Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Regioselective Formation of Six-Membered Platinacycles by C-X and C-H Oxidative Addition

Leave this area blank for abstract info.

Craig M. Anderson^{*,a}, Matthew Greenberg^a, Tedros A. Balema^a, Leila Duman^a, Nathaniel Oh^a, Asad Hashmi^a, Leah Ladner^a, Kyan Jain^a, David Yu^a, and Joseph M. Tanski^b

Regioselective Formation of Six-Membered Platinacycles by C-X and C-H Oxidative Addition

Craig M. Anderson^{*a}, Matthew Greenberg^a, Tedros A. Balema^a, Leila Duman^a, Nathaniel Oh^a, Asad Hashmi^a, Leah Ladner^a, Kyan Jain^a, David Yu^a, and Joseph M. Tanski^b

Bard College, 30 Campus Road, Annandale-on-Hudson NY 12504

Corresponding author. Tel.: +1-845-752-2356; fax: +1-845-752-2339

e-mail: canderso@bard.edu

ARTICLE INFO

Article history:

Received

Received in revised form

Accepted

Available online

Keywords:

platinum

synthesis

platinacycle

XRD

NMR

ABSTRACT

Several naphthyl-based N[^]N[^]C ligands were synthesized by strategically incorporating a bromide or iodide at the 8-position of the naphthyl ring. When allowed to react with the platinum tetra methyl dimer, PtMe₄(μ-SMe₂)₂, the more rare six-membered platinum(IV) platinacycles were formed by oxidative addition of the C(sp²)-X bond. In a separate case, C-H activation at the 8-position was encouraged by having the 2-position “blocked” with a methyl group thus a six-membered platinum(II) platinacycle was formed by C(sp²)-H activation at the 8-position. Products were characterized by XRD, NMR, UV/vis, emission spectroscopy, and HRMS. The platinum (IV) compounds were inert to thermolysis. The complexes appear to exhibit dual fluorescence and phosphorescence at room temperature in solution.

2009 Elsevier Ltd. All rights reserved.

Cyclometalated platinum complexes have been well known for quite some time now.^{1,2} These complexes have been implicated as intermediates in catalytic reactions,³ as potentially useful in artificial photosynthetic^{4,5}, and in material science as switches⁶ and sensors.⁷ Overwhelmingly the most prevalent ring size that platinacycles form are those containing five atoms, hence a five-membered ring.¹ Several examples of six-membered and even a few seven-membered platinacycles have been reported but they are much more rare than five-membered rings.^{8,9} Crespo reported a mixture of five-membered and six-membered rings formed by C-H activation when using anthracenyl based ligands, but exclusively five-membered metalated rings when using naphthyl-based ligands.^{2,10,11} Very recently, a report with exclusively five-membered rings has been published using naphthyl fused ring ligands.¹¹ Herein we report driving or forcing the regioselectivity to form exclusively six-membered rings when a bromide or iodide is present in the 8-position of a naphthyl ring, allowing for oxidative addition of the C-X bond. However, in a different reaction, a six-membered ring is formed exclusively when a methyl group is present in the 2-position and therefore sp² C-H activation at the 8-position gives the desired ring. Our reactions follow the selectivity/activity trend of C-X > C(sp²)-H > C(sp³)-H.

The C[^]N[^]N[^]C, tridentate ligands were formed in two steps (Scheme 1). For ligands **A** (bromo) and **B** (iodo) (Scheme 1), oxidation of the 8-halonaphthyl alcohol afforded the aldehyde, followed by condensation of the aldehyde with the appropriate amine to form the imine ligands. For ligand **C** (Scheme 1) only the condensation reaction was necessary as the aldehyde was

commercially available. Yields were reasonable and ligands were characterized by NMR spectroscopy. The metalated complexes **D**, **E**, and **G** were formed by reaction of the tetra methyl platinum dimer, [PtMe₄(μ-SMe₂)₂],¹² and the appropriate ligand. The dimethylsulfide ligands are quite labile and are easily substituted for by the two nitrogen donors of the imine ligands to afford a platinum(II) intermediate (Scheme 2) followed by oxidative addition of the C-X (**A** and **B**) or C-H (**C**) bond. The coordination platinum(II) intermediate can be isolated in the case of the ligand **C** and heat is necessary in order to drive the subsequent metalation step in order to produce compound **G**. Conversely, ligands **A** and **B** react quickly to give the final platinum(IV) products without the isolation or observation of the intermediate platinum(II) species.

Compound **E** was also characterized crystallographically and the molecular structure has a six coordinate environment with the three strong carbon donor atoms in a *fac* geometry as would be expected (Figure 1).^{13,14} The C[^]N[^]N[^]C ligand forms two fused rings, one five-membered with the N[^]N[^] chelate, and the other a six-membered metalated ring containing the C[^]N[^] chelate, with the two rings being relatively planar. The structure of compound **D**, (SI, Figure S1) could not be refined successfully, likely due to disorder caused by a mixture of enantiomers. However the connectivity could be confirmed and was analogous to that of compound **E**. The structure of **E**, has the bonds lengths and angles within the expected ranges for platinum(IV) organometallic complexes with N[^]N[^]C ligands.¹⁵

The metalated compounds were characterized by NMR spectroscopy, HRMS, and XRD. Platinum compounds **D** and **E**

appear to give two diastereomers (presumably in addition to the expected mixture of enantiomers for each) in each case as seen by parallel sets of peaks in the proton NMR (Supp. Info.). We speculate that the major isomer is the isomer that is observed in the XRD study and the second isomer is the isomer having the dimethyl amino group switched for the halide atom (Figure 2). Only two possibilities are considered given that the ligand is tridentate and the three strong carbon donors are necessarily *fac*. We have previously not observed such a situation with any of our platinum(IV) complexes with C[^]N[^]N ligands in the past.^{14,16-18} All prior examples with analogous ligands have the C[^]N[^]N atoms all in the same plane hence in the *mer* configuration. Therefore, here we suggest that the second diastereomer has the C[^]N[^]N ligand in the *fac* arrangement. The proton NMR spectra clearly have two sets of resonances observable for the characteristic protons, including the methyl and imine groups. For example, for compound **E**, resonances for the two methyl groups and the imine proton for the major isomer are observed at $\delta = 0.95$ ppm ($^2J(\text{Pt-H}) = 72$ Hz) and 1.49 ppm ($^2J(\text{Pt-H}) = 67$ Hz); and 8.56 ppm ($^3J(\text{Pt-H}) = 31$ Hz), respectively, and for the minor isomer, $\delta = 0.73$ ppm ($^2J(\text{Pt-H}) = 74$ Hz) and 1.27 ppm ($^2J(\text{Pt-H}) = 65$ Hz); and 8.61 ppm ($^3J(\text{Pt-H}) = 30$ Hz), respectively. Chemical shifts and platinum coupling constants are in the expected ranges for platinum(IV) species with all three carbon donors *fac*. Platinum (IV) complexes are known to have reduced coupling constants compared to platinum (II) species.¹⁹ In addition, this geometry avoids *trans* carbons which would result in a much more reduced platinum-hydrogen coupling constant than is observed.²⁰ With ligand **C**, the product **F** is easily identified by its proton NMR spectrum with two singlet methyl resonances with large platinum coupling constants characteristic of these platinum (II) species ($\delta = -3.08$ ppm, $^2J(\text{Pt-H}) = 90.3$ Hz and $\delta = 3.24$ ppm, $^2J(\text{Pt-H}) = 82.4$ Hz). Upon metalation to give the product **G**, the NMR spectrum shows only one methyl resonance with the appropriate coupling constant ($\delta = 0.98$ ppm, $^2J(\text{Pt-H}) = 78.5$ Hz).^{14,19}

The reactivity of the compounds was studied briefly with respect to thermolysis so as to compare to some previously reported C[^]N chelate ligand species. We have reported C-C coupling reactions from six coordinate platinum(IV) complexes that contain C[^]N ligands when the complexes were heated.^{21,22} **D** and **E** are not reactive in the same manner with respect to reductive elimination as the C[^]N ligands when heated, including to 110 °C in toluene, for several hours. This is similar to our findings for other C[^]N[^]N ligands that were also inert to thermolysis under similar conditions.

Scheme 1

Scheme 2

Figure 1. Molecular structure of compound **B**. Selected bond lengths (Å) and angles (deg.) with estimated standard deviations (ellipsoids at 50% probability) : Pt-C(1): 2.071(7); Pt-C(2): 2.075(8); Pt-C(3): 2.018(7); Pt-N(1): 2.084(6); Pt-N(2): 2.4279(7); Pt-I: 2.7574(6); C(1)-Pt-C(2): 87.2(4); C(1)-Pt-C(3): 93.7(3); C(3)-Pt-C(2): 87.3(3); C(1)-Pt-N(1): 173.4(4); C(2)-Pt-N(1): 91.1(3); C(3)-Pt-N(1): 92.6(3); C(1)-Pt-N(2): 92.4(3); C(2)-Pt-N(2): 93.6(3); C(3)-Pt-N(2): 173.8(2); C(1)-Pt-I: 91.3(3); C(2)-Pt-I: 174.8(2); C(3)-Pt-I: 87.9(2); N(1)-Pt-I: 90.9(2); N(2)-Pt-I: 91.4(2).

Figure 2: Possible Diastereomers

The platinum (IV) species **D** and **E** have UV/visible (UV/vis) spectra with the lowest energy peak at around 390 nm tailing into the visible to approximately 440 nm. This peak is most likely attributable to a MLCT band given the extinction coefficient of 5.3×10^3 and 1.1×10^4 L·mol⁻¹·cm⁻¹ for **D** and **E**, respectively.²³⁻²⁵ The cyclometalated products **G**, **D** and **E** exhibit, what we speculate to be, dual emission consisting of both fluorescence and phosphorescence (less pronounced in the case of **D**) at room temperature in solution (Fig. 3). For example, excitation with 415 nm light gave dual emission with peaks at 490 and 610 nm for complex **E**. The emission peak at 490 nm, for compound **E**, as it not appreciably shifted from the emission peak of the free ligand, may be thought to be due to contamination with trace amounts of excess ligand, **B**. However, the NMR spectra of the samples used for the emission spectroscopy do not show signs of the free ligand. Dual emission has been reported for platinum and iridium complexes with metalated ligands and the spectra show a resemblance to our spectrum of complex **E**, including an

additional shoulder on the lower energy peak.^{26,27} The peak in the emission spectrum of **E** at 490 nm is red-shifted approximately 100 nm compared to its absorbance peak and has a lifetime of 20 ns both observations supporting an assignment of fluorescence. The emission at 610 nm has a lifetime of 740 ns and is red-shifted by over 200 nm from the absorbance peak, indicating emission from a triplet state and hence phosphorescence.^{28,29} The emission data for **D** and **E** are interesting because, in a previous work, we observed a turning off of emission for platinum complexes when oxidized from platinum(II) to platinum(IV).³⁰ Platinum(IV) emitters at room temperature are much more rare than platinum(II) species. Therefore these results add to the data in this under-studied area.³¹ The platinum(II) compound **G** has similar spectra but with some notable differences. The emission spectrum has its highest energy peak at 480 nm, which is red-shifted 10 nm as compared to the emission of its free ligand thus ruling out contamination as its source. The lower energy peak has a shoulder discernable to the point that there appears to be two peaks: 610 and 670 nm. The three peaks have lifetimes of 40, 350, and 500 respectively therefore we tentatively make similar photophysical assignments as for **D** and **E**.

Computational studies using Gaussian '09 were conducted in order to obtain some insight into the relative thermodynamic stability of the proposed isomers in Figure 2. The *fac* and *mer* isomers were compared to each other and then the *fac* and *mer* isomers of a related hypothetical isomer with a five-membered ring (metalation at the 2-position) were compared (SI, Table S1). As stated, our numerous previous reports of platinum cyclometalated complexes with five-membered rings did not produce the isomeric mixture that is proposed for **D** and **E**. In both cases the isomer with a *mer* configuration is the lower energy isomer. The free energy difference between the *fac* and *mer* isomers of the six-membered rings **D** and **E** is about 3 kJ/mol less than the energy difference between the *fac* and *mer* isomers for the five-membered rings. This might suggest that the *fac* isomer is more accessible in the case of the six-membered ring compared to the five-membered ring. Unsurprisingly, our computation data clearly indicate that five-membered rings are more thermodynamically stable than the isomeric six-membered rings (SI, Table S1). However, the mixtures obtained experimentally may be a result of the accessibility of the transition state and the necessary orientation of the molecule during the formation of different sized rings.³²

In summary, we have managed to synthesize the rarer six-membered rings by exploiting (and confirming) the greater reactivity of C-X bonds over C-H bonds and of C(sp²)-H bonds over C(sp³)-H bonds, and record emission spectra for the Pt(IV) species, which are less precedented than Pt(II) species. Future studies are being pursued that include the synthesis of complexes with naphthyl-based ligands with C[^]N chelates, containing six-membered rings, followed by exploring the reactivity of the new complexes as a function of ligand architecture.

Acknowledgment This material is based upon work supported by the National Science Foundation under CHE-1058936 and CHE-1362858 (Craig M. Anderson (CMA), P.I.). The authors also thank the Bard Summer Research Institute (BSRI) for financial help and The Camille and Henry Dreyfus Foundation for a Henry Dreyfus Teacher-Scholar Award to CMA. Mass spectrometry was performed using instrumentation supported by funding from a National Science Foundation Major Research Instrumentation Grant (#1039659, Teresa A. Garrett, P.I.)

Figure 3: Emission spectra (Excitation wavelength: 405 nm) of Compounds **D**, **E**, and **G**. Intensity is measured in arbitrary units.

References

- (1) Albrecht, M. *Chemical Reviews*. **2010**, 576–623.
- (2) Crespo, M.; Evangelio, E. *Journal of Organometallic Chemistry*. **2004**, 1956–1964.
- (3) Jia, Y.-X.; Li, B.-B.; Li, Y.; Pullarkat, S. A.; Xu, K.; Hirao, H.; Leung, P.-H. *Organometallics*. **2014**, 6053–6058.
- (4) Ding, J.; Feng, K.; Tung, C.-H.; Wu, L.-Z. *The Journal of Physical Chemistry C*. **2011**, 833–839.
- (5) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorganic Chemistry*. **2005**, 6802–6827.
- (6) Boixel, J.; Guerchais, V.; Le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekkine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; Righetto, S.; De Angelis, R. *Journal of the American Chemical Society*. **2014**, 5367–5375.
- (7) Liu, C.; Song, X.; Rao, X.; Xing, Y.; Wang, Z.; Zhao, J.; Qiu, J. *Dyes and Pigments*. **2014**, 85–92.
- (8) Garner, K. L.; Parkes, L. F.; Piper, J. D.; Williams, J. A. G. *Inorganic Chemistry*. **2010**, 476–487.
- (9) Cortés, R.; Crespo, M.; Davin, L.; Martín, R.; Quirante, J.; Ruiz, D.; Messegue, R.; Calvis, C.; Beldomà, L.; Badia, J.; Font-Bardía, M.; Calvet, T.; Cascante, M. *European Journal of Medicinal Chemistry*. **2012**, 557–566.
- (10) Crespo, M.; Font-Bardía, M.; Pérez, S.; Solans, X. *Journal of Organometallic Chemistry*. **2002**, 171–178.
- (11) Rao, A. R. B.; Pal, S. *Journal of Organometallic Chemistry*. **2014**, 58–66.
- (12) Scott, J. D.; Puddephatt, R. J. *Organometallics*. **1983**, 1643–1648.
- (13) Rendina, L. M.; Puddephatt, R. J. *Chemical Reviews*. **1997**, 1735–1754.
- (14) Anderson, C. M.; Crespo, M.; Jennings, M. C.; Lough, A. J.; Ferguson, G.; Puddephatt, R. J. *Organometallics*. **1991**, 2672–2679.
- (15) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics*. **1992**, 1177–1181.
- (16) Anderson, C. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *Journal of the Chemical Society, Chemical Communications*. **1989**, 1297–1298.
- (17) Anderson, C.; Crespo, M. *Journal of Organometallic Chemistry*. **2004**, 1496–1502.
- (18) Anderson, C.; Crespo, M.; Font-Bardía, M.; Klein, A.; Solans, X. *Journal of Organometallic Chemistry*. **2000**, 22–33.
- (19) Anderson, C. M.; Crespo, M.; Tanski, J. M. *Organometallics*. **2010**, 2676–2684.
- (20) Lashanizadehgan, M.; Rashidi, M.; Hux, J. E.; Puddephatt, R. J.; Ling, S. S. M. *Journal of Organometallic Chemistry*. **1984**, 317–322.
- (21) Anderson, C. M.; Crespo, M.; Kfoury, N.; Weinstein, M. A.;

- Tanski, J. M. *Organometallics*. **2013**, 4199–4207.
- (22) Crespo, M.; Anderson, C. M.; Kfoury, N.; Font-Bardía, M.; Calvet, T. *Organometallics*. **2012**, 4401–4404.
- (23) Anderson, C. M.; Weinstein, M. A.; Morris, J.; Kfoury, N.; Duman, L.; Balema, T. A.; Kreider-Mueller, A.; Scheetz, P.; Ferrara, S.; Chierchia, M.; Tanski, J. M. *Journal of Organometallic Chemistry*. **2013**, 188–197.
- (24) Shao, P.; Li, Y.; Yi, J.; Pritchett, T. M.; Sun, W. *Inorganic Chemistry*. **2010**, 4507–4517.
- (25) Hu, J.; Yip, J. H. K.; Ma, D.-L.; Wong, K.-Y.; Chung, W.-H. *Organometallics*. **2009**, 51–59.
- (26) Zhang, K. Y.; Liu, H.-W.; Tang, M.-C.; Choi, A. W.-T.; Zhu, N.; Wei, X.-G.; Lau, K.-C.; Lo, K. K.-W. *Inorganic Chemistry*. **2015**, 6582–6593.
- (27) Kozhevnikov, D. N.; Kozhevnikov, V. N.; Shafikov, M. Z.; Prokhorov, A. M.; Bruce, D. W.; Gareth Williams, J. A. *Inorganic Chemistry*. **2011**, 3804–3815.
- (28) Turner, E.; Bakken, N.; Li, J. *Inorganic Chemistry*. **2013**, 7344–7351.
- (29) Kozhevnikov, V. N.; Durrant, M. C.; Williams, J. A. G. *Inorganic Chemistry*. **2011**, 6304–6313.
- (30) Anderson, C.; Freedman, D. A.; Jennings, M.; Gray, B. *Journal of Organometallic Chemistry*. **2005**, 168–176.
- (31) Juliá, F.; Bautista, D.; Fernández-Hernández, J. M.; González-Herrero, P. *Chemical Science*. **2014**, 1875.
- (32) Crumpton, D. M.; Goldberg, K. I. *Journal of the American Chemical Society*. **2000**, 962–963.