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Communication

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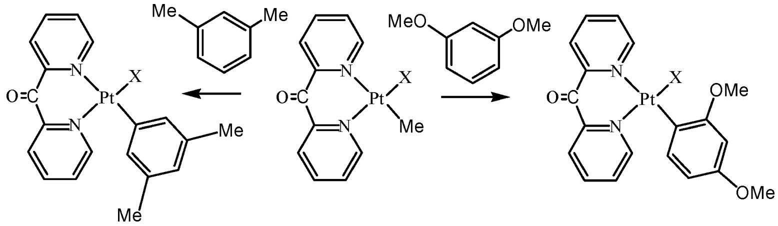

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Activation of C−H Bonds of Arenes: Selectivity and Reactivity in Bis(pyridyl) Platinum(II) Complexes

Fenbao Zhang, Christopher W. Kirby, Douglas W. Hairsine, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, The University of Western Ontario, London, Canada N6A 5B7

Received August 9, 2005; E-mail: pudd@uwo.ca

There has been rapid progress in understanding the factors that influence selectivity and reactivity in C−H bond activation in arenes or alkanes by organoplatinum(II) compounds.[1−4] The reactions with arenes are often reversible and proceed through "arene platinum(II)" and "aryl(hydrido)platinum(IV)" complex intermediates. In arene activation reactions, the rate-determining step can be arene coordination or C−H oxidative addition, and the C−H oxidative addition/reductive coupling steps can be reversible and either faster or slower than methane displacement. Since the design of catalysts for reactions involving C−H activation requires knowledge of the factors affecting reactivity and selectivity in C−H activation reactions, we are prompted to report an arene C−H bond activation reaction in which the chelate ring size of the bidentate ligand, NN, and its effect on the ligand geometry (Chart 1), is a critical factor. In addition, it is shown that methyl and methoxy substituents on the arene give opposite selectivity.

Reactions of $[PtMe_2(NN)]$, **1a**, NN = di-2-pyridyl ketone (DPK); **1b**, NN = di-2-pyridylamine (DPA); **1c**, NN = di-2-pyridylmethane (DPM); **1d**, NN = 4,4′-di-*tert*-butyl-2,2′-bipyridyl (bu_2bpy) (Chart 1), with $B(C_6F_5)_3/H_2O$ in CF_3CH_2OH occurred rapidly at room temperature with loss of methane to give the corresponding complexes $[PtMe\{HOB(C_6F_5)_3\}(NN)]$, **2a**−**2d**.[5] The anion $[HOB(C_6F_5)_3]^-$ acts as a good leaving group; replacement by CO gives the complexes $[PtMe(CO)(NN)][HOB(C_6F_5)_3]$, **3a**−**3d**, whose carbonyl stretching frequencies are 2119, 2105, 2109, and 2109 cm^{-1} when NN = DPK, DPA, DPM, and bu_2bpy, respectively, indicating that DPK is the weakest donor, while the other ligands have similar electronic effects. The structures of **2a** (Figure 1) and **3b** were confirmed crystallographically.[5]

Reactions of **2a**−**2c** (or, more conveniently, a mixture of **1a**−**1c** and $B(C_6F_5)_3/H_2O$) with benzene or with several methyl- or methoxy-substituted arenes Ar−H in CF_3CH_2OH gave the corresponding complexes $[PtArX(NN)]$, with $X = HOB(C_6F_5)_3$ and NN = DPK, DPA, or DPM. However, complex **2d**, NN = bu_2bpy, failed to react with arenes under these conditions. Because it is established that the ligands DPA, DPM, and bu_2bpy have similar electronic effects, the enhanced reactivity of **2a**−**2c** compared to that of **2d** must arise from the presence of bowed six-membered Pt(NN) chelate rings in **2a**−**2c** compared to the more planar five-membered chelate ring in **2d** (see Chart 1, which shows the different orientations of the *ortho*-hydrogen atoms of the chelate ligands).[6] The complexes **2a**−**2c**, with NN = $(2\text{-}C_5H_4N)_2X$ and X = CO, NH, and CH_2 respectively, show similar reactivity to arenes, although the carbonyl group is more electron-withdrawing than either the NH or CH_2 group, further suggesting that structural rather than electronic effects are responsible for the difference in reactivity of **2d** compared to that of **2a**−**2c**.

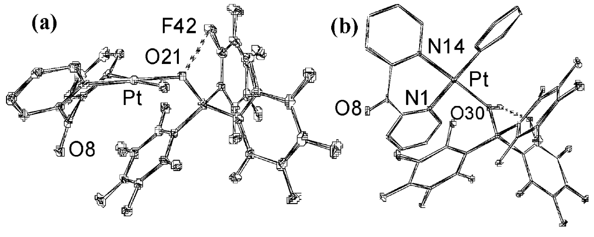
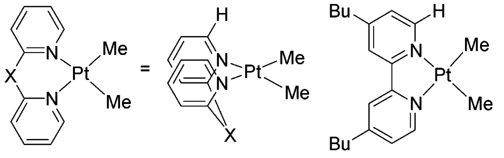


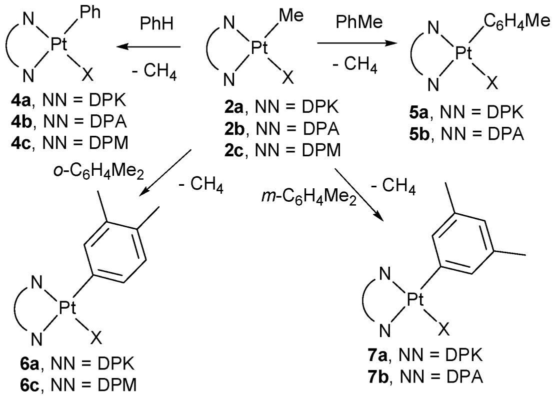
Figure 1. The structures of the methyl and phenylplatinum complexes $[PtRX(DPK)]$: (a) R = Me, **2a**; and (b) R = Ph, **4a**.

Chart 1. Planar and Bowed Bipyridine Groups in **1d** and **1a**−**1c**, Respectively (note the orientation of the *o*-hydrogen atoms in the plane in **1d** and out of the plane in **1a**−**1c**)



1a, X = CO; **1b**, X = NH; **1c**, X = CH_2 **1d**

Scheme 1. $X = HOB(C_6F_5)_3$



Benzene reacted with complexes **2a**−**2c** to give the corresponding phenyl complexes $[PtPhX(NN)]$, **4a**−**4c**,[5] while toluene reacted with **2a** or **2b** to give the corresponding complex $[Pt(C_6H_4Me)X(NN)]$, **5a**, NN = DPK; **5b**, NN = DPA (Scheme 1). NMR analysis showed that the tolyl complexes exist as a mixture of isomers with *meta*:*para*:*ortho* = 70:27:3 for **5a** and 75:22:3 for **5b**, consistent with results for related diimine complexes.[2−4] Reactions of **2a** or **2c** with *o*-xylene and of **2a** or **2b** with *m*-xylene gave only the isomers shown in Scheme 1,[5] with no products of *ortho* C−H or benzylic C−H bond activation detected. Mesitylene, which has only *ortho* and benzylic C−H bonds, failed to react with complex **2a** under similar conditions. The structures of **6a**, **6c**, and **7a** were confirmed crystallographically.[5]

Anisole reacted with **2a** to give $[Pt(C_6H_4OMe)X(DPK)]$, **8a**, as a mixture of *o*-, *m*-, and *p*-isomers in a ratio 90:8:2, from which the pure *ortho* isomer was crystallized, and *m*-dimethoxybenzene reacted to give $[Pt\{2,4\text{-}C_6H_3(OMe)_2\}X(DPK)]$, **9a**, respectively

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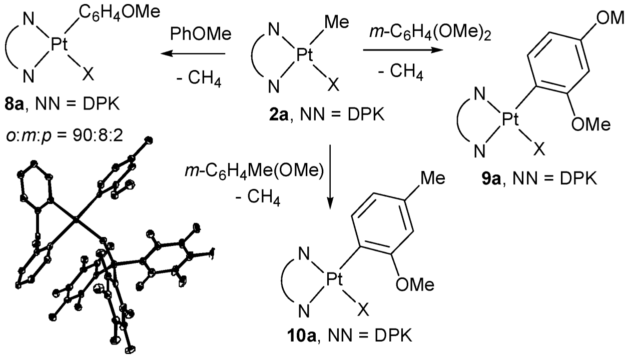
Scheme 2. X = $HOB(C_6F_5)_3$ (the inset shows the structure of **10a**)



(Scheme 2).[5] The prominence of *ortho*-metalation is obvious, but there is no associated acceleration of reaction. Thus, reaction of **2a** with an equimolar mixture of *m*-xylene and *m*-dimethoxybenzene gave **7a** and **9a** in a 3:2 ratio, and the reaction was slower than with *m*-xylene alone. Reaction of 3-methylanisole with **2a** gave [PtArX(DPK)], **10a**, with Ar = 2-MeO-4-Me-C_6H_3 (Scheme 2),[5] showing that, in the reagent that contains both methyl and methoxy substituents, the methoxy group controls the site of metalation.[7]

The reaction of **1a** and $B(C_6F_5)_3/H_2O$ in CF_3CH_2OH with *o*-xylene or anisole gave a kinetic isotope effect $k_H/k_D = 2.8$ or 3.6, respectively,[8] and the similar reactions with *o*-xylene-d_{10} or anisole-d_8 gave CH_4 and CH_3D, with only traces of CH_2D_2, indicating that the reductive coupling step to give methane is largely irreversible and that the C−H oxidative addition step is rate-determining.[2−4] In agreement, the arylplatinum product from reaction of **1** with *o*-xylene-d_{10} in CF_3CH_2OH was very largely **10**-d_9, with <2% H incorporation at the aromatic sites and no H incorporation at the methyl sites.[8]

In conclusion, it is shown that the chelate ring size of supporting bipyridyl ligands is an important factor in C−H activation of arenes and should be considered in the design of more active catalysts.[9] In addition, methyl and methoxy substituents on the arene are shown to give very different regioselectivities. It is interesting that the selectivity in toluene activation is similar in this case, in which C−H oxidative addition is product-determining, and with the ligand ArN═C(Me)C(Me)═NAr, in which the methane displacement step is most important.[1−4] The methoxy group is shown for the first time to give *o*-platination but without an associated rate acceleration.[10]

Acknowledgment. We thank the NSERC (Canada) for financial support.

Supporting Information Available: Experimental procedures, diagrams of X-ray structures, and spectroscopic data (PDF), X-ray data for complexes **2a**, **3b**, **4a**, **6a**−**10a**, and **6c** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Experimental details, including synthetic procedures, spectroscopic data, and X-ray data for complexes **2a**, **3b**, **4a**, **6a**−**10a**, and **6c**, are given in the Supporting Information. The NMR data for the complexes support the structures and show that the $[B(OH)(C_6F_5)_3]^-$ anion remains coordinated in CD_2Cl_2 solution. In each case, the OH proton appeared as a septet in the ^1H NMR at room temperature through coupling to all six *ortho*-fluorine atoms, and the ^{19}F NMR contained only three resonances (*o*, *m*, *p*). However, at −80 °C, all fluorine atoms were inequivalent due to restricted rotation about the B−O and B−C bonds. For example, complex **2a** gave at 20 °C $\delta(OH) = 3.30$, sept., $J(HF) = 3$ Hz, but at −80 °C, $\delta(OH) = 3.36$, d, $J(HF) =$ ca. 20 Hz, indicating H-bonding of the OH proton to only one *ortho*-fluorine atom at low temperature. At −80 °C, $\delta(o\text{-F}) = -127.0, -132$ (3F), $-139.6, -142.2$; $\delta(p\text{-F}) = -157.5, -160.0, -161.3$; $\delta(m\text{-F}) = -164.1, -164.4, -164.5, -164.6; -165.0$ (2F).

(6) Hill, G. S.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525. The carbonyl group in DPK is known to form hemiketals with alcohols, and this might affect reactivity, but we did not detect any reaction of either DPK or complex **4a** with trifluoroethanol, as indicated by NMR.

(7) If the methyl group controlled the site of metalation, the major product would be that with Ar = 3-MeO-5-Me-C_6H_3. We suggest that the methoxy group is a better ligand for platinum than the π-arene and directs metalation to the least hindered *ortho* site, though a transient arene complex is probably required for metalation.[1−4] In the isolated 2-methoxyarylplatinum products, the Pt···O distance is >3 Å, and there are no bond distortions that might suggest a bonding interaction between platinum and the methoxy substituent. The hydroxy proton was not directly located in **8a**−**10a**, but it lies close to the 2-methoxyaryl oxygen atom and to one or two *ortho*-fluorine atoms. For example, in **10a** (Scheme 2), the short contacts are O···O = 2.73, O···F = 2.65, 2.76 Å, all in the range for which a hydrogen bond is possible.

(8) The mechanistic implications of the presence or absence of multiple H−D exchange between aryl and methyl groups or between hydrocarbonyl groups and solvent have been discussed in refs 2−4. The isotope effects were determined by reaction of **1a** with equimolar amounts of *o*-xylene/*o*-xylene-d_{10} or anisole/anisole-d_8, with analysis of the H/D content of the isolated product by ^1H NMR. In the reaction of **1** with anisole-d_8 in CF_3CH_2OH, a greater degree of H−D exchange was observed in the 5- (ca. 8% H) and 3- (ca. 6% H) positions of the deuterated 2-methoxyphenylplatinum complex **8a**. This is attributed largely to H/D exchange through conventional electrophilic substitution *para* or *ortho* to the activating methoxy group, with a small preference for *para*. The arylplatinum complexes were inert to C−H activation; for example, **4a** failed to react with *o*-xylene or 3-methoxyanisole.

(9) The bowing of the six-membered chelate ring in the DPM complexes is not very easily inverted. Thus, the platinum(II) complexes give two well-separated resonances for the CH_2 protons [e.g., **1c**, $\delta(CH_2) = 4.00, 4.74$]. This bowing should reduce steric hindrance between *o*-substituents of the pyridyl and incipient aryl group in the transition state compared to planar bipyridine.

(10) Zhang, X.; Kanzelberger, M.; Emge, T. J.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13192. This article reviews some CH activation reactions of arenes, in which a substituent may give selectivity for *ortho* product as a result of either kinetic or thermodynamic control, as well as providing an elegant example of the second.

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