## **ORGANOMETALLICS**

# Nickel and Platinum PCP Pincer Complexes Incorporating an Acyclic Diaminoalkyl Central Moiety Connecting Imidazole or Pyrazole Rings

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#### Supporting Information

**ABSTRACT:** This work explores avenues toward PCP pincer complexes with acyclic diaminocarbene central moieties that are suitable for ligand-assisted reactivity involving the carbene carbon. For this purpose, diphosphine chelating ligands 1 and 2, with bis(imidazolyl)methyl and bis(pyrazolyl)methyl backbones, respectively, were prepared in two high-yield synthetic steps. Nickel(II) and platinum(II) dihalide complexes 3 and 6, incorporating 1, were prepared and converted into PCP pincer ligands 5 and 7 upon deprotonation with KHMDS. Chelated nickel(I) complex 4 was obtained as a byproduct to 3. Although the solid-state structures of 5 and 7 presented geometric strain at the diaminomethyl carbon, this moiety could not be converted into a diaminocarbene by proton or



hydride abstraction. 7 could be converted into platinum(IV) analog 8 by oxidation with  $PhICl_2$ . Ligand 2 proved more versatile than 1, or less dependable in its behavior, generating P,N-chelating cobalt(II) dibromide complex 9. Easily accessible ligands 1 and 2 provide a new and versatile PCP pincer platform.

#### ■ INTRODUCTION

The term "metal–ligand cooperativity" was added to the vocabulary of the discipline by Milstein in 2006,<sup>1</sup> although the concept has deeper roots in the chemistry literature. Over the past decade, it has developed into a flourishing chapter of the larger area of small-molecule activation and catalysis.<sup>2</sup> We have recently shown that, in stark contrast to the classical chemistry of *N*-heterocyclic carbenes (NHCs), which are quintessential ancillary ligands, the metal-coordinated carbene carbon in selected ligands can act as proton acceptor.<sup>3</sup> This enabled the ligand-assisted, reversible activation of ammonia on a nickel(0) NCN–pincer complex (Scheme 1). Derivatives featuring a

### Scheme 1. NHC-Ligand-Assisted Reversible Activation of Ammonia



diaminoalkyl fragment coordinated to a transition metal,  $N_2C(H)-ML_n$ , such as the ammonia activation product shown in Scheme 1, remain rare for five-<sup>4</sup> and six-membered<sup>5</sup> cyclic frameworks, where deprotonation with formation of NHC complexes ( $N_2C \rightarrow ML_n$ ) prevails. They are more common for acyclic systems, most notably in strongly folded,

nonclassical NCN pincer complexes with bis(pyrazolyl)methyl (Mo and W)<sup>6</sup> and bis(azaindolyl)methyl (Pt)<sup>7</sup> ligands.

Aiming to identify other NHC-based architectures suitable to metal-ligand cooperativity involving the carbon for small-molecule activation,<sup>8</sup> we focused on complexes of types A and **B** (Chart 1). The nitrogen lone pairs of electrons in these ligands are integrated in the  $\pi$  systems of the aromatic azole and pyrazole rings, respectively; consequently, the carbenic structure is less stabilized. To date, only two pincer ligands with central acyclic diaminocarbene moieties such as those envisaged in ligands A and B have been reported, in metal complexes C and D.<sup>9</sup> They have been obtained in serendipitous metal-templated self-assembly reactions, and their chemistry has not been further investigated. In contrast, pincer ligands featuring acyclic dialkyl and diarylcarbene moieties in the central positions have been pioneered by Shaw four decades ago (E, M = Ir)<sup>10</sup> and their chemistry is rather extensive. Ru and Os complexes E have been reported by Gusev.<sup>11</sup> The chemistry of derivatives F, first obtained via self-assembly in the coordination sphere of the metal by Roper (R = Ph, M = Ru),<sup>12</sup> has been examined extensively by Piers (R = iPr and tBu; R' =H; M= Ni, Rh, and Ir)<sup>13</sup> and Iluc (R = iPr; R' = H and tBu; M = Pd)<sup>14</sup> in recent years, and expanded by the former to analogs G.<sup>15</sup> Tantalum OCO-pincer complexes H, resulting from a sequential proton and hydride abstraction at the methylene

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Chart 1. Pincer Complexes with Acyclic Carbene Moieties in the Central Position



bridge, have been described by Kawaguchi.<sup>16</sup> Ruthenium OCC–pincer complexes featuring an acyclic diaminocarbene central moiety and NHC pendant arms have been reported by Blechert and Grubbs as decomposition products of olefin metathesis catalysts.<sup>17</sup>

Ruthenium and palladium complexes I (R = iPr), with a structure very similar to that proposed for A and B, have been described by Ozerov.<sup>18</sup> Metal carbene ( $Ar_2C \rightarrow ML_n$ ) and metal alkyl ( $Ar_2C(H)-ML_n$ ) species were identified for these systems, confirming that the constraining geometry of the ligand does not prevent their formation. Later work with iron, cobalt, and nickel complexes of less electron-rich PCP ligand analogs (R = Ph) was limited to the metal alkyl species.<sup>19</sup>

We identified ligands 1 and 2 (Scheme 2) as promising, easily accessible precursors for the synthesis of PCP-pincer

Scheme 2. Synthesis of Ligands 1 and 2



complexes via C–M bond formation upon deprotonation at the methylene bridge. For the reasons discussed above, these metal alkyl derivatives were postulated to have increased stability with respect to diaminocarbene pincer analogs **A** and **B** and potentially allow for carbene–carbon-assisted transformations. The synthesis and P,P', as well as N,N', coordination chemistry of diphenylphosphino analogs of ligands **1** and **2** have been described nearly two decades ago (Chart 2).<sup>20</sup> More recent investigations targeted the P,P', N,N', and P,N coordination chemistry of these ligands.<sup>21</sup> Remarkably, the potential of these ligands to generate pincer complexes via deprotonation or C–H bond activation has not been explored; our investigations of this chemistry will be described below.

Chart 2. P,P'- and N,N'-Complexes of Diphosphine Ligands with Bis(pyrazolyl)methane and Bis(imidazolyl)methane Backbones<sup>20</sup>



#### RESULTS AND DISCUSSION

Ligand Synthesis. Ligands 1 and 2 are easily accessible in two simple steps in a manner very similar to that used for the synthesis of their diphenylphosphino analogs (Scheme 2).<sup>20</sup> The bis(imidazolyl)- and bis(pyrazolyl)methane precursors were obtained in a neat reaction between the corresponding nitrogen heterocycles and stoichiometric dichloromethane in the presence of excess potassium hydroxide and a phase transfer catalyst.<sup>22</sup> We found that the mixture of nitrogen base, potassium hydroxide, and phase transfer catalyst liquefied easily and the viscous liquid solidified again within 60 min. The best yields were obtained when dichloromethane was added to the fluid mixture, although they were variable and in our hands never approached the reported 100%. These highly exothermic reactions were carried out in pressure glass reaction vessels. Addition of small amounts of water to aid liquefying and mixing led to a substantial drop in yields. The pure products were isolated easily via sublimation from the crude reaction mixtures.

Ligand synthesis was accomplished via double deprotonation of the bis(imidazolyl)- and bis(pyrazolyl)methane precursors in THF with *n*-butyl lithium, followed by reaction with 2 equiv of chlorodi(iso-propyl)phosphine, *i*Pr<sub>2</sub>PCl. It proved crucial for the success of this step that the starting materials were completely dissolved prior to lithiation. Bis(pyrazolyl)methane was well soluble, but its imidazole counterpart required a solvent to solute ratio of ca. 200:1. The crude products were reproducibly obtained in moderate (1) or high (2) yield as viscous oils with good solubility in organic solvents, including *n*-pentane. They had remarkably high purity and were used as such for complex synthesis. The ligands could be handled in air for brief periods of time but decomposed when exposed to air over several hours, especially in solution. They were characterized by  ${}^{31}P$  NMR resonances at -19.4 (1) and -20.8 (2) ppm. The triplet resonances corresponding to the methylene bridge were observed at 6.54 and 7.03 ppm, respectively, in the <sup>1</sup>H NMR spectra and at 55.3 and 61.0 ppm, respectively, in the <sup>13</sup>C NMR spectra.

**Nickel Complexes.** Complex 3 was obtained as a dark green microcrystalline product upon mixing 1 with Ni(dme)Br<sub>2</sub> in dichloromethane (Scheme 3). Its effective magnetic moment determined using Evans' method<sup>23</sup> had a value of 3.76, which is in the expected range for tetrahedral Ni(II) complexes.<sup>24</sup> Single-crystal X-ray analysis of the paramagnetic compound revealed the expected pseudotetrahedral geometry (Figure 1). Ligand 1 is strongly folded, with a dihedral angle of 100.5° between the imidazole rings and an NCN angle at the methylene bridge of 112.8(3)°. The methylene bridge is conveniently positioned for pincer coordination, only 3.666(3) Å away from the nickel center (cf. the sum of the van der Waals radii for carbon and nickel of 3.3 Å). However, heating to 110°C in toluene for 24 h failed to promote HBr elimination, and complex 3 was recovered unchanged.

Scheme 3. Synthesis of Ni Complexes 3 and 4 and Formation of 5



**Figure 1.** Solid-state structure of **3** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms except those on the methylene bridge were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–Br = 2.3332(8), 2.3722(7); Ni1–P = 2.3274(12), 2.3538(11); Ni1···C1 = 3.666(3); P1···P2 = 3.750(1); C1-N = 1.446(4); 1.452(4); P1–Ni1–P2 = 106.48(4); Br1–Ni1–Br2 = 117.38(3); N1–C1–N3 = 112.8(3).

Addition of 1 equiv of potassium hexamethyldisilazide (KHMDS) to a THF solution of 3 (Scheme 3) yielded a diamagnetic, air stable, orange compound featuring one <sup>31</sup>P NMR resonance at 31.5 ppm. The triplet resonance corresponding to the methine bridge proton was observed at 5.8 ppm, while the methyl protons of the isopropyl groups were characterized by virtual triplet signals typical for pincer coordination in ligands containing phosphine pendant arms. The number of resonances observed for the isopropyl groups corresponded to the expected  $C_s$  symmetry. Solid complex 3 does not show signs of decomposition when exposed to the air for months, and its solutions can be handled in the air without significant deterioration.

The solid-state structure of 4 confirmed the PCP-pincer coordination with a diaminomethyl moiety in the central position (Figure 2). Although the ligand backbone remained far from planar, the folding was reduced substantially upon pincer formation, with the dihedral angle between the imidazole rings in 4 being 148.4°. C–N bond formation has little impact on the geometry of the bridge carbon, with the NCN angle measuring 111.1(2)°. The tetrahedral bridge carbon atom, C1, sits 0.15 and 0.26 Å outside of the best plane of the two imidazole rings, reflecting substantial strain in the rigid structure. Very similar, strained geometries were identified in the closely related metal alkyl  $(Ar_2C(H)-ML_n)$  precursors to derivatives I (R = iPr; $ML_n = Ru(CO)_2Cl$ , PdCl, and PdOTf) where the dihedral angles between the pyrrole rings measured 154.9–159.6°, while the deviation of the bridge carbon from the best plane of the pyrrole rings was between 0.10 and 0.31 Å.18



**Figure 2.** Solid-state structure of **4** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms except those on the methine bridge were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–Br1 = 2.3275(7); Ni1–P = 2.1710(11), 2.1802(12); Ni1–C1 = 1.965(3); P1···P2 = 4.328(1); C1–N = 1.471(4); 1.483(4); P1–Ni1–P2 = 168.25(4); Br1–Ni1–C1 = 172.81(10); N1–C1–N3 = 111.1(2).

Paramagnetic Ni(I) complex 5 was identified by single-crystal X-ray crystallography (Figure 3), owing to its propensity to



**Figure 3.** Solid-state structure of **5** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms except those on the methylene bridge were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–Br1 = 2.2997(5); Ni1–P = 2.2088(10), 2.2242(9); Ni1···C1 = 3.448(1); P1···P2 = 3.694(1); C1–N = 1.448(4); 1.458(4); P1–Ni1–P2 = 112.87(4); Br1–Ni1–P = 115.55(3), 131.57(3); N1–C1–N3 = 112.3(3).

crystallize preferentially from mixtures, as a minor byproduct in the formation of 4 via deprotonation. Its presence led to line broadening in the NMR spectra of impure samples of 4. It was not isolated on a large scale, and targeted synthesis was not pursued. A number of Ni(I) halide complexes with chelating phosphine ligands have been described, and they feature very similar geometry at the trigonal planar nickel center.<sup>25</sup> The reductive properties of alkali metal amides have been documented,<sup>26</sup> and it is assumed that the side reaction involves the formation of the highly unstable bis(trimethylsilyl)aminyl radical.<sup>27</sup> The solid-state structure of **5** reveals a trigonal planar nickel center and a strongly folded ligand conformation, very similar to that observed in the structure of 3. The dihedral angle formed by the imidazole rings measures 108.7°, and the NCN angle corresponding to the methylene bridge remains relatively unchanged at 113.2(3)°. The Ni-Br bond in Ni(I) complex 5 (2.30 Å) is only marginally shorter than those in Ni(II) complexes 3 (2.35 Å) and 4 (2.33 Å). The decrease in the length of the Ni-P bond upon pincer formation is much more drastic, from 2.34 Å in 3 to 2.17 Å in 4, where it is even shorter than in tricoordinate complex 5 (2.21 Å). These values fall within the ranges that are typical for the respective compound classes.

Deprotonation of 4 at the methylene bridge to yield a PCP pincer complex with a central, acyclic diaminocarbene moiety was attempted using KHMDS, KH, MeLi, LDA, or tBuOK in toluene and THF. KHMDS was also employed in the presence of Lewis bases (PPh<sub>3</sub>, PCy<sub>3</sub>, and tBuNC) meant to cap the nickel coordination site vacated by the bromide ion. All attempts were unsuccessful, leading to multiple unwanted decomposition products. Hydride abstraction with trityl tetrakis(pentafluorophenyl)borate ( $[CPh_3][B(C_6F_5)_4]$ ) in toluene, as reported for Pd complex I (R = iPr, L = Cl),<sup>18b</sup> did not meet with success either, leading to a complex mixture of products that was not further investigated. Numerous nickel(II) pincer complexes featuring dialkylmethyl central platforms are known,<sup>28</sup> but none of these was converted to a carbene complex. Remarkably, a PCP-pincer system with a diarylmethyl backbone was recently shown to stabilize both diarylmethyl and diarylcarbene complexes of nickel.<sup>13b</sup>

**Platinum Complexes.** Platinum(II) chelate complex 6 was obtained upon combination of ligand 1 with platinum dichloride in THF (Scheme 4). Both the platinum dichloride

Scheme 4. Synthesis of Pt Complexes 6-8



reagent and the product had low solubility in organic solvents and purification was best accomplished via Soxhlet extraction. According to the <sup>1</sup>H NMR spectrum, the chelated platinum complex had time-averaged  $C_s$  symmetry, with the inequivalent methylene bridge protons featured as doublet resonances. Deprotonation of 6 with KHMDS in toluene led to clean formation of pincer complex 7 (Scheme 3), as indicated by the emergence in the <sup>1</sup>H NMR spectrum of a resonance featuring platinum satellites at 6.43 ppm, corresponding to the diaminomethyl group bonded to the metal. The four doublet of doublet signals attributed to the methyl groups in 6 converted upon deprotonation to an equal number of doublets of virtual triplets typical of PCP pincer complexes with diisopropylphosphine moieties. The <sup>31</sup>P NMR resonance shifts downfield from -19.4 ppm in 1 to 6.9 ppm in 6 and 35.6 ppm in 7, and the magnitude of the  ${}^{1}J^{_{195}}_{Pt}{}^{_{31}}_{P}$  coupling constant increases upon pincer formation from 2242 Hz in 6 to 2756 Hz in 7. Very few platinum pincer complexes with methine central moieties are known,<sup>29</sup> and only one of these features a diaminomethyl central group.<sup>30</sup>

The solid-state structure of 7 (Figure 4) confirms pincer formation and is very similar to the structure of the analogous nickel pincer 4, with the exception of the longer bonds involving the square-planar metal. The best planes of the imidazole rings form a dihedral angle of  $147.1^{\circ}$ , and the methine carbon lies 0.13 and 0.25 Å outside of these planes, implying structural strain. In line with the observations made on 4, the acidity of the diaminomethine hydrogen in 7 is low, and this compound does not react with KHMDS in toluene or THF in the presence or absence of Lewis bases (PPh<sub>3</sub> and



**Figure 4.** Solid-state structure of 7 with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms except those on the methine bridge were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1–Cl1 = 2.3587(6); Pt1–P = 2.2724(6), 2.2748(6); Pt1–C1 = 2.065(2); P1…P2 = 4.514(1); C1-N = 1.473(3); 1.492(3); P1–Pt1–P2 = 166.23(2); Cl1–Pt1–C1 = 177.16(7); N1–C1–N3 = 113.0(2).

*t*BuNC). Similarly, hydride abstraction with trityl tetrakis-(pentafluorophenyl)borate in toluene failed to yield a cationic PCP-pincer carbene complex.

In anticipation of an increase in the acidity of the diaminomethine hydrogen upon oxidation of the platinum center, the synthesis of platinum(IV) complex 8 by oxidation of 7 with  $PhICl_2$  was easily achieved (Scheme 4). A few diphosphine trihalide complexes of platinum(IV) with a similar coordination geometry at the metal have been reported and were shown to be susceptible to photoreduction,<sup>31</sup> but none of these were pincer derivatives. Several NCN pincer complexes of platinum(IV) are however known,<sup>32</sup> and CCP analogs have been reported as well.<sup>33</sup> The <sup>31</sup>P NMR resonance at 35.6 ppm in 7 shifted slightly to 24.5 ppm in 8 upon oxidation, and the  ${}^{1}J^{_{195}}_{Pt}{}^{_{31}}_{P}$  coupling constant in this compound measured 2266 Hz. This was significantly larger than in the reported Pt(IV) CCP pincer complexes (1371 and 1427 Hz)<sup>33</sup> and mirrored the difference in the magnitude of the coupling constants observed for the respective Pt(II) precursors. The time-averaged  $C_s$ symmetry of the compound was maintained upon oxidation, and the  $J_{195}_{Pt}{}^{13}_{C}$  and  ${}^{2}J_{195}{}^{19}_{Pt}{}^{1}_{H}$  coupling constants (652.5 and 86.8 Hz, respectively) observed for the resonances corresponding to the methine bridge confirmed that the Pt-C bond remained intact. Attempted deprotonation of 8 with KHMDS resulted in quantitative reduction to 7, which was identified based on its NMR signature.

Due to the presence of more Lewis basic sites, ligand 2 promises a more varied coordination chemistry in comparison to 1. Its reaction with  $CoBr_2$  (Scheme 5) yielded teal-colored

Scheme 5. Synthesis of Co Complex 9



paramagnetic complex 9, with an effective magnetic moment of 4.77, as determined using Evans' method;<sup>23</sup> this is in good agreement with a pseudotetrahedral geometry at the metal.<sup>24</sup> A structural determination based on single-crystal X-ray diffraction revealed P,N-chelation with the formation of a sevenmembered metallacycle that adopted a boat conformation in the solid state (Figure 5). The metal was even closer to the methylene carbon than in the nickel complex 3 (3.24 vs 3.67 Å). Given that the PP bite of the ligand is easily adaptable to



**Figure 5.** Solid-state structure of **9** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms except those on the methylene bridge were omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1–Br = 2.3547(7), 2.3775(10); Co1–P1 = 2.3916(11); Co1–N4 2.017(3); Co1—C1 = 3.238(3); C1–N = 1.446(4); 1.465(4); P1–Co1–N4 = 101.68(9); Br1–Co1–Br2 = 115.98(3); N1–C1–N3 = 113.2(3).

the size and geometry of the metal, it is likely that the coordination mode involving the pyrazole nitrogen reflects the preference of Co(II) for mixed ligation<sup>34</sup> and not steric strain.

#### CONCLUSIONS

Ligands 1 and 2, easily accessible via two high-yield synthetic steps from commercially available starting materials, proved to have a diverse coordination chemistry. Most notably, the chelated complexes of Ni(II) (3) and Pt(II) (6) incorporating ligand 1 were converted to PCP pincer analogs 4 and 7, respectively, in the presence of KHMDS. Ni(I) chelate complex 5 was obtained as a side product in the formation of 4. The methine bridge hydrogen in complexes 4 and 7 proved to be remarkably robust and could not be removed as either a proton or a hydride to yield carbene-based PCP pincer complexes.

This research started from the premise that the involvement of the nitrogen lone pair in the  $\pi$  electron system of the aromatic imidazole ring would lead to weak stabilization of the diaminocarbene structure and increase the stability of the diaminomethyl complexes. The validity of this premise was confirmed, and diaminomethyl complexes 4 and 7 were shown to be stable toward air and moisture and survive reflux in toluene. It is nevertheless surprising that the diaminomethyl proton in complexes 4 and 7 cannot be removed with strong bases, especially given the related chemistry outlined in Scheme 1, as well as that described for analogs F, G, and especially  $L^{(13-15,18)}$  The lack of such an observable derivative does not preclude the involvement of such an intermediate in a ligandassisted catalytic process, and investigations in this direction are pending. Notable for ligand 1 is the easily variable P...P ligand "bite", which measures 3.69, 3.75, 4.33, and 4.52 Å in 5, 3, 4 and 7, respectively, as well as the stability of its Ni(II) derivatives in the air. Further investigations of ligands based on the bis(imidazolyl)- and bis(pyrazolyl)methane frameworks are in progress.

#### EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise specified, all operations were carried out with careful exclusion of air and moisture using standard Schlenk and glovebox techniques. The solvents were dried and deoxygenated prior to use. Starting materials were purchased from commercial suppliers and used as received. All NMR spectra were run on either a Bruker Avance RDQ-400 instrument and chemical shifts are reported in  $\delta$  units (ppm) using the solvent as an internal reference: CH<sub>2</sub>Cl<sub>2</sub>-d<sub>1</sub> (5.32 ppm, <sup>1</sup>H) and CH<sub>2</sub>Cl<sub>2</sub>-d<sub>2</sub> (54.00 ppm, <sup>13</sup>C); THF-d<sub>7</sub> (3.58 ppm, <sup>1</sup>H) and THF-d<sub>8</sub> (67.57 ppm, <sup>13</sup>C); toluene $d_7$  (2.09 ppm, <sup>1</sup>H) and toluene- $d_8$  (20.4 ppm, <sup>13</sup>C). All <sup>13</sup>C and <sup>31</sup>P NMR spectra were acquired broad-band proton decoupled.

**Synthesis of Methylenebis(imidazole).**<sup>22</sup> Imidazole (20.00 g, 134.98 mmol), *n*-butylammonium bromide (2.43 g, 7.53 mmol), and finely ground KOH (32.97 g, 582.75 mmol) were mixed in a thick-walled round-bottomed flask equipped with a magnetic stirring bar. The reaction mixture liquefied upon mixing and when the viscosity started to increase again (30–60 min),  $CH_2Cl_2$  (9.4 mL, 146.90 mmol) was added, the flask sealed, and the highly exothermic reaction allowed to proceed overnight. The pure product was isolated as a colorless crystalline solid (13.397 g, 61.56%) via sublimation from the crude reaction mixture at 170 °C and 10<sup>-3</sup> bar. A similar procedure was used for the synthesis of methylenebis(pyrazole).

**Synthesis of Ligand 1.** Methylenebis(imidazole) (2.00 g, 13.50 mmol) was dissolved in THF (400 mL) in a swivel frit apparatus attached to vacuum line. The solution was cooled to -55 °C using a liquid N<sub>2</sub>/ethanol bath. Then, *n*BuLi (18.1 mL, 28.90 mmol) was added dropwise, and the mixture was allowed to slowly warm up to -20 °C under continuous stirring. After 1 h at this temperature, the reaction mixture was cooled again to -55 °C, and *i*Pr<sub>2</sub>PCl was added (4.12 g, 27.81 mmol) and allowed to react for 12 h. Solid NH<sub>4</sub>Cl (1.40 g, 26 mmol) was added to quench excess unreacted *n*BuLi, and the reaction mixture was stirred for another 1 h. The solvent was removed in vacuo, and the remaining brown solid was extracted with pentane (200 mL). The product was obtained as a pale yellow thick oil (3.16 g, 61.44%) of satisfactory purity upon removal of the pentane in vacuo.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K): δ 0.97 (12H, dd,  ${}^{3}J_{PH} = 12.6$  Hz,  ${}^{3}J_{HH} = 6.9$  Hz, CH<sub>3</sub>), 1.11 (12H, dd,  ${}^{3}J_{PH} = 15.9$  Hz,  ${}^{3}J_{HH} = 7.1$  Hz, CH<sub>3</sub>), 2.35 (4H, dsep,  ${}^{3}J_{HH} = 7.0$  Hz,  ${}^{2}J_{PH} = 2.1$  Hz, CH), 6.55 (2H, t,  ${}^{4}J_{PH} = 3.3$  Hz, CH<sub>2</sub>), 7.16 (s, 2H, CH), 7.26 (s, 2H, CH).  ${}^{13}C$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz, 298 K):  $\delta$  19.5 (d,  ${}^{2}J_{PC} = 8.8$  Hz, CH<sub>3</sub>), 20.1 (d,  ${}^{2}J_{PC} = 18.3$  Hz, CH<sub>3</sub>), 25.0 (d,  ${}^{1}J_{PC} = 5.8$  Hz, CH), 55.3 (t,  ${}^{3}J_{PC} = 16.7$  Hz, CH<sub>2</sub>), 121.0 (vt,  $J_{PC} = 3.0$  Hz, CH), 131.4 (s, CH), 147.1 (d,  ${}^{1}J_{PC} = 16.8$  Hz, PC).  ${}^{31}P{}^{1}H$  NMR (toluene- $d_{8}$ , 162 MHz, 298 K):  $\delta$  –19.44 (s).

Synthesis of Ligand 2. In a 100 mL two-necked round-bottomed flask, 1,1'-methylenebis(pyrazole) (500 mg, 3.37 mmol) was dissolved in THF (70 mL). The solution was subsequently cooled to -78 °C, treated dropwise with 1.6 M nBuLi in hexanes (4.22 mL, 6.74 mmol), and stirred for 2 h, while being allowed to warm up to -25 °C. After cooling back to -78 °C, the mixture was treated dropwise with iPr<sub>2</sub>PCl (1.03 g, 6.95 mmol) and allowed to warm up to room temperature overnight. Solid ammonium chloride (370 mg, 6.87 mmol) was added, the mixture stirred for another hour, and the solvent removed in vacuo. The solid residue was extracted with pentane (80 mL), yielding a light yellow solution. After filtration, the solvent was removed in vacuo, leaving behind the product as a yellow transparent oil (1.20 g, 93%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K):  $\delta$ 0.97 (12H, dd,  ${}^{3}J_{PH} = 12.0$  Hz,  ${}^{3}J_{HH} = 7.2$  Hz,  $CH_{3}$ ), 1.02 (12H, dd,  ${}^{3}J_{PH} = 12.0$  Hz,  ${}^{3}J_{HH} = 7.2$  Hz,  $CH_{3}$ ), 1.94 (4H, dsep,  ${}^{3}J_{HH} = 6.8$  Hz,  ${}^{2}J_{\rm PH}$  = 1.6 Hz, CH), 6.16 (d, 2H,  ${}^{3}J_{\rm HH}$  = 1.8 Hz, CH), 7.03 (2H, t,  ${}^{4}J_{\rm PH}$ = 3.2 Hz, *CH*<sub>2</sub>), 7.56 (2H, d,  ${}^{3}J_{HH}$  = 1.8 Hz, *CH*).  ${}^{13}C$  NMR (*C*<sub>6</sub>*D*<sub>6</sub>, 101 MHz, 298 K):  $\delta$  19.6 (d,  ${}^{2}J_{PC}$  = 10.1 Hz, *CH*<sub>3</sub>), 20.0 (d,  ${}^{2}J_{PC}$  = 17.2 Hz, *CH*<sub>3</sub>), 24.6 (d,  ${}^{1}J_{PC}$  = 9.1 Hz, *CH*), 61.0 (t,  ${}^{3}J_{PC}$  = 15.2 Hz, *CH*<sub>2</sub>), 11.6 (t,  ${}^{2}J_{PC}$  = 15.2 Hz, *CH*<sub>2</sub>) 111.6 (s, CH), 139.8 (dd,  ${}^{1}J_{PC} = 24.2$ ,  ${}^{5}J_{PC} = 2.4$  Hz, PC), 140.2 (s, CH). <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  –20.8 ppm (s).

**Synthesis of Ni(II) Complex 3.** Ni(dme)Br<sub>2</sub> (520 mg, 1.68 mmol) was added to a solution of 1 (650 mg, 1.69 mmol) in toluene (50 mL), and the reaction mixture was stirred for 12 h at room temperature. The solvent was subsequently removed in vacuo, and the solid was washed with pentane, leaving the product behind as a dark green crystalline solid (919 mg, 91.2%). The magnetic susceptibility  $\mu_{\text{eff}}$  was determined to be 3.76 by Evans' method using the chemical shift of SiMe<sub>4</sub> in toluene-*d*<sub>8</sub> solution and a concentration of 3 of 9.13 mg/mL, 298 K. Elemental analysis (%): Calcd for C<sub>19</sub>H<sub>34</sub>N<sub>4</sub>Br<sub>2</sub>NiP<sub>2</sub>: C 38.10, H 5.72, N 9.25. Found: C 37.86, H 5.76, N 8.44. Single crystals suitable for X-ray crystallography were obtained via slow evaporation of a THF solution.

**Synthesis of Ni(II) Complex 4.** Solid KHMDS (336 mg, 1.68 mmol) was added at room temperature to a solution of 3 (873 mg, 1.46 mmol) in THF in a swivel frit setup. The reaction mixture was allowed to stir for 2 h at room temperature, and the solvent was subsequently removed in vacuo. The product was extracted with toluene, the solvent removed in vacuo, and the remaining solid washed with pentane. The product was isolated by filtration as a light brown powder (656 mg, 86.9%). Ni(I) byproduct **5** was removed by exposing a suspension of crude **4** in hexane to the air and subsequently subjecting the resulting mixture to Soxhlet extraction using hexane for **48** h. Pure **5** separated in the collection flask as an orange powder.

<sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, 298 K): δ 1.07 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, *J*<sub>PH</sub> = 7.5 Hz, *CH*<sub>3</sub>), 1.26 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, *J*<sub>PH</sub> = 8.4 Hz, *CH*<sub>3</sub>), 1.40 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, *J*<sub>PH</sub> = 8.4 Hz, *CH*<sub>3</sub>), 1.40 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, *J*<sub>PH</sub> = 8.4 Hz, *CH*<sub>3</sub>), 1.42 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, *J*<sub>PH</sub> = 8.4 Hz, *CH*<sub>3</sub>), 1.42 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, *J*<sub>PH</sub> = 8.4 Hz, *CH*<sub>3</sub>), 2.40 (2H, m, *CH*), 2.68 (2H, m, *CH*), 5.84 (1H, s, NiCH), 6.85 (2H, s, *CH*), 7.39 (2H, s, *CH*). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 101 MHz, 298 K): δ 17.7 (s, *CH*<sub>3</sub>), 18.2 (s, *CH*<sub>3</sub>), 18.4 (s, *CH*<sub>3</sub>), 18.5 (s, *CH*<sub>3</sub>), 24.4 (vt, *J*<sub>PC</sub> = 14.9 Hz, *CH*), 25.7 (vt, *J*<sub>PC</sub> = 12.8 Hz, *CH*), 65.6 (t, <sup>3</sup>*J*<sub>PC</sub> = 17.3 Hz, NiCH), 121.4 (s, *CH*), 137.6 (vt, *J*<sub>PC</sub> = 3.5 Hz, *CH*), 148.1 (vt, *J*<sub>PC</sub> = 31.3 Hz, N<sub>2</sub>CP). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 162 MHz, 298 K): δ 31.5 (s). Elemental analysis (%): Calcd for C<sub>19</sub>H<sub>33</sub>N<sub>4</sub>BrNiP<sub>2</sub>: C 44.05, H 6.42, N 10.82. Found: C 44.78, H 6.35, N 11.02. Single crystals suitable for X-ray crystallography were obtained via vapor diffusion of pentane into a toluene solution.

Synthesis of Pt(II) Complex 6. THF (120 mL) was condensed onto a mixture of ligand 1 (808 mg, 2.12 mmol) and  $PtCl_2$  (565 mg, 2.12 mmol). The reaction vessel was immersed in an ultrasonic bath for 1 h and then stirred at room temperature for 16 h. The solvent was removed in vacuo, and the residue was washed with pentane (2 × 50 mL) and subsequently extracted with dichloromethane over 24 h in a Soxhlet apparatus. Removal of the solvent yielded 6 (840 mg, 61%) as a tan powder.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K): δ 0.87 (6H, dd,  ${}^{3}J_{HH} = 6.6$  Hz,  ${}^{3}J_{PH} = 15.7$  Hz, CH<sub>3</sub>), 1.26 (6H, dd,  ${}^{3}J_{HH} = 7.0$  Hz,  ${}^{3}J_{PH} = 15.8$  Hz, CH<sub>3</sub>), 1.35 (6H, dd,  ${}^{3}J_{HH} = 6.8$  Hz,  ${}^{3}J_{PH} = 19.2$  Hz, CH<sub>3</sub>), 1.52 (6H, dd,  ${}^{3}J_{HH} = 6.9$  Hz,  ${}^{3}J_{PH} = 17.8$  Hz, CH<sub>3</sub>), 2.92 (2H, m, br, CH), 3.68 (2H, m, br, CH), 6.09 (1H, d,  ${}^{2}J_{HH} = 13.7$  Hz, CH<sub>2</sub>), 7.16 (2H, s, CH), 7.38 (2H, s, CH), 7.89 (1H, d,  ${}^{2}J_{HH} = 14.1$  Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz, 298 K): δ 18.6 (s, CH<sub>3</sub>), 19.5 (s, CH<sub>3</sub>), 20.8 (s, CH<sub>3</sub>), 21.6 (s, CH<sub>3</sub>), 27.1 (d,  ${}^{1}J_{PC} = 36.6$  Hz, CH), 29.0 (d,  ${}^{1}J_{PC} = 39.0$  Hz, CH), 57.1 (s, CH<sub>2</sub>), 125.1 (s, CH), 131.4 (d,  ${}^{3}J_{PC} = 10.0$  Hz, CH), 136.4 (d,  ${}^{1}J_{PC} = 70.6$  Hz, N<sub>2</sub>CP).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K): δ 6.9 (s,  ${}^{1}J_{PH} = 2242.1$  Hz). Elemental analysis (%): Calcd for C<sub>19</sub>H<sub>34</sub>N<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>Pt: C 35.30, H 5.30, N 8.67. Found: C 35.74, H 5.68, N 8.20.

**Synthesis of Pt(II) Complex 7.** Toluene (70 mL) was condensed onto a mixture of 6 (683 mg, 1.06 mmol) and KHMDS (211 mg, 1.06 mmol), and the suspension was stirred at room temperature for 24 h. The solids were filtered off, and the toluene was removed in vacuo. The residue was triturated with pentane (25 mL), which was then removed in vacuo. This operation was repeated three times to fully remove excess HMDS. The solid was washed with pentane (50 mL), and 7 was isolated as an off-white powder (505 mg 78%).

<sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 400 MHz, 298 K): δ 0.91 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, *J*<sub>PH</sub> = 8.8 Hz, CH<sub>3</sub>), 1.17 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, *J*<sub>PH</sub> = 8.8 Hz, CH<sub>3</sub>), 1.35 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, *J*<sub>PH</sub> = 9.2 Hz, CH<sub>3</sub>), 1.38 (6H, dvt, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, *J*<sub>PH</sub> = 7.2 Hz, CH<sub>3</sub>), 2.52 (2H, m, CH), 2.90 (2H, m, CH), 6.43 (1H, s, <sup>2</sup>*J*<sub>PH</sub> = 84.8 Hz, PtCH), 6.97 (2H, d, <sup>3</sup>*J*<sub>HH</sub> = 0.8 Hz, CH), 7.54 (2H, d, <sup>3</sup>*J*<sub>HH</sub> = 0.8 Hz, <sup>5</sup>*J*<sub>PtH</sub> = 12.0 Hz, CH<sub>3</sub>), 18.1 (vt, *J*<sub>PC</sub> = 2.5 Hz, CH<sub>3</sub>), 18.3 (s, <sup>3</sup>*J*<sub>PtC</sub> = 10.5 Hz, CH<sub>3</sub>), 18.7 (s, <sup>3</sup>*J*<sub>PtC</sub> = 17.9 Hz, CH<sub>3</sub>), 23.6 (vt, *J*<sub>PC</sub> = 17.3 Hz, <sup>2</sup>*J*<sub>PtC</sub> = 21.9 Hz, CH), 26.9 (vt, *J*<sub>PC</sub> = 15.6 Hz, <sup>2</sup>*J*<sub>PtC</sub> = 22.4 Hz, CH), 54.2 (t, <sup>3</sup>*J*<sub>PtC</sub> = 41.2 Hz, CH), 137.8 (vt, *J*<sub>PC</sub> = 4.7 Hz, CH), 147.3 (vt, *J*<sub>PC</sub> = 37.5 Hz, N<sub>2</sub>CP). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 162 MHz, 298 K): δ 35.6 (s, <sup>1</sup>*J*<sub>PtP</sub> = 2755.6 Hz). Elemental analysis (%): Calcd for C<sub>19</sub>H<sub>33</sub>N<sub>4</sub>ClP<sub>2</sub>Pt: C 37.41, H 4.45, N 9.19. Found: C 37.12, H 5.22, N 8.80.

Synthesis of Pt(IV) Complex 8. A solution of PhICl<sub>2</sub> (95 mg, 0.35 mmol) in dichloromethane (25 mL) was added dropwise at room

temperature to a solution of 7 (202 mg, 0.33 mmol) in the same solvent (25 mL). The mixture was stirred for 6 h, and the volatiles were removed in vacuo. The residue was washed twice with pentane (25 mL) and collected, yielding 8 (104 mg, 46%) as a microcrystalline solid.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K): δ 0.90 (6H, dd,  ${}^{3}J_{HH} = 7.0$  Hz,  ${}^{3}J_{PH} = 17.2$  Hz, CH<sub>3</sub>), 1.66 (6H, dd,  ${}^{3}J_{HH} = 7.2$  Hz,  ${}^{3}J_{PH} = 20.6$  Hz, CH<sub>3</sub>), 1.76 (6H, dd,  ${}^{3}J_{HH} = 7.4$  Hz,  ${}^{3}J_{PH} = 18.1$  Hz, CH<sub>3</sub>), 1.77 (6H, dd,  ${}^{3}J_{HH} = 6.9$  Hz,  $J_{PH} = 17.2$  Hz, CH<sub>3</sub>), 2.79 (2H, m, CH), 4.01 (2H, m, CH), 6.91 (1H, s,  ${}^{2}J_{PH} = 86.8$  Hz, PtCH), 7.51 (2H, s, CH), 7.52 (2H, d, CH).  ${}^{13}$ C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz, 298 K): δ 19.7 (s, CH<sub>3</sub>), 19.8 (s, CH<sub>3</sub>), 20.5 (s, CH<sub>3</sub>), 18.3 (s, CH<sub>3</sub>), 21.3 (s, CH<sub>3</sub>), 31.6 (d,  ${}^{1}J_{PC} = 28.3$  Hz,  ${}^{2}J_{PtC} = 15.2$  Hz, CH), 32.9 (d,  ${}^{1}J_{PC} = 33.3$  Hz,  ${}^{2}J_{PtC} = 16.7$  Hz, CH), 57.9 (s,  ${}^{1}J_{PtC} = 652.5$  Hz, PtCH), 123.3 (s,  ${}^{3}J_{PtC} = 28.2$  Hz), 138.1 (d,  ${}^{3}J_{PC} = 11.1$  Hz, CH), 147.3 (d,  $J_{PC} = 94.9$  Hz, N<sub>2</sub>CP).  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K): δ 24.5 (s,  ${}^{1}J_{PtP} = 2266.4$  Hz).

**Synthesis of Co Complex 9.** Solid cobalt(II) bromide (286 mg, 1.31 mmol) was added at -78 °C to a THF (60 mL) solution of **2** (500 mg, 1.31 mmol). The mixture was allowed to warm up to room temperature overnight with stirring, during which time the color turned from light green to dark teal. The mixture was filtered, and the solvent was removed in vacuo. The solid teal colored residue was washed with pentane (50 mL) and collected by filtration (715 mg, 91%). Its effective magnetic moment was determined by Evans' method ( $\mu_{\rm eff}$  = 4.77) using a 16.7 mM solution in CD<sub>2</sub>Cl<sub>2</sub>. Elemental analysis (%): Calcd for C<sub>19</sub>H<sub>34</sub>N<sub>4</sub>Br<sub>2</sub>P<sub>2</sub>Co: C 38.09, H 5.72, N 9.35. Found: C 38.17, H 5.83, N 8.73.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00396.

Complete NMR spectra for all new diamagnetic compounds, as well as the relevant crystallography tables (PDF)

Cartesian coordinates (XYZ)

#### Accession Codes

CCDC 1552638–1552642 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, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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