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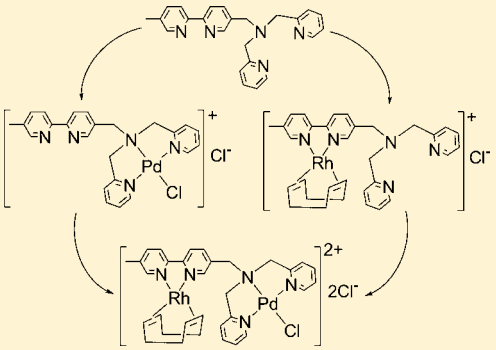
Evaluation of Multisite Polypyridyl Ligands as Platforms for the Synthesis of Rh/Zn, Rh/Pd, and Rh/Pt Heterometallic Complexes

Sarah K. Goforth, Richard C. Walroth, and Lisa McElwee-White*

Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

Supporting Information

ABSTRACT: Ligands containing linked dipicolylamine (dpa) and bipyridine (bpy) sites have been utilized in the synthesis of monometallic and heterometallic complexes. The two sites have different selectivities for metal binding, which allows preferential formation of singly metalated complexes. The dpa site of the ligands has been observed to bind selectively to Zn^{2+}, Pd^{2+}, and Pt^{2+}, while the bpy site binds selectively to Rh^{+}. Addition of a second metal then results in the formation of heterometallic products. In the presence of CD_3OD, the heterometallic Rh/Pt and Rh/Pd complexes undergo rapid selective H/D exchange of one of the diastereotopic protons of the dpa methylene group.



INTRODUCTION

The use of heterobimetallic complexes as catalysts has arisen as a potentially useful motif in organometallic catalysis.[1−6] The rationale behind these catalysts is that the two different metals involved can interact cooperatively to achieve new reactivity not possible with one metal center. In some cases, each metal is an active site for different steps in the reaction. In others, the connection between the two metals through one or more bridging ligands alters the electronic properties of the active metal site. Heterobimetallic catalysts have been utilized in many reaction types including carbonylation,[7,8] C−C coupling,[9−11] alcohol oxidation,[12] and ethylene polymerization.[13] Heterometallic complexes have also been successful in the area of tandem catalysis. For example, Cu/Pd catalysts were employed for tandem click/Sonogashira reactions,[14] and Ir/Pd complexes were found to catalyze Suzuki-coupling/transfer hydrogenations.[15]

Though heterobimetallic complexes have been proven to be useful catalysts, their synthesis is challenging. One approach is the use of multisite ligands whose sites have different binding affinities for different metals.[16−20] There have been several recent examples of multisite polypyridyl ligands (Figure 1) which often display differing site selectivities for various metals.[16,17,21−29] This property is often found in ligands containing dipicolylamine (dpa) along with either a phenanthroline (phen) or bipyridine (bpy) moiety. The ligand L1 was reported to selectively bind Zn^{2+} at its dipicolylamine (dpa) site as evidenced by X-ray crystallography.[21] The binding selectivity was found to remain consistent for a variety of L1 derivatives which were then used as Zn^{2+} sensors with large dynamic ranges. Similarly, selective dpa binding by $Zn(NO_3)_2$ has been reported for the L2 ligand.[19,22,23] Ligands L3 and L4 were also found to bind Zn^{2+} as well as Cu^{2+} at their dpa sites followed by subsequent addition at their bpy site as monitored by UV−visible spectroscopy.[24,25] Though the complexes were not isolated, they were further characterized by comparison with model compounds. Ligand L3 has also been used in the

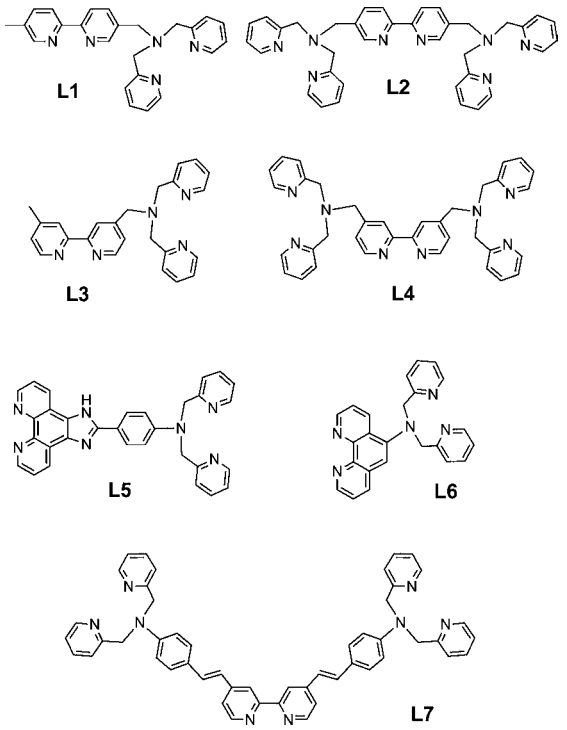


Figure 1. Examples of multisite polypyridyl ligands.

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formation of Ru/Mn complexes in which the Ru is first bound to the bpy site.[26] However, the Ru was bound to a monobromomethyl-2,2-bipyridine moiety followed by reaction with dpa to give $[Ru(bpy)_2(L3)]^{2+}$. Similar methods were employed in the formation of $[Ru(bpy)_2(L5)]^{2+}$.[27] Ligands L6 and L7 can also bind metal exclusively at their bidentate site when reacted with cyclometalated $[Ir_2(C^{\wedge}N)_4Cl_2]$ complexes (where C^N is a derivative of 2-phenylpyridine).[28,29]

On the basis of these precedents, we have chosen L1 and L2 as model systems for the study of selective metalation of polypyridyl ligands in the synthesis of heterobimetallic complexes. In this work, we have probed the reactivity of L1 and L2 with Zn, Rh, Pd, and Pt sources, resulting in selective preparation of several heterometallic complexes. NMR techniques, ESI-MS analysis, and elemental analysis were used to determine the binding site preferences of these metals.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all reactions were performed under an inert atmosphere using standard Schlenk line and glovebox techniques. All anhydrous solvents were stored over 3 Å molecular sieves. Dichloromethane, hexane, and toluene were passed through an MBraun MB-SP solvent purification system prior to use. Other solvents were distilled from sodium/benzophenone (tetrahydrofuran, diethylether), CaH_2 (DMSO), or magnesium turnings and I_2 (ethanol, methanol). Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, stored over 3 Å molecular sieves, and used without further purification. The Pd(COD)Cl_2 and $Na_2[PtCl_4]$ were purchased from Strem Chemicals, and all other reagents were obtained from Aldrich and Fisher. The syntheses of L1, L2, and L2′ were all modified from procedures described by Zhu and co-workers for the preparation of L1.[21] Complex **3** was synthesized using the method of Hamachi and co-workers.[23] Syntheses of model complexes Zn(dpa)Cl_2, [Pd(dpa)Cl]Cl, and [Pt(dpa)Cl]Cl were modified from those of their L1 and L2 analogues, and the procedures are included in the Supporting Information.

All ^{1}H NMR and ^{13}C NMR spectra were obtained using either a 300 MHz Mercury, a 300 MHz Gemini, or a 500 MHz INOVA instrument while all gHMBCAD spectra were collected using the 500 MHz INOVA instrument. High resolution mass spectrometry (HRMS) data were recorded on an electrospray ionization, time-of-flight (ESI-TOF) mass spectrometer. Elemental analyses of [**4**](**PF$_6$**), [**5**](**PF$_6$**)$_2$, [**7**](**PF$_6$**)$_2$, **13**, and **17** were performed by Complete Analysis Laboratories in Parsippany, New Jersey, while that of **12** was performed at the University of Florida. For compounds **16** and **18**, repeated attempts to obtain elemental analyses (including duplicate analyses of the same sample by the same laboratory and duplicate analyses of portions of the same sample by different laboratories) afforded inconsistent results.

Synthesis of Monometallic and Homobimetallic Complexes. *(L1)ZnCl$_2$* ***(1)***. This synthesis was modified from that of Zhu and co-workers.[21] Ligand L1 (0.3017 g, 0.790 mmol) was dissolved in CH_2Cl_2 (6.0 mL) and was added to a CH_3CN (10.0 mL) solution of $ZnCl_2$ (0.1078 g, 0.790 mmol). The solvent was immediately removed by rotary evaporation to give a white powder (0.3842 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.37 (dd, J = 5.4, 1.0 Hz, 2H), 8.51 (d, J = 1.9 Hz, 1H), 8.40 (d, J = 1.9 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 7.91 (td, J = 7.7, 1.7 Hz, 2H), 7.66 (dd, J = 8.2, 1.9 Hz), 7.64 (dd, J = 8.2, 1.9 Hz, 2H), 7.52 (ddd, J = 7.4, 5.2, 1.0 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 4.11 (br s, 4H), 3.90 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.3, 153.4, 152.4, 150.7, 150.5, 149.8, 140.2, 139.6, 137.7, 134.2, 127.4, 124.8, 123.7, 120.6, 120.6, 55.5, 53.0, 18.5.

(L2)(Zn(OAc)$_2$)$_2$ ***(2)***. A methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.0124 g, 0.0565 mmol) was added to a methanolic solution of L2 (0.0186 g, 0.0321 mmol) open to the air. The solvent was removed under reduced pressure to afford **2** as a pale yellow solid (0.0163 g, 61%). ^{1}H NMR (300 MHz, CD_3OD): δ 8.78 (d, J = 4.2 Hz, 4H), 8.55 (br s, 2H), 8.36 (d, J = 7.6 Hz, 2H), 8.06 (t, J = 7.5 Hz, 4H), 7.94 (br s, 2H), 7.61 (t, J = 6.3 Hz, 4H), 7.56 (d, J = 8.0 Hz, 4H), 4.36–3.99 (m, 8H), 3.90 (br s, 4H), 2.01 (s, 11H). ^{13}C NMR (126 MHz, CD_3OD): δ 179.3, 154.8, 151.1, 148.6, 140.6, 140.0, 128.8, 124.6, 124.2, 120.7, 55.4, 53.2, 21.8.

[(L1)(PtCl)](PF$_6$) ***([4](PF$_6$))***. $Na_2[PtCl_4]{\cdot}xH_2O$ (0.0231 g, 0.0606 mmol) and L1 (0.0232 g, 0.0606 mmol) were suspended in 1.5 mL of DMSO-d_6 and allowed to stir at room temperature overnight. The addition of 16 mL of acetone resulted in the precipitation of an NMR silent impurity (most likely NaCl) which was removed by filtration. The acetone was removed from the filtrate by rotary evaporation. Excess aqueous KPF_6 was added to the yellow residue, yielding the product as an off-white solid (0.0440 g, 96%) which was collected by vacuum filtration and washed with methanol and diethyl ether. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.98 (s, 1H), 8.64 (d, J = 5.4 Hz, 2H), 8.48 (s, 1H), 8.30 (d, J = 7.3 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 8.10 (t, J = 8.4 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 7.9 Hz, 2H), 7.52–7.42 (m, 2H), 5.42 (d, J = 15.6 Hz, 2H), 4.99 (d, J = 16.2 Hz, 2H), 4.45 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.9, 156.0, 153.3, 152.3, 150.1, 149.5, 141.6, 141.4, 138.1, 134.6, 127.7, 125.4, 124.1, 120.8, 119.3, 68.4, 64.3, 18.3. HRMS (ESI-TOF) for $C_{24}H_{23}ClF_6N_5PPt$ calcd.: $[M - PF_6]^+$ 612.1281. Found: 612.1287. Anal. Calcd for $C_{24}H_{23}ClF_6N_5PPt$: C, 38.08; H, 3.06; N, 9.25. Found: C, 38.12; H, 3.08; N, 9.22.

[(L2)(PtCl)$_2$]Cl$_2$ ***([5]Cl$_2$)***. A 50 mL Schlenk flask was charged with L2 (0.3027 g, 0.523 mmol), $Na_2[PtCl_4]{\cdot}xH_2O$ (0.4009 g, 1.05 mmol), and anhydrous DMSO (20 mL), giving a dark burnt orange mixture. After stirring at room temperature overnight, the reaction produced a white solid suspended in a yellow solution. The reaction mixture was filtered in the air through a fine fritted funnel to afford the product as a white powder (0.490 g, 84%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.90 (s, 2H), 8.64 (d, J = 5.5 Hz, 4H), 8.35 (d, J = 8.3 Hz, 2H), 8.13 (t, J = 7.7 Hz, 4H), 7.87 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 7.7 Hz, 4H), 7.55–7.45 (m, 4H), 5.51 (d, J = 16.0, 4H), 5.00 (d, J = 14.9, 4H), 4.41 (br s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.9, 154.8, 153.4, 149.5, 141.8, 141.3, 128.7, 125.4, 124.1, 120.0, 68.5, 64.3. HRMS (ESI-TOF) for $C_{36}H_{34}Cl_4N_8Pt_2$ calcd.: $[M - 2Cl]^{2+}$ 519.5779. Found: 519.5785.

[(L2)(PtCl)$_2$](PF$_6$)$_2$ ***([5](PF$_6$)$_2$)***. Complex [**5**]**Cl$_2$** (0.0505 g, 0.0455 mmol) was dissolved in DMSO/H_2O (5:3) and treated with excess aqueous KPF_6 (sat.). The white precipitate was collected by vacuum filtration and washed with methanol and diethyl ether (0.0283 g, 47%). Anal. Calcd for $C_{36}H_{34}Cl_2F_{12}N_8P_2Pt_2$: C, 32.50; H, 2.58; N, 8.43. Found: C, 32.59; H, 2.67; N, 8.34.

[(L1)PdCl]PF$_6$ ***([6]PF$_6$)***. L1 (0.0213 g, 0.0558 mmol) and Pd(COD)Cl_2 (0.0151 g, 0.0529 mmol) were dissolved in methanol (10 mL) and allowed to stir overnight. Solvent was removed from the resulting pale yellow solution, and the pale yellow residue was redissolved in 1 mL of CD_3OD for NMR characterization revealing product [**6**]**Cl** and trace amounts of L1. The addition of 0.425 M aqueous KPF_6 (0.25 mL, 0.11 mmol) to this solution resulted in the precipitation of [**6**]**PF$_6$**. The product was collected by vacuum filtration and washed with diethylether yielding a white powder (0.0274 g, 78%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.05 (s, 1H), 8.49 (s, 1H), 8.42 (d, J = 5.7 Hz, 2H), 8.36 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 8.07 (t, J = 7.7 Hz, 2H), 8.04 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 7.7 Hz, 2H), 7.45 (m, 2H), 5.58 (d, J = 16.1 Hz, 2H), 4.70 (d, J = 16.2 Hz, 2H), 4.39 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 164.6, 156.4, 152.2, 151.9, 150.4, 149.3, 141.0, 140.8, 137.8, 134.8, 128.0, 124.3, 123.1, 120.9, 120.0, 67.4, 63.7, 16.8. HRMS (ESI-TOF) for $C_{24}H_{23}Cl_2N_5Pd$ calcd.: $[M - Cl]^+$ 524.0670. Found: 524.0682.

[(L2)(PdCl)$_2$]Cl$_2$ ***([7]Cl$_2$)***. A 100 mL Schlenk flask was charged with Pd(COD)Cl_2 (0.0990 g, 0.347 mmol) and L2 (0.100 g, 0.173 mmol). The reagents were combined with 60 mL of anhydrous THF. The reaction mixture was stirred for 24 h, at which point a white precipitate had formed. The supernatant was removed, and the solid was rinsed with anhydrous THF (20 mL) to yield [**7**]**Cl$_2$** as an off-white powder (0.150 g, 93%). ^{1}H NMR (300 MHz, CD_3OD): δ 9.08 (d, J = 1.7 Hz, 2H), 8.58 (dd, J = 5.8, 1.0 Hz, 4H), 8.45 (dd, J = 8.2, 2.3 Hz, 2H), 8.01 (td, J = 7.8, 1.5 Hz, 2H), 7.97 (d, J = 8.8 Hz, 4H), 7.60 (d, J = 7.9 Hz,

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4H), 7.41 (ddd, J = 7.2, 5.7, 1.0 Hz, 4H), 5.53 (d, J = 16.1 Hz, 4H), 4.73 (d, J = 15.5 Hz, 4H), 4.42 (s, 4H). ^{13}C NMR (126 MHz, CD_3OD): δ 164.6, 155.3, 152.4, 150.5, 141.1, 141.0, 128.9, 124.4, 123.2, 120.5, 67.4, 63.6. HRMS (ESI-TOF) $C_{36}H_{34}Cl_4N_8Pd_2$ calcd.: $[M - 2Cl]^{2+}$ 431.0175. Found: 431.0165. Calcd.: $[M - Cl]^+$ 897.0039. Found: 897.0040. Calcd. $[M - HCl_2]^+$ 861.0277. Found: 861.0270.

*[(L2)(PdCl)$_2$](PF$_6$)$_2$ ([**7**](PF$_6$)$_2$).* Complex [**7**]**Cl$_2$** (0.0207 g, 0.0222 mmol) was dissolved in 4 mL of methanol. Upon the addition of excess KPF_6, the product precipitated and was collected by vacuum filtration. After washing with methanol and ether, the product was collected as an off-white solid (0.0127 g, 50%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.99 (s, 2H), 8.38 (d, J = 5.3 Hz, 4H), 8.33 (d, J = 7.4 Hz, 2H), 8.02 (t, J = 7.7 Hz, 4H), 7.87 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.0 Hz, 4H), 7.41 (t, J = 6.8 Hz, 4H), 5.54 (d, J = 15.8 Hz, 4H), 4.66 (d, J = 16.1 Hz, 4H), 4.33 (s, 4H). Anal. Calcd for $C_{36}H_{34}Cl_2F_{12}N_8P_2Pd_2$: C, 37.52; H, 2.97; N, 9.72. Found: C, 37.46; H, 3.04; N, 9.68.

*[(L2′)(PtCl)$_2$]Cl$_2$ ([**8**]Cl$_2$).* L2′ (0.0205 g, 0.0350 mmol) and $Na_2[PtCl_4]\cdot xH_2O$ (0.0269 g, 0.0702 mmol) were each combined separately with 1 mL of DMSO-d_6. The $Na_2[PtCl_4]\cdot xH_2O$ suspension was added to the ligand solution, and the reaction mixture was allowed to stir at room temperature. NMR analysis revealed the reaction mixture to have reached equilibrium when a ratio of 1.0:0.27 [**8**]**Cl$_2$**/L2′ was present. The addition of excess aqueous KPF_6 (sat.) did not result in the formation of a precipitate. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.57 (dd, J = 5.8, 1.0, 4H), 8.05 (td, J = 7.8, 1.5 Hz, 4H), 7.79 (d, J = 8.3 Hz, 4H), 7.60 (d, J = 7.9 Hz, 4H), 7.47−7.42 (m, 4H), 7.06 (d, J = 8.2 Hz, 4H), 5.47 (d, J = 15.9 Hz, 4H), 4.98 (d, J = 15.9 Hz, 4H), 4.35 (s, 4H). The ^{1}H NMR data were obtained from a mixture with L2′ starting material, but only the signals from [**8**]**Cl$_2$** were reported.

*[(L2′)(PdCl)$_2$]Cl$_2$ ([**9**]Cl$_2$).* Anhydrous THF (20 mL) was added to a 50 mL Schlenk flask containing Pd(COD)Cl_2 (0.0199 g, 0.0697 mmol) and L2′ (0.0202 g, 0.0350 mmol). The yellow solution quickly began to form a white precipitate. After allowing the reaction mixture to stir overnight at room temperature, the precipitate was allowed to settle, and the supernatant was removed. The white product was washed once with 20 mL of anhydrous THF to afford pure product (0.0220 g, 69%). ^{1}H NMR (300 MHz, CD_3OD): δ 8.57 (dt, J = 5.9, 0.8 Hz, 4H), 8.02 (td, 7.8, 1.1 Hz, 4H), 7.93 (d, J = 8.2 Hz, 4H), 7.55 (d, J = 7.9 Hz, 4H), 7.44 (t, J = 6.8 Hz, 4H), 7.22 (d, J = 8.2 Hz, 4H), 5.48 (d, J = 15.9 Hz, 4H), 4.66 (d, J = 15.9 Hz, 4H), 4.31 (s, 4H). ^{13}C NMR (126 MHz, CD_3OD): δ 164.8, 150.3, 141.1, 140.8, 132.8, 131.4, 126.9, 124.1, 123.0, 67.5, 66.4. HRMS (ESI-TOF) for $C_{38}H_{36}Cl_4N_6Pd_2$ calcd.: $[M - HCl_2]^+$ 859.0373. Found: 859.0397. Calcd.: $[M - H_2Cl_3]^+$ 823.0612. Found: 823.0634.

*[(COD)Rh(L1)]Cl (**10**).* To a 25 mL Schlenk flask containing L1 (0.0392 g, 0.103 mol) and $[Rh(COD)Cl]_2$ (0.0268 g, 0.0544 mmol) was added 16 mL of anhydrous THF. The mixture was allowed to stir at room temperature for one hour, at which point ^{1}H NMR indicated conversion to product with a small amount of L1 still present. The solvent was removed by reduced pressure yielding 0.0569 g (88% crude yield) of a rust-colored powder. Longer reaction times did not yield further conversion, and overnight reaction resulted in discoloration of the product to a dark wine red color. Purification by recrystallization from anhydrous CH_2Cl_2 and hexanes was unsuccessful. Performing the same procedure in refluxing toluene resulted in no reaction while the room temperature reaction in EtOH yielded the same product as the THF reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.23 (d, J = 8.5 Hz, 1H), 9.16 (d, J = 8.5 Hz, 1H), 8.54 (d, J = 4.8 Hz, 2H), 8.25 (dd, J = 8.4 and 1.7 Hz, 1H), 8.11 (dd, J = 8.5, 1.5 Hz, 1H), 7.88 (s, 1H), 7.71 (td, J = 7.7, 1.7 Hz, 2H), 7.49 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.20(d, J = 6.9, 5.3 Hz, 2H), 4.55 (br s, 3H), 3.83 (s, 4H), 3.74 (s, 2H), 2.70−2.45 (m, 4H), 2.41 (s, 3H), 2.22−2.10 (m, 4H). Note that in the ^{1}H NMR data listed here, only the peaks corresponding to product are listed, although the ligand L1 starting material was also present. ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.1, 155.4, 154.1, 149.1, 148.0, 147.2, 142.1, 141.6, 138.5, 137.4, 136.7, 125.1, 124.6, 123.4, 122.4, 84.2, 59.8, 54.2, 30.3, 18.6. HRMS (ESI-TOF) for $C_{32}H_{35}ClN_5Rh$ calcd.: $[M - Cl]^+$ 592.1942. Found: 592.1928.

*[(COD)Rh(L2)]Cl (**11**).* $[Rh(COD)Cl]_2$ (0.149 g, 0.0302 mmol) was added along with L2 (0.362 g, 0.0302 mmol) to a 10 mL Schlenk flask. The reagents were dissolved in 8 mL of anhydrous THF and stirred at room temperature for 45 min. The solvent was removed under reduced pressure, leaving the product as a shiny red solid which adhered strongly to the sides of the flask. Purification was attempted by recrystallization from CH_2Cl_2 with hexanes and also from CH_2Cl_2 with toluene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.37 (d, J = 8.2 Hz, 2H), 8.53 (d, J = 4.2 Hz, 4H), 8.26 (d, J = 7.9 Hz, 2H), 7.86 (br s, 2H), 7.70 (t, J = 8.0 Hz, 4H), 7.47 (d, J = 7.9 Hz, 4H), 7.24−7.08 (m, 4H), 4.59 (br s, 4H), 3.82 (s, 8H), 3.73 (s, 4H), 2.74−2.50 (m, 4H), 2.28−2.19 (m, 4H). The ^{1}H NMR data were obtained from a mixture with L2 starting material, but only the peaks for **11** were reported. ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.1, 155.4, 149.1, 148.0, 141.7, 138.6, 136.7, 125.2, 123.4, 122.4, 84.3, 59.8, 54.3, 30.4. HRMS (ESI-TOF) for $C_{44}H_{46}ClN_8Rh$ calcd.: $[M - Cl]^+$ 789.2895. Found: 789.2914.

*[Rh(bpy0)COD]Cl (**12**).* To a 50 mL Schlenk flask containing 5,5′-dimethyl-2,2′-bipyridine (bpy0, 0.0786 g, 0.427 mmol) and $[Rh(COD)Cl]_2$ (0.1029 g, 0.209 mmol) was added 20 mL of anhydrous THF. The reactants dissolved immediately into a red-orange solution. Within seconds, a neon-orange solid precipitated. The mixture was allowed to stir overnight, and the solvent was removed in vacuo, leaving a neon-orange solid (0.154 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (d, J = 8.2 Hz, 2H), 8.08 (dd, J = 8.3, 1.4 Hz, 2H), 7.51 (s, 2H), 4.49 (br s, 4H), 2.74−2.53 (m, 4H), 2.42 (s, 6H), 2.24−2.05 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.5, 147.3, 142.3, 137.4, 125.0, 84.3, 30.5, 18.9. Anal. Calcd for $C_{20}H_{24}ClN_2Rh$: C, 55.76; H, 5.62; N, 6.50. Found: C, 55.62; H, 5.71; N, 6.33.

Synthesis of Heterometallic Complexes. *[(COD)Rh(L1)ZnCl$_2$]Cl (**13**).* To a 50 mL Schlenk flask containing **1** (0.0309 g, 0.0597 mol) and $[Rh(COD)Cl]_2$ (0.0147 g, 0.0298 mol) was added 16 mL of anhydrous THF resulting in an orange solution. A pink-orange solid began to precipitate within three hours. The mixture was allowed to stir at room temperature overnight, at which point solvent was removed in vacuo to give pure product (0.0219 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$, −45 °C): δ 9.40 (d, J = 5.3 Hz, 2H), 8.98 (d, J = 8.3 Hz, 1H), 8.42 (s, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0, 2H), 7.50−7.44 (m, 5H), 4.65 (d, J = 16 Hz, 2H), 4.57 (br s, 4H), 4.51 (s, 2H), 4.01 (d, J = 16.0 Hz), 2.76−2.51 (m, 4H), 2.46 (s, 3H), 2.27−2.17 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.6, 154.8, 153.7, 151.6, 149.7, 147.6, 144.7, 141.7, 140.3, 137.7, 134.7, 124.7, 124.1, 123.9, 123.4, 85.3, 57.0, 55.9, 30.3, 18.7. HRMS (ESI-TOF) for $C_{32}H_{35}Cl_3N_5RhZn$ calcd.: $[M - Cl]^+$ 728.0585. Found: 728.0608. Anal. Calcd for $C_{32}H_{35}Cl_3N_5RhZn$: C, 50.29; H, 4.62; N, 9.16. Found: C, 50.18; H, 4.58; N, 8.96.

*[(COD)Rh(L2)]·Zn$_2$(NO$_3$)$_4$Cl (**14**).* A solution of L2 (0.0160 g, 0.0276 mmol) in 5 mL of methanol was prepared in a 25 mL round-bottom flask open to the air. To this was added a solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.0162 g, 0.0544 mmol) also dissolved in methanol. The solvent was removed under reduced pressure, and the round-bottom flask was charged with argon. Anhydrous THF was added to the flask, but not all of the solids dissolved. The white suspension was cannula transferred to a Schlenk flask containing an orange solution of $[Rh(COD)Cl]_2$ (0.0068 g, 0.014 mmol) in anhydrous THF. The reaction mixture turned yellow, but not everything went into solution. Solvent was removed under reduced pressure, yielding **14** as a tan solid containing some unidentified impurities (0.0201 g, 61%). ^{1}H NMR (300 MHz, CD_3OD): δ 8.76 (ddd, J = 5.2, 1.3, 0.7 Hz, 4H), 8.32 (d, J = 8.2 Hz, 2H), 8.28 (dd, J = 8.5, 1.3 Hz, 2H), 8.14 (td, J = 7.6, 1.6 Hz, 4H), 7.90 (s, 2H), 7.74 (ddd, J = 8.0, 5.0, 0.9 Hz, 4H), 7.63 (d, J = 7.9 Hz, 4H), 4.68 (br s, 4H), 4.39 (br d, J = 16 Hz, 4H), 4.13 (s, 4H), 4.08 (br d, J = 20 Hz, 4H), 2.72−2.67 (m, 4H), 2.29−2.23 (m, 4H). The ^{1}H NMR data were obtained from an impure sample, but only peaks from **14** were reported. ^{13}C NMR (126 MHz, CD_3OD): δ 159.7, 159.0, 154.8, 152.2, 147.5, 145.7, 137.3, 129.1, 129.0, 126.9, 60.2, 58.4, 33.9.

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[(COD)Rh(L1)]·Zn(NO$_3$)$_2$Cl (**15**). L1 (0.0206 g, 0.0540 mmol) and [Rh(COD)Cl]$_2$ were dissolved in anhydrous ethanol (8 mL) in a 25 mL Schlenk flask and allowed to stir at room temperature for 30 min. A 5 mL ethanolic solution of Zn(NO$_3$)$_2$·6H$_2$O (0.0163 g, 0.0548 mmol) was then cannula transferred into the 25 mL Schlenk flask resulting in the immediate precipitation of a fine pink-orange solid. The solvent was removed in vacuo, and the product was collected as a dark brown-red powder containing some unidentified impurities (0.0368 g, 83%). ^{1}H NMR (300 MHz, CD$_3$OD): δ 8.89 (d, J = 4.8 Hz, 2H), 8.25 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 1H), 8.12−7.94 (m, 4H), 7.77 (s, 1H), 7.72−7.61 (m, 2H), 7.50 (d, J = 7.4 Hz, 2H), 4.66 (br s, 4H), 4.24 (br s, 4H), 4.18 (s, 2H), 2.80−2.52 (m, 4H), 2.45 (s, 3H), 2.36−2.13 (m, 4H). ^{13}C NMR (126 MHz, CD$_3$OD): δ 156.2, 155.2, 153.1, 150.9, 149.0, 148.5, 143.3, 141.3, 141.2, 139.0, 133.4, 124.8, 124.5, 122.7, 122.0, 85.4, 556.7, 55.7, 29.8, 17.0.

[(COD)Rh(L1)PdCl]Cl$_2$ (**16**). L1 (0.0509 g, 0.133 mmol) and [Rh(COD)Cl]$_2$ (0.0328 g, 0.0665 mmol) were dissolved in anhydrous EtOH (20 mL) in a 200 mL Schlenk flask and allowed to stir for 35 min. A 54 mL anhydrous ethanolic solution of Pd(COD)Cl$_2$ (0.0165 g, 0.0578 mmol) was then cannula transferred into the reaction Schlenk flask. The reaction mixture was stirred at room temperature for 12 h, at which point the solvent was reduced to approximately 3 mL. The product was precipitated upon the addition of 40 mL of anhydrous diethylether, collected by filtration, and washed with anhydrous diethylether (10 mL). The product was collected as a brown-red powder (0.0810 g, 75%). ^{1}H NMR (300 MHz, CD$_3$OD): δ 8.83 (s, 1H), 8.64 (dd, J = 5.7, 1.2 Hz, 2H), 8.43 (dd, J = 8.3, 1.9 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.12−7.96 (m, 4H), 7.79 (s, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.43 (m, 2H), 5.56 (d, J = 16.4 Hz, 2H), 4.86 (br s, 4H), 4.80 (d, J = 16.1 Hz, 2H), 4.50 (s, 2H), 2.78−2.63 (m, 4H), 2.45 (s, 3H), 2.34−2.21 (m, 4H). ^{13}C NMR (126 MHz, CD$_3$OD, −20 °C): δ 164.6, 156.6, 152.5, 150.3, 149.4, 143.9, 141.4, 141.2, 139.5, 132.2, 124.6, 123.5, 123.0, 122.0, 86.0, 67.2, 62.4, 30.0, 17.0. HRMS (ESI-TOF) for C$_{32}$H$_{35}$Cl$_3$N$_5$PdRh calcd.: [M − Cl]$^+$ 770.0350. Found: 770.0348.

[(COD)Rh(L2)(PdCl)$_2$]Cl$_3$ (**17**). A 50 mL Schlenk flask was charged with [Rh(COD)Cl]$_2$ (0.0106 g, 0.0215 mmol) and [7]Cl$_2$ (0.0400 g, 0.0429 mmol). The reagents were suspended in 30 mL of anhydrous ethanol. After 50 min, all reagents had dissolved into a red-orange solution. Solvent was removed under reduced pressure giving **17** as a brown powder (0.0375 g, 79%). ^{1}H NMR (300 MHz, CD$_3$OD): δ 8.84 (s, 2H), 8.63 (d, J = 5.4 Hz, 4H), 8.45 (dd, J = 8.3, 1.1 Hz, 2H), 8.05 (d, J = 2.3 Hz, 2H), 8.07 (td, J = 7.8, 1.5 Hz, 4H), 7.66 (d, J = 7.6 Hz, 2H), 7.49 (m, 4H), 5.56 (d, J = 16.4 Hz, 4H), 5.06 (br s, 4H), 4.83 (d, J = 16.4 Hz, 4H), 4.53 (s, 4H), 2.79 (m, 4H), 2.35 (m, 4H). ^{13}C NMR (126 MHz, CD$_3$OD): δ 164.4, 155.2, 152.8, 150.5, 144.1, 141.4, 133.3, 124.7, 123.5, 123.0, 87.2, 67.4, 62.5, 30.0. HRMS (ESI-TOF) for C$_{44}$H$_{46}$Cl$_5$N$_8$Pd$_2$Rh calcd.: [M − Cl]$^+$ 1144.9714. Found: 1144.9680. Calcd.: [M − 2Cl]$^{2+}$ 554.0015. Found: 554.0021. Anal. Calcd for C$_{44}$H$_{46}$Cl$_5$N$_8$Pd$_2$Rh: C, 44.79; H, 3.93; N, 9.50. Found: C, 44.58; H, 4.02; N, 9.26.

[(COD)Rh(L2)(PtCl)$_2$]Cl$_3$ (**18**). [Rh(COD)Cl]$_2$ (0.0099 g, 0.0201 mmol) and [**5**]**Cl$_2$** (0.0445 g, 0.0401 mmol) were dissolved in anhydrous methanol (17.5 mL) in a 50 mL Schlenk flask. The bright orange solution became burnt orange-red in color after stirring at room temperature for 2 h. The solvent was reduced to approximately 7 mL, and anhydrous diethylether (40 mL) was added to precipitate the product. The solid was allowed to settle, and the supernatant was removed followed by two diethylether washes of 40 and 20 mL, respectively. The residual solvent was removed in vacuo yielding a pink-brown solid (0.0319 g, 59%). ^{1}H NMR (300 MHz, CD$_3$OD): δ 8.81 (d, J = 5.7 Hz, 4H), 8.77 (s, 2H), 8.40 (d, J = 7.9 Hz, 2H), 8.08 (t, J = 8.0 Hz, 4H), 7.98 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.6 Hz, 4H), 7.55−7.42 (m, 4H), 5.37 (d, J = 15.9 Hz, 4H), 5.06 (d, J = 15.7 Hz, 4H), 4.99 (br s, 4H), 4.55 (s, 4H), 2.81−2.67 (m, 4H), 2.38−2.21 (m, 4H). ^{13}C NMR (126 Hz, CD$_3$OD): δ 165.2, 154.8, 153.7, 149.2, 149.2, 144.2, 141.0, 132.5, 125.0, 123.6, 122.9, 68.4, 63.2, 30.2. HRMS (ESI-TOF) for C$_{44}$H$_{46}$Cl$_5$N$_8$Pt$_2$Rh calcd.: [M − Cl]$^+$ 1321.0922. Found: 1321.0920.

Kinetic Studies of H/D Exchange in Complex 18. A 4.9 mg sample of complex **18** was dissolved in 0.70 mL of CD$_3$OD at a time designated t = 0 s. Using a 300 MHz Mercury instrument regulated at 25 °C, ^{1}H NMR spectra of the sample were recorded every 1 to 2 min. As the proton signals for most of the molecule remain unchanged throughout the exchange process, no other standard was needed for determining the remaining concentration of **18** as it reacted to form the H/D exchange product **18^D** ([(COD)Rh(L2-d_4)(PtCl)$_2$]Cl$_3$). The aromatic region of the spectra, which is uninterrupted by solvent signals, served as the standard against the disappearing dpa methylene peak at 5.37 ppm. Data points were collected past four half-lives. The same procedure was followed for a 2.3 mg sample of complex **18**.

RESULTS AND DISCUSSION

Ligands L1 and L2 and Their Models. Ligands L1 and L2 and model ligand L2′ (Figures 1 and 2) were synthesized as previously reported by substitution of dpa onto appropriate bromomethyl bipyridine or biphenyl precursors.[19,21,30] As expected, L1 and L2 always showed essentially the same reactivity, with any major difference in reaction workups being the result of the lower solubility of L2 and its complexes. The higher solubility of the L1 complexes makes them more attractive for future applications as heterobimetallic complexes for use in homogeneous catalysis, but utilization of L2 allows for more facile determination of binding site preferences. Because L2 has a 2:1 ratio of dpa/bpy sites, we can often gather information about the binding site simply by considering the quantity of metal reagent taken up by the ligand in the reaction. Binding site preferences were also probed by comparison of complexes of L1 and L2 with those of the model ligands bpy0 and L2′ (Figure 2).

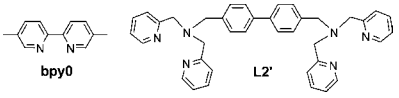

Figure 2. Simplified models for L1 and L2.

Binding Site Determination by NMR. Reaction of L1 and L2 with Zn^{2+}, Pd^{2+}, and Pt^{2+} sources afforded complexes in which metal was bound exclusively at the dpa site. In contrast, Rh$^+$ complexes of L1 and L2 were found to exhibit metal binding only at the bipyridine site. All of these products were characterized by ESI-MS and ^{1}H NMR. Additionally, gHMBCAD NMR was employed to identify the carbon shifts and establish the connectivity along the ligand backbone in each complex. In all cases, the equivalents of metal reagent employed matched the number of its preferred binding sites available in the ligand. The resulting proton shifts of L1 and L2 complexes were similar, providing evidence for a consistent binding site preference. Additionally, the symmetry of L2, as determined by considering the aromatic region of the ^{1}H NMR spectra, did not change upon reaction with 1 equiv of Rh$^+$ or with 2 equiv of Zn^{2+}, Pd^{2+}, or Pt^{2+}. If after the addition of 1 equiv of metal reagent the symmetry of the L2 complex is retained, then the metal preferentially binds at the bpy site. If 2 equiv can be used to produce a symmetric product, then binding is occurring exclusively at the dpa site.

Complex **1** was synthesized by the method of Zhu et al.[21] Though an X-ray crystal structure of L1 with Zn^{2+} bound at the dpa site has been reported,[21] comparison of the NMR spectrum of **1** with that of L1 provides evidence that **1** is also the dominant species in solution (Figure 3). Specifically, the peaks corresponding to the dpa site (A1−A4) are significantly shifted

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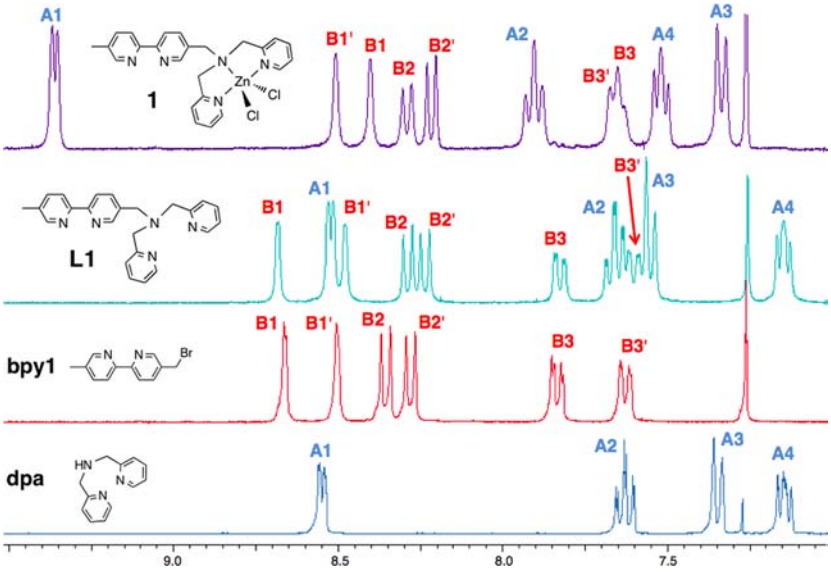

Figure 3. ^{1}H NMR comparison of dpa, bpy1, L1 and **1**. The peaks A1−A4 correspond to the dipicolylamine site, and the B1−B3 and B1′−B3′ correspond to the bipyridine site.

while the peaks corresponding with the bpy site (B1−B3, B1′−B3′) retain essentially the same chemical shifts after metalation.

Reaction of 2 equiv of $ZnCl_2$ with L2 resulted in the formation of a product which was insoluble in all common organic solvents. Therefore, $Zn(OAc)_2$ and $Zn(NO_3)_2$ were employed to obtain the soluble Zn/L2 complexes **2** and **3**, which were characterized by ^{1}H NMR. In both the case of the previously known complex **3** and the case of the new complex **2**, 2 equiv of Zn reagent were reacted with ligand, and the products were characterized without purification. No loss of ligand symmetry was observed in the products.

The ^{1}H NMR peaks associated with the dpa methylene groups display a range of splitting patterns between **1**, **2**, and **3** (Figure 4). In the $Zn(NO_3)_2$ L2 complex **3**, the dpa methylene peaks are split into two distinct diastereotopic doublets (J = 16), while the other extreme is observed in the case of the $ZnCl_2$ L1 complex **1**, in which only a singlet is observed. The $Zn(OAc)_2$ L2 complex **2** lies between these two extremes, displaying a very broad doublet. These results indicate a range of conformational flexibility around the dpa methylene site arising from the changing lability of Zn^{2+}. The trend can be explained as a counterion effect. As the counterion becomes more strongly coordinating from NO_3^- to OAc^- to Cl^-, the Zn^{2+} becomes more electron-rich and therefore more labile. In all cases, the proton chemical shift of the methylene linker between the dpa and bipyridine sites is around 3.90 ppm. Diastereotopic methylene protons, as observed in **3**, have been previously reported for dpa complexes[16,17,19,22,23] and this splitting pattern, which is also found in the ^{1}H NMR spectra of the Pd and Pt complexes of L1 and L2, is confirmation of metal binding at the dpa site.

Pd and Pt Complexes. Reactions of $Na_2[PtCl_4]$ with 1 equiv of L1 or 0.5 equiv of L2 in DMSO afforded complexes **4** and **5** (Figure 5). In the case of **5**, the crude chloride salt precipitated directly from the reaction mixture after 24 h. The addition of aqueous KPF_6 to a concentrated DMSO solution of **[5]Cl$_2$** or the **4** reaction mixture resulted in formation of the pure PF_6^- salts of the complexes. The replacement of $Na_2[PtCl_4]$ with $Pt(COD)Cl_2$ in the presence of $Ag(PF_6)$ or

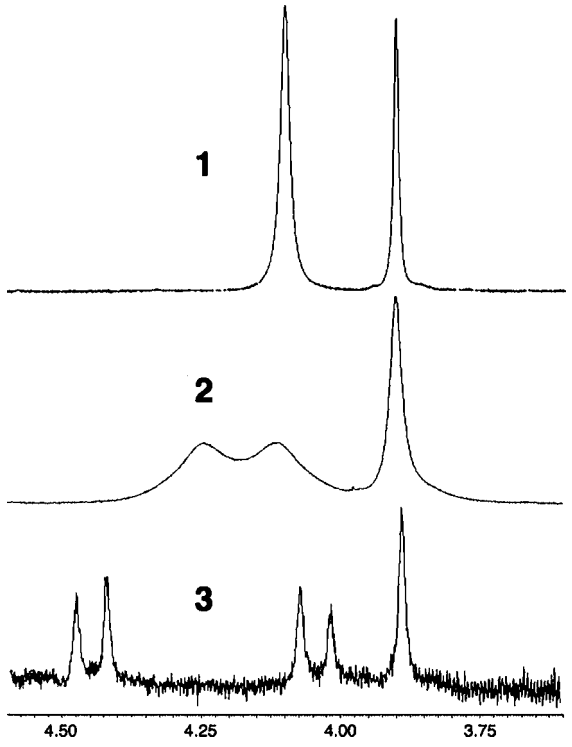

Figure 4. Methylene region of the ^{1}H NMR spectra of **1**, **2**, and **3**.

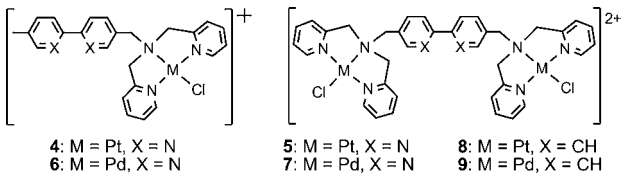

Figure 5. Pt and Pd complexes **4**−**9**.

$Ag(NO_3)_2$ resulted in a mixture of unidentified products, but in the absence of a Ag reagent, no reaction occurred.

In contrast, Pd complexes **6** and **7** (Figure 5) were readily obtained by reaction of $Pd(COD)Cl_2$ with 1 equiv of L1 or 0.5

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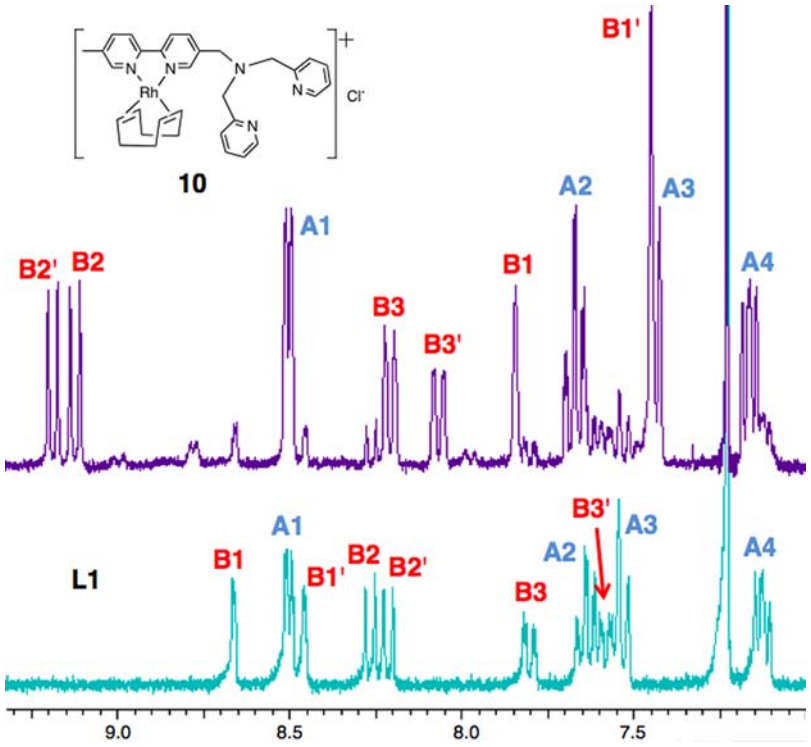

Figure 6. ^{1}H NMR comparison of L1 and **10**. The peaks A1−A4 correspond to the dipicolylamine site, and the B1−B3 and B1′−B3′ correspond to the bipyridine site.

equiv of L2 in methanol or THF. Each reaction was allowed to proceed at room temperature overnight, resulting in the formation of the product as the chloride salt. In the case of the THF reactions, the products precipitated out of the reaction mixture and could be purified by washing the solid in THF to remove remaining ligand starting material as well as COD. In all cases, further purification was possible by converting the products to their PF_6^- salts by treating their concentrated solutions with excess aqueous KPF_6 (sat.).

For all Pt and Pd complexes **4**−**7**, metal binding at the dpa site was confirmed by the diastereotopic methylene protons (J = 16 Hz) in the ^{1}H NMR spectrum. As further proof of this binding preference by Pt and Pd, the ligand model L2′, in which the bipyridine of L2 is replaced with a biphenyl group, was subjected to the same reaction conditions as its L2 counterpart. In the resulting products, **8** and **9**, the chemical shifts associated with the dpa pyridines were identical to those for **5** and **7**, respectively. The ESI-mass spectrometry data for **5**, **7**, and **9** confirmed the presence of ions containing two Pd's or two Pt's bound to the ligand. There was no evidence of ions containing three bound metals in the ESI-mass spectrometry data of **5** and **7**, consistent with a lack of binding at the bpy site. As further evidence of this fact, mixtures containing **6**/$[Pd_2(L1)Cl_3]Cl$ or **7**/$[Pd_3(L2)Cl_4]Cl_2$ were produced and revealed clear spectroscopic distinctions between mono- and dipalladated L1 complexes and between di- and tripalladated L2 complexes. Specifically, all the ^{1}H NMR aromatic peaks of the dipalladated L1 product and the tripalladated L2 product were observed to have chemical shifts downfield of those of their more monopalladated L1 and dipalladated L2 counterparts.

Rh Complexes. Rhodium complexes of L1 and L2, **10** and **11**, were obtained by reaction of the ligands with 0.5 equiv of $[Rh(COD)Cl]_2$ in either THF or EtOH. Unfortunately, the products were mixed with small amounts of starting material and sometimes trace amounts of unidentified material. The reaction did not progress any further after 20 min, and extending the reaction time to overnight led to decomposition when THF was the solvent. Although pure **10** and **11** could not be obtained by recrystallizations or chromatography, it was possible to determine the binding site by ^{1}H NMR spectroscopy. In contrast to what was observed for **1**, the dpa peaks in the spectrum of **10** remain in place while the bpy peaks are significantly shifted (Figure 6). In fact, they shift in a manner identical to that of the bpy peaks in the analogous reaction of bpy0 with $[Rh(COD)Cl]_2$ to obtain **12** (Figure 7). Analogous shifts are observed in the spectrum of the L2 complex, **11**. Both **10** and **11** were also characterized by ESI-TOF mass spectrometry, and their ^{1}H and ^{13}C NMR peaks were fully assigned via gHMBCAD NMR (see Supporting Information).

Heterometallic Complexes. With the binding preferences of Zn^{2+}, Pd^{2+}, Pt^{2+}, and Rh^+ determined, it was reasonable to assume that the metals would display the same selectivity whether or not the ligands were already bound to another metal. If that were the case, it would then be possible to produce Rh/Zn, Rh/Pd, and Rh/Pt complexes without scrambling of metals between binding sites (Figure 8).

Preparation of the Rh/Zn L1 complex, **13**, went to completion upon reaction of 0.5 equiv of $[Rh(COD)Cl]_2$ with **1** in EtOH or THF, and no further purification was required. This result is in contrast to that of performing the same reaction with L1 instead of the Zn-bound complex **1**, in which a portion of the L1 starting material always remained unreacted. Reaction of 0.5 equiv of $[Rh(COD)Cl]_2$ with **3** achieves similar results though the complex **14** is only sparingly soluble in CH_3OH and could not be purified. Complex **14** and its L1 analogue **15** can also be obtained by reaction of $Zn(NO_3)_2$ with the Rh complexes **10** or **11**. This ability to alter the order of the metalation steps and still produce the same

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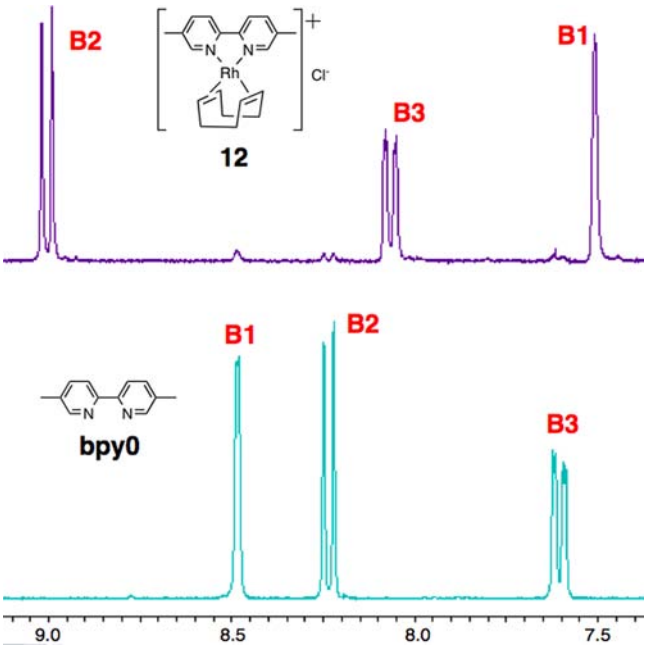


Figure 7. ^{1}H NMR comparison of bpy0 and **12**. The peaks B1−B3 correspond to the bipyridine ring protons.

product is confirmation that the metals retain their original binding site preferences even in the presence of the other metal. At room temperature, the proton NMR spectra of both **14** and **15** in CD_3OD show the diastereotopic dpa methylene protons as the expected pair of mutually coupled doublets. The dpa methylenes of **13** appear as two broad singlets at 4.20 and 4.58 ppm in CD_3OD and are present as a very flat and broad peak stretching from approximately 3.50 to 4.75 ppm in the baseline in $CDCl_3$. At −45 °C in $CDCl_3$, however, the dpa methylene groups are present as two doublets at 4.01 and 4.65 ppm.

Rh/Pd complexes of L1 and L2, **16** and **17**, respectively, can be prepared by either addition of $[Rh(COD)Cl]_2$ to the Pd complexes **6** or **7** or by addition of $Pd(COD)Cl_2$ to the Rh complexes **10** or **11** (Figures 9 and 10). Though the same major product is formed in either case, addition of Pd to Rh complexes **10** or **11** redissolved in THF does not result in full conversion. Complete conversion to product occurs when either the $[Rh(COD)Cl]_2$ is added to the Pd complexes **6** or **7** or when the entire reaction is done as a one pot synthesis in EtOH with Rh addition first (Figure 10).

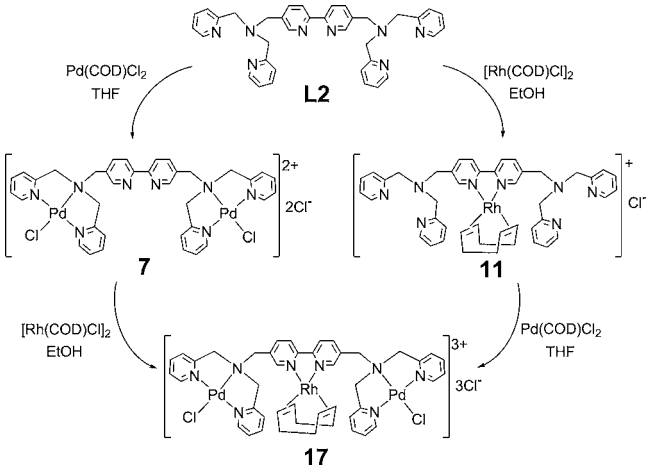


Figure 9. Complementary routes for the synthesis of **17**.

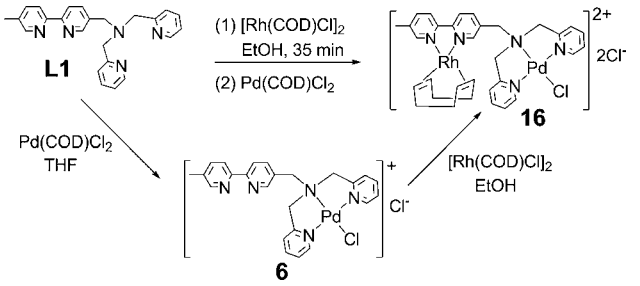
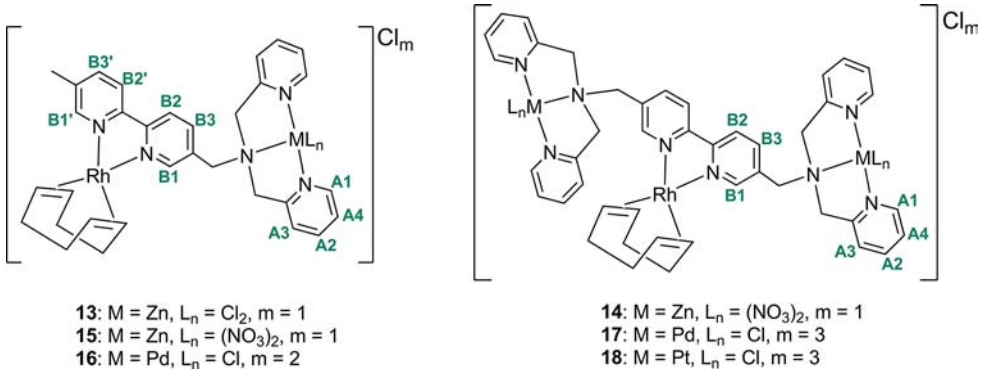


Figure 10. Complementary routes for the synthesis of **16**.

Similar reactions to produce Rh/Pt complexes were made difficult by the limited solubility of the available Pt starting materials $Na_2[PtCl_4]$, $[4]PF_6$, $[5](PF_6)_2$, and $[5]Cl_2$. In particular, $[5](PF_6)_2$ was not soluble in THF, ethanol, methanol, water, or DMSO, and both $Na_2[PtCl_4]$ and $[4]PF_6$ were only soluble in DMSO. DMSO was not regarded as a good option since the Rh/Pd complex **17** had quickly decomposed in DMSO, presumably because DMSO is known to readily displace COD on Rh^+.[31] Therefore, only the complex $[5]Cl_2$, which is sparingly soluble in methanol, was employed. Reaction of this complex with $[Rh(COD)Cl]_2$ at room temperature for 5.5 h resulted in the formation of **18**.

Hydrogen−Deuterium Exchange in Heterometallic Complexes. When dissolved in CD_3OD at room temperature, complexes **16**−**18** undergo hydrogen/deuterium exchange for one of the two hydrogens at their dpa methylene sites. For each



13: M = Zn, L_n = Cl_2, m = 1
15: M = Zn, L_n = $(NO_3)_2$, m = 1
16: M = Pd, L_n = Cl, m = 2

14: M = Zn, L_n = $(NO_3)_2$, m = 1
17: M = Pd, L_n = Cl, m = 3
18: M = Pt, L_n = Cl, m = 3

Figure 8. Heterometallic complexes **13**−**18**.

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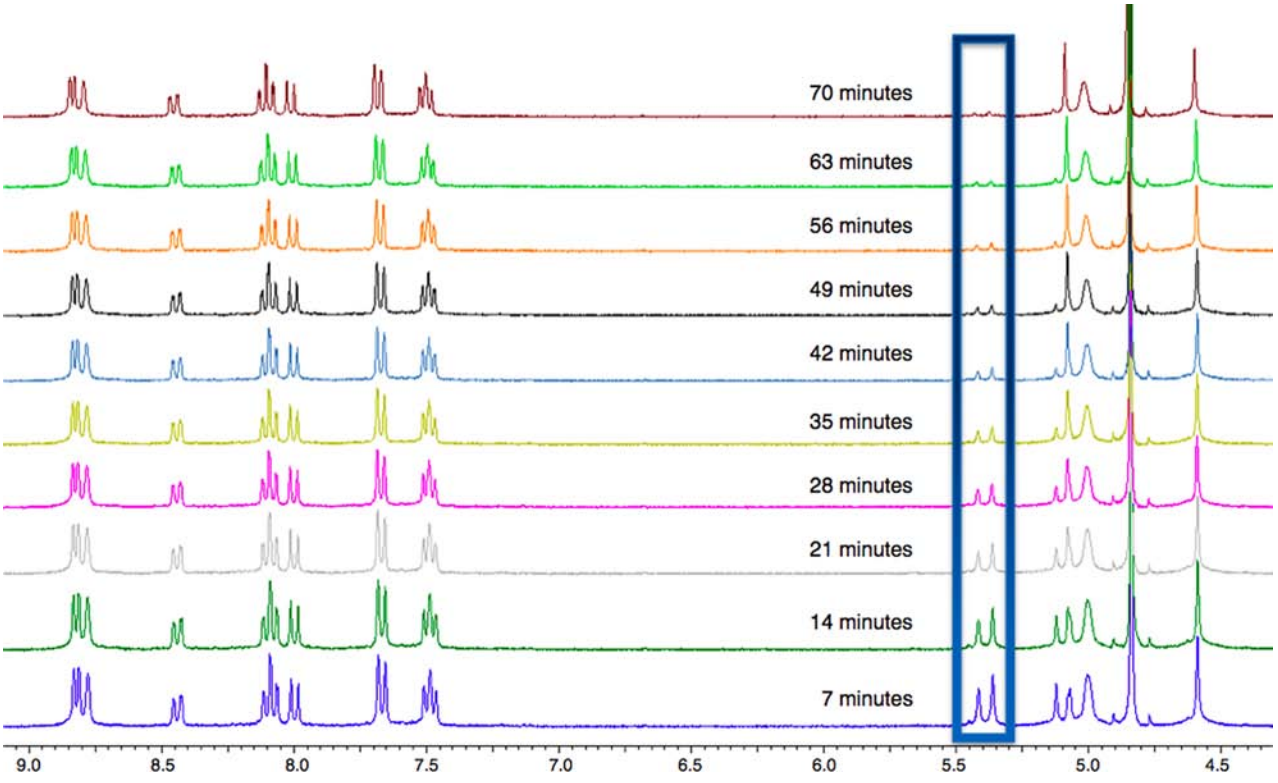

Figure 11. ^{1}H NMR spectra of **18** in CD_3OD at 25 °C as one of the dpa methylene protons is exchanged with deuterium.

complex, the downfield dpa methylene doublet at approximately 5.5 ppm is observed initially and then disappears over time while its upfield partner at around 4.6 ppm morphs into a singlet (Figure 11). The remaining proton shifts are unaffected, indicating that the only change occurring is the replacement of hydrogen by deuterium. Exchange was also observed when employing CH_3OD as the NMR solvent with suppression of the CH_3 signal. This confirms incorporation of the acidic proton of the methanol and rules out mechanisms involving β-hydride elimination from coordinated methoxide. The exchange was found to be reversible when the deuterated solvent was removed and replaced with CH_3OH or CH_3CH_2OH. Variable temperature NMR studies of complex **16** established that the exchange does not occur at −20 °C. The selectivity for exchange of only one of the dpa hydrogens observed in the Rh/Pd and Rh/Pt complexes indicates that the Pd and Pt moieties remain firmly bound to the dpa site while in solution.

This rapid hydrogen/deuterium exchange is not observed in the monometallic L1 or homobimetallic L2 counterparts of these complexes. The dpa-bound Pt and Pd complexes **4**−**7** all retain their dpa methylene peaks even after remaining in CD_3OD over several days. The Rh/Zn complex **13** also retains both diastereotopic dpa methylene peaks in the proton NMR at −40 °C after dissolution in CD_3OD for over a week at room temperature. These results are consistent with both metals being necessary for the exchange process. To further probe the participation of the two metals in the exchange process, monometallic complexes $Zn(dpa)Cl_2$, [Pd(dpa)Cl]Cl, and [Pt(dpa)Cl]Cl were synthesized by the same methods as their L1 and L2 analogues and then analyzed by ^{1}H NMR in CD_3OD. One equivalent of the bpy0 bound Rh complex **12** was added to each solution. As expected, no H/D exchange occurred for the $Zn(dpa)Cl_2$ complex. Rapid H/D exchange was observed at the dpa-methylene site of [Pd(dpa)Cl]Cl, but there was no selectivity between the methylene hydrogens. H/D exchange was also observed with [Pt(dpa)Cl]Cl in the presence of **12**, but the selectivity could not be determined due to coincidence of one of the diasterotopic proton signals with the methanol solvent peak. These experiments demonstrate that H/D exchange of the methylene protons of a (dpa)Pd or (dpa)Pt moiety occurs in the presence of the (bpy)Rh species **12**. The two metals need not be bound into the same complex for H/D exchange to occur. However, the selectivity between the diastereotopic methylene protons for H/D exchange in the heterometallic complexes **16**−**18** suggests that the geometric constraints and preorganization in these complexes can control their reactivity.

Kinetic studies of the H/D exchange in Pt/Rh complex **18** were carried out by recording NMR spectra of two methanolic solutions of **18** with concentrations of 2.4 mM and 5.2 mM (Figure 12). Good linear fits were found for the plots of $\ln[\mathbf{18}]_t$ versus time. As the deuterium source methanol is the solvent, these data indicate pseudo-first-order reaction kinetics for the exchange. Setting the intercepts at $-\ln[\mathbf{18}]_0$, the rate constants found for both the 2.4 mM and 5.2 mM solutions were both 5.2×10^{-4} s^{-1} with R^2 values of 0.99. The first order dependence on concentration of the heterometallic complex is consistent with an intramolecular process as opposed to a reaction involving the Rh portion of one molecule and the Pt portion of another, which would be expected to be second-order in the heterometallic complex.

To explore the source for the geometric constraints which lead to selectivity, the Pt L2 complex **5** was also mixed with Rh complex **12** in a 1:1 ratio in CD_3OD at 25 °C. No observable H/D exchange occurred within the first 2.5 h. This finding supports an intramolecular process for exchange in the heterometallic Rh/Pt L2 complex **18** as that process occurs well within this time range. After 11 h, the same downfield

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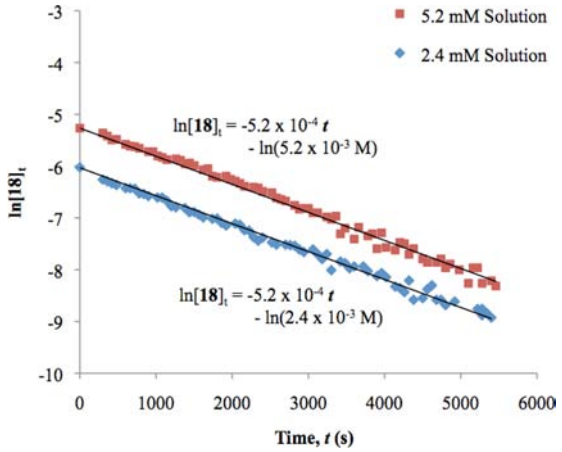

Figure 12. Plots of $\ln[\mathbf{18}]_t$ versus time for two solutions with initial concentrations of 5.2 mM and 2.4 mM.

proton which exchanged in the heterometallic cases was also fully deuterated in the Pt L2 case. Since no such selectivity is observed in the [Pt(dpa)Cl]Cl complex, the basis for the selectivity in this Pt L2 case is probably the steric constraints added by the bpy moiety. Simple molecular modeling using Spartan[32] indicates a facile approach from the Rh center to the dpa methylene proton which is furthest from the bpy moiety (see the Supporting Information). There is no evident approach for the dpa methylene proton closest to the bpy ring which would involve reasonable overlap with empty orbitals on the Rh center. Observation of H/D exchange is consistent with either C−H activation to produce a Rh hydride or formation of an agostic intermediate followed by H/D exchange with the acidic deuterium of CD_3OD and release of the C−D bond from the metal.[33,34] The contribution of the Pt to the reaction is likely to be electronic in nature—especially considering the lack of H/D exchange reactivity in the Rh/Zn complex.

CONCLUSIONS

The metal-binding selectivity of the dpa and bpy sites of ligands L1 and L2 was probed using NMR spectroscopy, ESI-MS, elemental analysis, and comparison with model complexes. Rh^+ was found to bind selectively at the bipyridine site, while Zn^{2+}, Pd^{2+}, and Pt^{2+} were found to bind at the dpa site. These selectivities were exploited in the synthesis of heterometallic Rh/Zn, Rh/Pt, and Rh/Pd complexes **13**−**18**. Selective hydrogen/deuterium exchange was observed when the heterometallic Rh/Pd and Rh/Pt complexes **16**−**18** were dissolved in CD_3OD. For the Rh/Pt complex, the exchange was found to obey first order kinetics suggesting an intramolecular process. This is evidence of cooperativity between the two metal sites as control experiments involving homometallic analogues as well as the Rh/Zn complex **13** indicate that both the Rh and Pt or Pd metals are required for the H/D exchange.

ASSOCIATED CONTENT

Supporting Information

Tables of gHMBCAD data, additional syntheses, more H/D exchange studies, and Spartan modeling results. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lmwhite@chem.ufl.edu.

Notes

The authors declare no competing financial interest.

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