in THF produced the methyl

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Table 1. Crystallographic Data and Refinement Parameters[a]

	4	5	6
empirical formula	$C_{30}H_{26}ClNNiP_2$	$C_{31}H_{29}NNiP_2$	$C_{33}H_{29}F_3N_2NiO_3P_2S$
fw (g/mol)	556.62	536.20	694.25
temperature (K)	98(2)	98(2)	98(2)
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
unit cell dimens (Å, deg)			
a (Å)	14.391(6)	14.261(2)	9.3166(9)
b (Å)	16.192(6)	16.269(2)	23.499(2)
c (Å)	11.431(5)	11.528(2)	15.009(1)
β (deg)	107.556(7)	106.917(8)	103.738(7)
volume (Å^3)	2539.6(2)	2558.8(6)	3191.8(5)
Z	4	4	4
calcd density (g/cm^3)	1.456	1.392	1.445
abs coeff (mm^{-1})	1.02	0.904	0.826
F(000)	1152	1120	1430
cryst size (mm^3)	0.35 × 0.24 × 0.03	0.45 × 0.16 × 0.15	0.20 × 0.19 × 0.09
θ range (deg)	2.25−26.00	3.11−25.50	3.04−25.50
limiting indices	$-17 \le h \le 15$, $-19 \le k \le 19$, $-13 \le l \le 14$	$-17 \le h \le 17$, $-19 \le k \le 16$, $-10 \le l \le 13$	$-10 \le h \le 11$, $-28 \le k \le 28$, $-18 \le l \le 18$
reflns collected/unique	15750/4978 (R_{int} = 0.039)	13313/4752 (R_{int} = 0.027)	17146/5873 (R_{int} = 0.054)
completeness to θ (%)	99.7	99.8	98.7
abs corrn	multiscan *ABSCOR*	multiscan *ABSCOR*	multiscan *ABSCOR*
min and max transmn	0.813 and 1.000	0.811 and 1.000	0.229 and 1.000
data/restraints/param	4978/0/316	4752/0/316	5873/0/454
GOF on F^2	1.002	1.011	1.036
final R indices [$I > 2\sigma(I)$]	R1 = 0.0397, wR2 = 0.0993	R1 = 0.0294, wR2 = 0.0809	R1 = 0.0613, wR2 = 0.1320
R indices (all data)	R1 = 0.0455, wR2 = 0.1053	R1 = 0.0321, wR2 = 0.0830	R1 = 0.0789, wR2 = 0.1415
largest diff peak and hole (e/Å^3)	0.634 and −0.517	0.543 and −0.641	0.916 and −0.608

[a]The refinement method was full-matrix least squares on F^2; wavelength = 0.71073 Å. R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

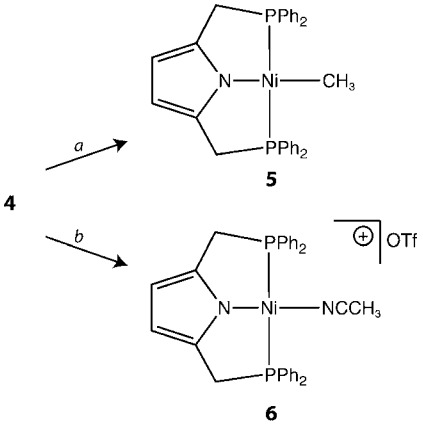
Table 2. Selected Crystallographic Bond Distances (Å) and Angles (deg) for Complexes 4−6

	4	5	6
Ni(1)−N(1)	1.856(2)	1.898(1)	1.820(3)
Ni(1)−P(1)	2.198(1)	2.1910(6)	2.211(1)
Ni(1)−P(2)	2.208(1)	2.1824(6)	2.203(1)
Ni(1)−X	2.1768(9)	1.999(2)	1.838(4)
P(1)−Ni(1)−P(2)	166.19(3)	165.59(2)	163.96(5)
N(1)−Ni(1)−X	175.83(7)	177.01(7)	172.0(2)
Ni(1)−N(2)−C(31)	n/a	n/a	167.1(4)

complex [Ni(CH$_3$)(P$_2^{Ph}$Pyr)] (**5**). This species is yellow and displays a ^{1}H NMR resonance for the methyl protons at −0.05 ppm in benzene-d_6. The solid-state structure of complex **5** is nearly isomorphous to that of **4** (Figure 2 and Tables 1 and 2), displaying a Ni−C bond length of 1.999(2) Å comparable to that of other nickel(II) alkyl complexes.[57] The Ni−PNP bond metrics are similar to those of **4** except for a slightly elongated Ni−N distance of 1.898(1) Å.

Removal of the chloride ligand in **4** with AgOTf, TlOTf, or $AgBF_4$ in the presence of CH_3CN afforded the cationic solvent adducts [Ni(CH$_3$CN)(P$_2^{Ph}$Pyr)](X) [X = OTf (**6**) or BF_4 (**6′**)]. These red-orange species are insoluble in benzene but dissolve readily in more polar solvents such as THF, CH_2Cl_2, and CH_3CN. IR spectroscopy of the triflate salt (**6**) revealed a CN stretch for the coordinated acetonitrile ligand at 2293 cm^{-1} in KBr. The solid-state structure of complex **6** is depicted in Figure 3 (see also Tables 1 and 2). As expected, the cationic

Scheme 2. Nickel(II) Complexes Prepared from 4



(*a*) CH$_3$MgCl, THF; (*b*) AgOTf, CH$_2$Cl$_2$/CH$_3$CN

nature of [Ni(CH$_3$CN)(P$_2^{Ph}$Pyr)]$^+$ results in a slightly contracted Ni−N$_{pyrrole}$ distance of 1.820(3) Å [cf. 1.856(2) and 1.898(1) Å for the chloro and methyl complexes, respectively]. The complex also displays a short Ni−N$_{nitrile}$ distance of 1.838(4) Å comparable to other reported CH_3CN adducts.[58] The remaining metric parameters of the PNP ligand are unremarkable with respect to those of the chloro and methyl complexes.

To explore the possible redox chemistry of the nickel(II) complexes, we next examined their electrochemical behavior. The cyclic voltammogram of complex **4** in CH_2Cl_2 displays an

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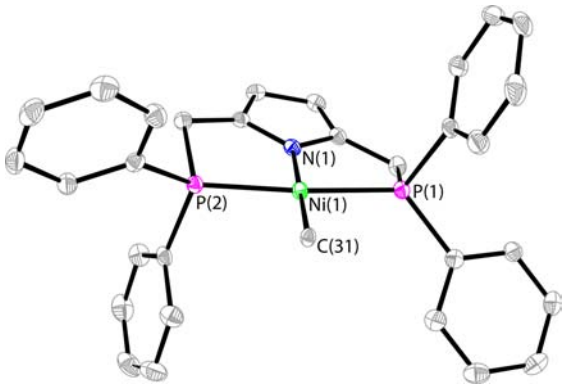

Figure 2. Thermal ellipsoid drawing (50%) of **5**. Hydrogen atoms are omitted for clarity. See Table 2 for selected bond lengths and angles.

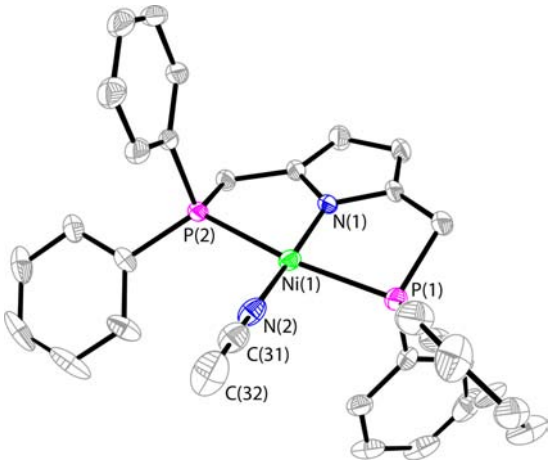

Figure 3. Thermal ellipsoid drawing (30%) of the cation of **6**. Hydrogen atoms and minor components of the disorder are omitted for clarity. See Table 2 for selected bond lengths and angles.

irreversible anode process at +0.45 V (all potentials reported vs ferrocene/ferrocenium), which we assign as oxidation to nickel(III) based on observations with other $Ni^{II}PXP$ systems (X = N or C).[59−61] Upon scanning to negative potentials, complex **4** exhibits a catalytic current wave near −2.1 V, suggesting that reduction of the complex to nickel(I) results in reactivity with the methylene chloride solvent. To examine this process in more detail, increasing amounts of CH_2Cl_2 were added to a THF solution of **4** and cyclic voltammetry (CV) was repeated (Figure 4). Consistent with a catalytic process, the current response was found to increase with larger concentrations of CH_2Cl_2.

Conducting CV in pure THF results in a similar irreversible anode process at +0.38 V, but no catalytic event is observed within the solvent window. Instead, an irreversible cathodic event takes place at −2.06 V, which gives rise to a new irreversible anodic event at −0.37 V (Figure 5). Furthermore, a quasi-reversible cathodic process centered at −2.53 V is also observed in THF upon scanning to lower potentials (Figure 5, inset).

Taken together, these observations are consistent with a process involving one-electron reduction of **4** followed by rapid loss of the Cl^- ligand. In CH_2Cl_2, the resulting $[Ni^I(P_2^{Ph}Pyr)]$ fragment appears to be capable of chlorine atom abstraction from solvent, which regenerates the nickel(II) chloride complex, leading to an electrocatalytic dechlorination sequence

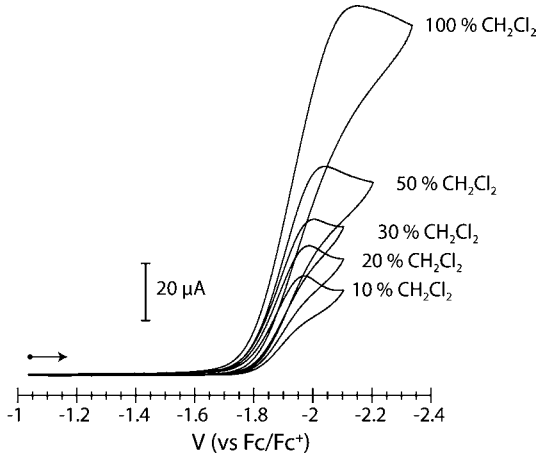

Figure 4. Cyclic voltammogram of **4** in THF (1.8 mM) at a glassy carbon electrode demonstrating the catalytic current wave observed upon an increase in the concentration of CH_2Cl_2. The scan rate is 50 mV/s, and the supporting electrolyte is 0.15 M Bu_4NPF_6.

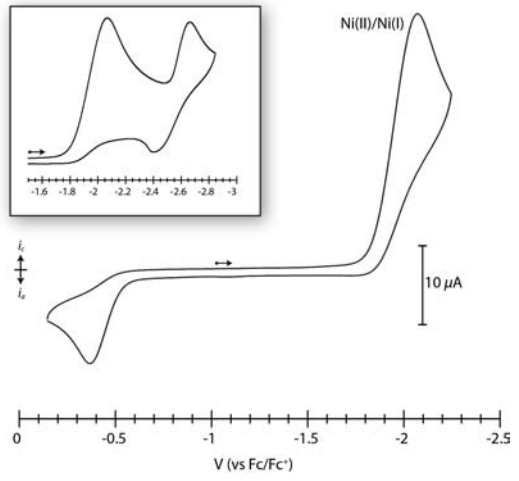

Figure 5. Cyclic voltammogram of **4** in THF (2.0 mM) at a glassy carbon electrode displaying the irreversible reduction at −2.06 V and its corresponding return wave at −0.37 V. The inset displays the quasi-reversible couple at −2.53 V. The scan rate is 100 mV/s, and the supporting electrolyte is 0.15 M Bu_4NPF_6.

(Scheme 3). In THF, a nickel(I) species is formed irreversibly, which demonstrates a further quasi-reversible process at −2.53 V. The new nickel(I) species is observed to undergo oxidation at a potential of −0.37 V, perhaps resulting in regeneration of **4**.

The electrochemical properties of **6** show notable differences with those of complex **4**. Similar to **4**, complex **6** displays an irreversible oxidation to nickel(III) in CH_2Cl_2 albeit at a slightly higher potential of +0.52 V, consistent with more difficult oxidation in the cationic complex. Interestingly, however, complex **6** shows no electrocatalytic activity when scanned to lower potentials in CH_2Cl_2. Instead, an irreversible cathodic reduction at −1.40 V takes place for **6** similar to that observed for **4** in THF (see Supporting Information). Thus, formation of the nickel(I) complex from **6** produces a species that is stable to CH_2Cl_2 on the electrochemical timescale. Scanning to more negative potentials (in CH_3CN) reveals a quasi-reversible process centered at −2.40 V also similar to that observed for **4** in THF. It therefore appears that analogous reduced nickel(I) species may result from the reduction of complex **4** or **6**.

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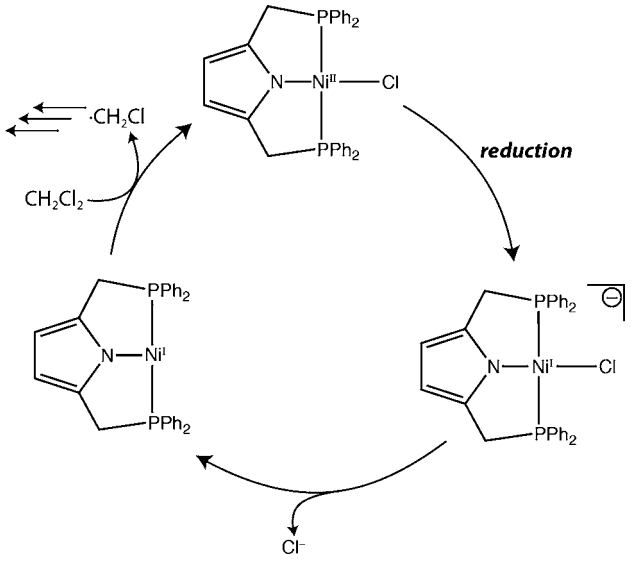
Scheme 3. Possible Catalytic Sequence for the Electrochemical Reactivity of 4 in CH_2Cl_2



However, reactivity with CH_2Cl_2 is *only* observed in the case of **4**, suggesting that the initial product of reduction is not the same in both cases.

CONCLUSIONS

In conclusion, we have prepared a new PNP pincer ligand featuring a central pyrrolide unit. The synthesis of the ligand is accomplished from a general precursor without the need of protecting group chemistry at pyrrole and is therefore well suited to the preparation of other alkylphosphine derivatives (*t*-Bu, cyclohexyl, etc.). The borane-protected species, **2**, is especially promising in this regard because alkylphosphine derivatives are expected to demonstrate even greater air sensitivity than the phenyl derivative reported here. The pincer ligand is delivered to nickel(II) via its borane adduct, giving rise to diamagnetic square-planar complexes. The electrochemistry of these complexes reveals a rich reduction chemistry. Further work will examine the small-molecule reactivity of these reduced nickel complexes and the coordination chemistry of the ligand with other metals.

EXPERIMENTAL SECTION

General Comments. Manipulations of air- and moisture-sensitive materials were performed under an atmosphere of nitrogen gas using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Tetrahydrofuran, diethyl ether, pentane, dichloromethane, toluene, and acetonitrile were purified by sparging with argon and passage through two columns packed with 4 Å molecular sieves or activated alumina (CH_3CN). Benzene and benzene-d_6 were dried over sodium ketyl and vacuum-distilled prior to use. Dichloromethane-d_2 and acetonitrile-d_3 were sparged with nitrogen and stored over 4 Å molecular sieves prior to use. Chloroform-*d* was used as received. NMR spectra were recorded on Varian spectrometers operating at 300 or 500 MHz (^{1}H) and referenced to the residual ^{1}H or ^{13}C resonance of the solvent. For ^{31}P, ^{19}F, and ^{11}B NMR spectra, external standards of neat 85% H_3PO_4(aq), neat $CFCl_3$, and 10% $BF_3{\cdot}Et_2O$ in benzene-d_6 were used, respectively (δ = 0.00 ppm). UV−vis spectra were recorded on a Cary 60 spectrophotometer in airtight Teflon-capped quartz cells. IR spectra were recorded as pressed KBr windows on a Nicolet iS10 FTIR spectrometer. CV was performed at 23 °C on a CH Instruments 620D electrochemical workstation. A three-electrode setup was employed comprising a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl quasi-reference electrode. Triply recrystallized Bu_4NPF_6 was used as the supporting electrolyte. All electrochemical data were referenced internally to the ferrocene/ferrocenium couple at 0.00 V. Elemental analyses were performed by Midwest Microlab, LLC, in Indianapolis, IN.

Materials. Pyrrole was purchased from commercial suppliers (Aldrich or Acros) and distilled prior to use. Anhydrous nickel(II) chloride, diphenylphosphine, methylmagnesium chloride solution (THF), lithium aluminum hydride, sodium borohydride, cerium(III) chloride, silver tetrafluoroborate, and silver triflate were purchased from Strem Chemicals Inc. and used as received.

Pyrrole-2,5-dicarbaldehyde. The dialdehyde was prepared by the two-step method of Knizhnikov et al.[47] In our hands, Soxhlet extraction of the crude product with hexanes was found to give material of insufficient purity, so an alternate purification method was developed. The crude material was purified by flash chromatography on alumina using hexanes/ethyl acetate (75:25) as the eluent. The resulting pure dialdehyde was found to be a white solid. Spectroscopic features matched those reported previously. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.67 (br s, N*H*), 9.79 (s, 2C*H*O), 7.04−6.99 (m, 2pyr-C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 181.83, 136.04, 119.82.

*[(Pyrrole-2,5-diyl)dimethylene]bis(diphenylphosphine oxide) (**1**).* A round-bottomed flask was charged with 2.87 mL (16.5 mmol) of diphenylphosphine and 1.0 mL of concentrated HCl under an atmosphere of dinitrogen. In a separate flask, 1.0 g (8.1 mmol) of pyrrole-2,5-dicarbaldehyde was dissolved in 8 mL of methanol under an atmosphere of dinitrogen. The methanolic solution of dialdehyde was added dropwise to the mixture containing diphenylphosphine. After the addition was complete, the reaction mixture was heated at reflux overnight. After cooling, methanol was removed by rotary evaporation, and the remaining residue was extracted into dichloromethane (3 × 75 mL). The combined extracts were dried over Na_2SO_4 and evaporated to dryness. The remaining residue was washed thoroughly with diethyl ether (4 × 15 mL) to afford 2.70 g (67%) of diphosphine oxide as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (br s, N*H*), 7.63 (m, 8*o*-*H*), 7.50 (t, 4*p*-*H*), 7.41 (t, 8*m*-*H*), 5.68 (s, 2pyr-C*H*), 3.59 (d, 4CH_2, J_{HP} = 12 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 132.30 (d, J_{CP} = 98.9 Hz), 132.01, 131.22 (app m), 128.71 (app m), 121.25 (m), 108.97 (m), 30.57 (d, CH_2, J_{CP} = 69.6 Hz). ^{31}P{^{1}H} NMR (202 MHz): δ 27.5. ESI-MS (negative mode). Calcd for [M − H]$^-$: *m*/*z* 494.1. Found: *m*/*z* 494.1.

*2,5-Bis[(diphenylphosphino)methyl]pyrrole with Borane Adduct, H(P_2^{Ph}Pyr)·2BH_3 (**2**).* A round-bottomed flask was charged with 1.45 g (5.88 mmol) of anhydrous $CeCl_3$, 0.227 g (6.00 mmol) of $NaBH_4$, and 15 mL of THF. The mixture was was cooled to −30 °C, at which point 0.495 g (1.00 mmol) of diphosphine oxide was added followed by 0.152 g (4.00 mmol) of $LiAlH_4$ in portions. The reaction mixture was allowed to warm to room temperature and stir for 15 h under an atmosphere of dinitrogen. The mixture was diluted with 25 mL of benzene and poured slowly onto 150 mL of ice−water containing 4 mL of concentrated HCl. The aqueous layer was extracted twice with 25 mL of benzene. The combined extracts were dried over Na_2SO_4 and evaporated to dryness. The resulting residue was purified by chromatography on alumina, eluting with 90:10 hexane/ethyl acetate to afford 0.295 g (60%) of diphosphinoborane as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 8.48 (br s, N*H*), 7.52 (t, 8Ar-*H*), 7.00 (m, 12Ar-*H*), 5.68 (s, 2H, pyr-C*H*), 3.16 (d, 4CH_2, J_{HP} = 10 Hz), 2.1−1.3 (v br m, 6BH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 133.12 (d, J_{CP} = 8.9 Hz), 131.55 (d, J_{CP} = 2.0 Hz), 129.90 (d, J_{CP} = 52.9 Hz), 129.21 (d, J_{CP} = 9.7 Hz), 122.47 (app m), 110.15 (d, J_{CP} = 4.3 Hz), 27.54 (d, J_{CP} = 34.3 Hz). ^{31}P{^{1}H} NMR (202 MHz): δ 16.0 (br m). ^{11}B NMR (150 MHz): δ −40.9. ESI-MS (negative mode). Calcd for [M − H]$^-$: *m*/*z* 490.2. Found: *m*/*z* 490.1.

*2,5-Bis[(diphenylphosphino)methyl]pyrrole, H(P_2^{Ph}Pyr) (**3**).* The free diphosphine was prepared by refluxing phosphinoborane in methanol. The volatiles were then removed in vacuo to afford diphosphine as a colorless oil in quantitative yield. Because of the air sensitivity of the material, it was used immediately without further purification. ^{1}H NMR (300 MHz, C_6D_6): δ 7.45 (br s, N*H*), 7.35 (m, 8Ar-*H*), 7.05 (m, 12Ar-*H*), 5.85 (d, 2pyr-C*H*, *J* = 2.0 Hz), 3.11 (s, 4

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CH_2). $^{13}C\{^1H\}$ (75 MHz, C_6D_6): δ 139.56 (d, J_{CP} = 15.9 Hz), 133.50 (d, J_{CP} = 18.5 Hz), 129.14, 129.02 (app m, J_{CP} = 6.5 Hz), 126.49 (d, J_{CP} = 14.1 Hz), 108.52 (d, J_{CP} = 5.3 Hz), 28.90 (d, J_{CP} = 15.7 Hz). $^{31}P\{^1H\}$ NMR (202 MHz): δ −16.2. Attempted observation by liquid chromatography−mass spectrometry yielded the monooxidized product. ESI-MS (positive mode). Calcd for $[M(O) + H]^+$: m/z 480.2. Found: m/z 479.9.

[NiCl(P$_2^{Ph}$Pyr)] (**4**). A flask was charged with 0.122 g of **2** (0.248 mmol) and 0.064 g of anhydrous $NiCl_2$ (0.49 mmol). The solids were suspended in 20 mL of THF, and 0.52 mL of Et_2NH was added. The mixture was stirred for 18 h at room temperature, during which time it became dark brown. All volatiles were removed in vacuo, leaving a dark-colored residue that was extracted into 25 mL of benzene. The benzene extract was filtered through a pad of Celite to give an orange-red solution. The solution was evaporated to dryness to afford 0.085 g (62%) of the desired nickel complex. Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a saturated benzene solution of the complex. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.91 (m, 8Ar-*H*), 7.46 (m, 12Ar-*H*), 5.93 (s, 2pyr-C*H*), 3.58 (app t, 4CH_2, J_{HP} = 5.1 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 136.69 (app t, J_{CP} = 7.4 Hz), 133.20 (app t, J_{CP} = 5.6 Hz), 131.25, 130.84 (app t, J_{CP} = 21.0 Hz), 129.18 (app t, J_{CP} = 10.5 Hz), 106.51 (app t, J_{CP} = 5.6 Hz), 31.98 (app t, CH_2, J_{CP} = 13.5 Hz). $^{31}P\{^1H\}$ NMR (202 MHz): δ 30.3. Anal. Calcd for $C_{30}H_{26}ClNNiP_2$: C, 64.73; H, 4.71; N, 2.52. Found: C, 64.44; H, 4.77; N, 2.60.

[Ni(CH$_3$)(P$_2^{Ph}$Pyr)] (**5**). A flask was charged with 0.111 g (0.199 mmol) of **4** and 20 mL of THF, and the resulting orange solution was cooled to −30 °C. To the cooled solution was added 66 μL (0.20 mmol) of CH_3MgCl (3.0 M in THF). The mixture was allowed to stir at room temperature for 2 h, during which time the mixture lightened. All volatiles were removed in vacuo, leaving a yellow residue, which was extracted into 10 mL of benzene and filtered through a pad of Celite. The benzene was removed in vacuo and the resulting solid washed with Et_2O to afford 0.095 g (85%) of the desired product as a yellow microcrystalline solid. Crystals suitable for X-ray diffraction were grown by pentane diffusion into a saturated benzene solution of the complex. ^1H NMR (500 MHz, C_6D_6): δ 7.59 (m, 8Ar-*H*), 6.97 (m, 12Ar-*H*), 6.58 (s, 2pyr-C*H*), 3.65 (app t, 4CH_2, J_{HP} = 4.7 Hz), −0.05 (t, 3CH_3, J_{HP} = 8.0 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 135.08 (app t, J_{CP} = 7.3 Hz), 133.79 (app t, J_{CP} = 18.9 Hz), 133.45 (app t, J_{CP} = 6.0 Hz), 130.39, 129.18 (app t, J_{CP} = 4.7 Hz), 106.14 (app t, J_{CP} = 5.4 Hz), 35.93 (app t, CH_2, J_{CP} = 13.0 Hz), −18.76 (t, CH_3, J_{CP} = 21.3 Hz). $^{31}P\{^1H\}$ NMR (202 MHz): δ 31.1. Anal. Calcd for $C_{31}H_{29}NNiP_2$: C, 69.44; H, 5.45; N, 2.61. Found: C, 69.89; H, 5.74; N, 2.66.

[Ni(CH$_3$CN)(P$_2^{Ph}$Pyr)](OTf) (**6**). A flask was charged with 0.100 g (0.181 mmol) of **4** and 0.046 g (0.18 mmol) of AgOTf. The solids were dissolved in 15 mL of CH_2Cl_2 containing 0.5 mL of CH_3CN. The resulting red-orange mixture was stirred for 5 h at room temperature. The mixture was filtered through a pad of Celite and evaporated to dryness. The resulting residue was washed thoroughly with benzene to afford 0.090 mg (70%) of a red powder. Crystals suitable for X-ray diffraction were grown by vapor diffusion of Et_2O into a saturated CH_2Cl_2 solution of the complex. ^1H NMR (500 MHz, CD_3CN): δ 7.79 (m, 8Ar-*H*), 7.65 (t, 4Ar-*H*), 7.57 (t, 8Ar-*H*), 5.91 (s, 2pyr-C*H*), 3.73 (app t, 4CH_2, J_{HP} = 5.5 Hz), 1.96 (s, 3 CH_3CN). $^{31}P\{^1H\}$ NMR (202 MHz): δ 43.1. ^{19}F NMR (470 MHz): −79.1. IR (KBr, cm^{-1}): 2293 (C≡N). Anal. Calcd for $C_{33}H_{29}F_3N_2NiO_3P_2S$: C, 55.72; H, 4.11; N, 3.94. Found: C, 55.60; H, 3.96; N, 3.29.

Alternatively, the BF_4 salt could be prepared in a similar fashion starting from $AgBF_4$. The NMR features were nearly identical (±0.02 ppm) with those of the triflate salt.

X-ray Data Collection and Structure Solution Refinement. Crystals suitable for X-ray diffraction were mounted in Paratone oil onto a glass fiber and frozen under a cold nitrogen stream maintained by an X-Stream low-temperature apparatus. The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo Kα radiation (λ = 0.71073 Å). Data collection and unit cell refinement were performed using *CrystalClear* software.[63] The total number of data were measured in the range $3.0 < \theta < 27.6°$ using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with *CrystalClear* and *ABSCOR*,[64] respectively. All structures were solved by direct methods and refined on F^2 using full-matrix least-squares techniques with *SHELXL-97*.[65,66] Non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen-atom positions were determined by geometry and refined by a riding model. The structure of **6** was found to contain an unbound chloride counterion in partial occupancy with the triflate. Refinement of the cooccupancy to 85% OTf/15% Cl resulted in a satisfactory structure. In addition, the structure of **6** was also found to contain substantial disorder about the phenyl rings. Diffraction experiments utilizing the BF_4 salt (**6′**) also resulted in disordered structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional spectra, cyclic voltammograms, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

After this paper was submitted, alternative syntheses of ligand **3** and complex **4** were reported by Gade et al.[62] In that work, the chemical reduction of **4** was demonstrated to result in a dimeric nickel(I) complex featuring a Ni−Ni bond. The formation of such a species in THF and subsequent quasi-reversible one-electron reduction are fully consistent with the data presented above. However, the reactivity of the nickel(I) dimer with CH_2Cl_2 was not reported.

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