Regioselective C-H/C-X Activation of Naphthyl-Derived Ligands to form Six-Membered Palladacycles

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ABSTRACT

Imine N[^]N[^]C-type pincer ligands were reacted with palladium(II) acetate and palladium(0) bis(dibenzylideneacetone) and the regioselective C-H and C-X activation was studied. C-X bonds that formed six-membered rings were selectively activated over C-H bonds; in addition sp² C-H bonds were selectively activated over sp³ CH bonds. The formation and regioselectivity of the cyclometalated palladium(II) complexes were characterized by NMR, MS, and XRD. Photoluminescence studies of cyclopalladated complexes were conducted.

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Palladium pincer complexes are well known in many organic transformations.¹ Most of the metalacycle rings are five-membered rings as these appear to form preferentially.²⁻⁸ It has been suggested that the reactivities and photophysical properties of these cyclometalated complexes depend on metalacycle size and the oxidation state of the metal, as well as a number of other aspects of the metal and ligands in the coordination sphere; therefore varying the ligand and the structure of the complexes, including metalacycle size and oxidation state, may affect the reactivity of the complexes and allow for new modes of interaction.⁹⁻¹⁵ The photophysical properties of cyclometalated and polypyridal metal compounds are well-known to be attractive in areas of artificial photosynthesis and molecular devices.¹⁶⁻¹⁸ Palladium is much under-represented in the area of photophysics compared to the larger member of Group 10, platinum.¹⁹⁻²³ Thus we have synthesized palladium compounds based on naphthyl ligands to give regioselective formation of the rarer six-membered metalacycles of palladium and have also studied the emission spectroscopy of the palladium compounds.

Chart 1: Structure of Ligands

Br)CH=NCH₂CH₂N(CH₃)₂ , **L3**, were synthesized from condensation reactions as reported previously²⁴, and (2-C₁₀H₆-1-Br)CH=NCH₂CH₂N(CH₃)₂ , **L4** was synthesized similarly. The ligands **L2** and **L3** were chosen to regioselectively form six-membered rings as opposed to five-membered rings, as the aromatic halide bonds at the 8-position are expected to be activated by the palladium preferentially over the C-H bonds at the 2-position. The methyl group in **L1** is employed to direct C-H bond activation at the 8-position, forming a six-membered ring, by blocking the 2-position. Finally, **L4** was employed to show that the five-membered ring is regioselectively formed by palladium activation of the bromide in the 1-position preferentially over the C-H bond at the 3-position. These ligands were reacted with Pd(OAc)₂ for several hours at 110 °C to give the final palladium(II) N[^]N[^]C pincer-type cyclometalated products, **Pd1-4**. (Scheme 1). When the ligands **L2-L4** were combined with the palladium salt and allowed to stir at room temperature, an intermediate was observed that was assigned as initial chelation of the N[^]N dimethylethylene moiety to palladium (Scheme 1). These coordination intermediates were assigned based on NMR data, however, they could not be isolated. Scheme 1 illustrates the proposed reactivity described above. The cyclometalated species, **Pd2-Pd4**, could also be formed, in better yields, using the palladium(0) species, Pd(dba)₂ (dba = dibenzylideneacetone), as a starting material (Scheme 2). The palladium products were characterized by multi-nuclear NMR (See SI), elemental analysis, and mass spectrometry. For example, the proton NMR spectrum of **Pd1** has five aromatic resonances, the imine resonance at 8.68 ppm, as well as the two methylenes and the dimethylamino resonance. In addition, the

NOESY has cross peaks showing the interaction of the imine with the methyl group on the naphthyl ring. The proton NMR spectrum of **Pd2** and **Pd3** are similar for the imine and dimethyl ethylene moiety, but six aromatic resonances are observed along with the dimethylamino resonances at 2.8 ppm. The COSY shows cross peaks for the imine proton and the aromatic proton at the seven position of the ring. In both the coordination intermediate and final cyclometalated product, ^1H NMR peaks associated with the ligand resonances are shifted compared to the free ligand indicating coordination. For example, the imine and the dimethylamino resonances shift upfield approximately 0.25 ppm upon coordination.

Chart 2: Structure of the Cyclometalated Complexes

Scheme 1: Formation of the Palladium Products

Scheme 2: Reactions with starting material $\text{Pd}(\text{dba})_2$

Two six-membered palladacycles (**Pd1** and **Pd2**) were characterized crystallographically by XRD (Figures 1 and 2). The structures clearly show two fused rings, one the six-membered metalacycle derived from the activation of the group at the 8-position of the naphthyl ring and the other being the five-membered ring expected from the dimethylethylene group. To date, very few $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ imine palladium compounds have been characterized by XRD and are thus quite novel.²⁵⁻²⁷ The bond lengths and angles appear reasonable for palladium (II) species with cyclometalated groups.²⁶⁻³⁰ As all the ligands form $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ pincer-type complexes, the cyclometalated group is thus trans to the dimethylamino group, while the imine nitrogen is trans to the acetate in **Pd1** and the iodide in **Pd2**. The Pd-N bond length

trans to the carbon donor is longer than that the Pd-N trans to the halide as would be expected due to the stronger trans influence of the naphthyl ligand.²

Figure 1. ORTEP of Compound **Pd1** (50% probability thermal ellipsoids). Selected bonds lengths (Å) and angles (°): Pd-N(1): 1.967(2); Pd-C(1): 1.999(2); Pd-O(1): 2.055(2); Pd-N(2): 2.185(2); C(1)-Pd-N(1): 91.50(7); C(1)-Pd-O(1): 94.60(7); N(1)-Pd-O(1): 171.55(7); N(1)-Pd-N(2): 84.35(7); C(1)-Pd-N(2): 175.85(7); O(1)-Pd-N(2): 89.54(6).

Figure 2. ORTEP of Compound **Pd2** (50% probability thermal ellipsoids). Selected bonds lengths (Å) and angles (°): Pd-N(1): 2.007(3); Pd-C(1): 2.015(4); Pd-I: 2.6347(6); Pd-N(2): 2.204(4); C(1)-Pd-N(1): 91.8(2); C(1)-Pd-I: 95.8(1); N(1)-Pd-I: 166.9(1); N(1)-Pd-N(2): 82.3(1); C(1)-Pd-N(2): 173.3(2); I-Pd-N(2): 90.7(1).

The UV/vis spectra of **Pd1** through **Pd4** were taken and lowest energy peaks were observed between 410 nm and 440 nm (Table 1) with extinction coefficients in the $4\text{--}6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ range and are thus assigned as MLCT bands.^{31,32} The room temperature emission spectra of the complexes **Pd2**, **Pd3**, and **Pd4** were run using the lowest energy absorbance energies from the visible spectra as the excitation wavelengths. The spectra showed no discernible emissions. However, complex **Pd1** had very weak peaks, which were red-shifted from its absorbance peak of 410 nm about 200 nm.

At low temperature (77 K) all four compounds had emission spectra with very similar set of peaks between 600-607 nm with a shoulder between 655-665 nm (Table 2). The large red-shift of around 200 nm probably indicates emission from a triplet MLCT excited state.^{19,33-38}

Table 1: Selected UV/vis Data for Pd Complexes

Compound	Wavelength (nm)	Concentration (mM)	Extinction coefficient ($M^{-1}cm^{-1}$)
Pd1	414	0.050	5600
Pd2	410	0.050	4090
Pd3	409	0.050	5590
Pd4	416	0.050	2300
	440		1970

Table 2: Selected Emission Data for Pd Complexes at 77 K

Compound	Excitation (nm)	Concentration (mM)	λ at Max Intensity (nm)
Pd1	410	0.50	605, 660
Pd2	410	0.50	602, 660
Pd3	410	0.50	600, 655
Pd4	410	0.50	607, 665

Figure 3: Selected UV/vis Spectra for Pd Complexes

Figure 4: Selected Emission Spectra for Pd Complexes

In summary we have synthesized several palladium complexes with $N^{\wedge}N^{\wedge}C$ type pincer ligands. The cyclometalated ring of three of the complexes is the rarer six-membered ring formed by judicious choice of ligand allowing for regioselective formation. Weak emission was observed at room temperature for the complex **Pd1** and at low temperature (77 K) for all four metalated complexes. This data adds to the under-represented data for emission spectroscopy of palladium cyclometalated complexes, especially those with six-membered metalacycles. Reactivity studies of the complexes are currently underway.

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Notes

The authors declare no competing financial interest.

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