

Intermolecular Hydroarylation of Unactivated Olefins Catalyzed by Homogeneous Platinum Complexes**

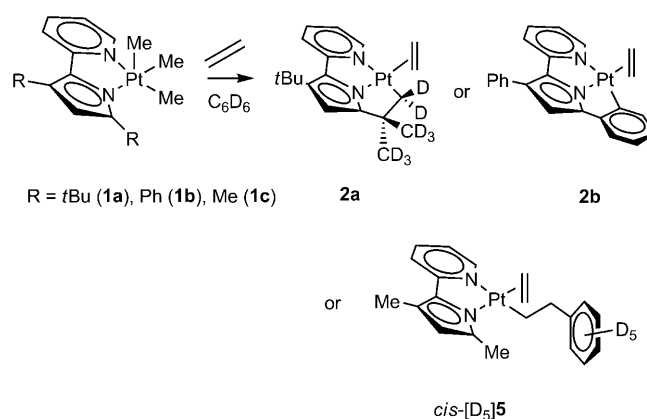
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The hydroarylation of olefins is a valuable C–C bond forming reaction used to produce alkyl arenes.^[1] Olefin hydroarylation can be catalyzed by Lewis acids, but such reactions proceed through a Friedel–Crafts type mechanism involving an intermediary carbocation. Thus, these reactions give predominantly Markovnikov products, and *ortho*, *meta*, and *para* selectivity is determined by the substituents on the aromatic ring. In contrast, the use of transition-metal catalysts can afford different regioselectivities acting via a mechanism of arene C–H bond activation and olefin insertion.^[1] While in the past transition-metal-catalyzed olefin hydroarylation reactions were primarily limited to activated arenes wherein a chelating functionality on the arene was available to assist and direct the C–H bond activation step,^[1] recently Ir^{III} and Ru^{II} catalysts have demonstrated hydroarylation with unactivated arenes and olefins.^[2,3] Mechanistic and computational studies on these Ir^{III} and Ru^{II} catalysts suggest that the hydroarylation does not proceed through a Friedel–Crafts type activation but through olefin insertion followed by oxidative hydrogen migration. In addition, selectivity for anti-Markovnikov over Markovnikov products (ca. 60:40) was observed. However, significantly higher selectivities and turnover numbers (TONs) are needed to make these processes economical, so a broadly tunable system that can be modified both sterically and electronically is likely needed.

One promising metal for olefin hydroarylation is platinum. There is considerable precedent for both arene C–H bond activation and olefin insertion at Pt^{II},^[4,5] however, attempts at olefin hydroarylation with Pt^{II} have been disappointing.^[6] Selectivities consistent with an electrophilic Friedel–Crafts type pathway were observed using a mixed Ag–Pt catalyst system.^[7] With a related Pt^{II} catalyst, the hydroarylation of norbornene was reported, but other olefins were found to be unreactive.^[8] Finally, tridentate chelation of a tris(pyrazolyl)borate ligand stabilized a potential Pt^{IV} intermediate preventing catalytic turnover.^[5] Herein, we describe the rational development of an effective Pt^{II} system for intermolecular hydroarylation with unactivated arenes

and olefins and present mechanistic evidence consistent with a pathway involving aryl–olefin insertion and C–H bond oxidative addition at Pt^{II}. While Markovnikov products are favored, anti-Markovnikov products are observed, and the mechanistic insight gained is promising for rational design of more selective and productive Pt^{II} catalysts for these reactions.

We recently reported that thermolysis of the five-coordinate Pt^{IV} complexes [(LX)PtMe₃] {LX = dtbpy [3,5-di-*tert*-butyl-2-(2-pyridyl)pyrrolide] (**1a**) or dppp [3,5-diphenyl-2-(2-pyridyl)pyrrolide] (**1b**)} at 85–100 °C in C₆D₆ in the presence of C₂H₄ (9–60 equivalents) led to the release of ethane and methane and formation of Pt^{II} complexes **2a** or **2b**, which contain a cyclometalated substituted pyrrolide group and C₂H₄ (Scheme 1).^[9] This indicates that the (pyridyl)pyrrolide



Scheme 1.

ligand on Pt^{II} effectively promoted two key reaction steps needed for hydroarylation: C–H bond activation and olefin coordination. The stability of the cyclometalated complexes, however, prevents further reaction. A complex containing a ligand that does not form a stable cyclometalation product may be expected to show different reactivity, and so [(dmpp)PtMe₃] [dmpp = 3,5-dimethyl-2-(2-pyridyl)pyrrolide (**1c**)] was prepared. Deprotonation of dmpp-H (**3**)^[10] with KH in THF yielded green dmpp-K (**4**). Reaction of **4** with [(PtMe₃OTf)₄] (OTf = SO₃CF₃[−]) in Et₂O produced a yellow solution of **1c**.^[11] Although an X-ray crystal structure of **1c** reveals a non-centrosymmetric dimeric structure in the solid state with a long bond [2.518(8) Å] between the C4-pyrrolide carbon and a second Pt center (see Figure S16 in the Supporting Information), the ¹H NMR spectrum of **1c** in CD₂Cl₂ at room temperature is consistent with a fluxional five-coordinate complex.^[12]

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Remarkably, the change to methyl substituents on the (pyridyl)pyrrolide ligand allowed for the observation of Pt-catalyzed intermolecular hydroarylation of unactivated olefins. Similar to the thermolyses of **1a** and **1b**, upon thermolysis of **1c** at 100 °C for 5 h in C₆D₆ in the presence of C₂H₄ (70 equiv) ethane and methane (CH₄ and CH₃D) were released. However, rather than a cyclometalated Pt^{II} species, the Pt^{II} product [(dmpp)Pt(CH₂CH₂C₆D₅)(C₂H₄)] (*cis*-[D₅]**5**) was observed in a 48% yield by ¹H NMR spectroscopy (Scheme 1). The configuration (*cis*) was assigned by NOESY^[11] and refers arbitrarily to the position of the 2-phenethyl ligand with respect to the pyrrolide group. Notably, the product of hydroarylation, C₆D₅CH₂CH₂D ([D₆]ethylbenzene), was also observed in the ¹H NMR spectrum, and the concentration of this organic product continued to increase upon further heating for an additional 12 h.

However, complex *cis*-[D₅]**5** decomposed significantly over this time to intractable products. The organic product, C₆D₅CH₂CH₂D, was identified by ¹H NMR spectroscopy and GC-MS. When C₆D₁₂ was used as the solvent with C₂H₄ and C₆H₆ (0.21 M) added as reagents, no evidence of hydroarylation (or hydroalkylation) was observed in the ¹H NMR spectrum. Instead, decomposition of **1c** to Pt⁰ was observed with evidence of numerous unidentified compounds in the ¹H NMR spectrum.

A related Pt^{II} catalyst precursor compound [(dmpp)Pt(SMe₂)Ph] (*trans*-**6**) was prepared by the reaction of **3** with [{Me₂Pt(μ-SMe₂)}₂] in C₆H₆.^[13] The relative configuration, phenyl *trans* to pyrrolide, was confirmed by NOESY.^[11] Heating a C₆D₆ solution of *trans*-**6** at 100 °C caused partial isomerization to *cis*-**6** (greater than 2:1 *cis/trans* after 133 h).^[11] Upon pressurization of a C₆D₆ solution of *trans*-**6** with C₂H₄ and subsequent heating at 59 °C for 14 h, conversion to *cis*-[D₅]**5** (59%) was observed in the ¹H NMR spectrum. Heating of either *cis*-[D₅]**5** or *trans*-**6** under C₂H₄ in C₆D₆ at 100 °C produced the hydroarylation product C₆D₅CH₂CH₂D. Similar attempts to synthesize [(dmpp)Pt-{(C₃H₆)C₆H₅}(C₃H₆)] by heating *trans*-**6** in C₆D₆ at 59 °C under an atmosphere of C₃H₆ were unsuccessful. However, *trans*-**6** can act as a precatalyst for the hydroarylation of C₃H₆ with C₆H₆ or C₆H₅CH₃ (Table 1).^[14]

Table 1: Products and TONs for the hydroarylation of olefins.^[a]

Arene	Olefin	Cat.	TON	<i>o/m/p</i>	<i>iPr/nPr</i>
C ₆ H ₆	C ₂ H ₄	1c	26		
	C ₃ H ₆		8		86:14
	cyclohexene		8		
	norbornene		10		
C ₆ H ₅ CH ₃	C ₂ H ₄	<i>trans</i> - 6	4	7:93 ^[b]	
	C ₃ H ₆		2	10:63:27	85:15
C ₆ H ₅ CF ₃	C ₂ H ₄		2	6:62:32	
C ₆ H ₆	C ₂ H ₄		36		
	C ₃ H ₆		18		85:15
C ₆ H ₅ CH ₃	C ₂ H ₄		12	6:94	
	C ₃ H ₆		3	9:66:25	84:16

[a] Reaction conditions: 100–110 °C, 1–3 mol% of **1c** or *trans*-**6**, 17–50 h.^[11,17] [b] *meta* and *para* isomers could not be resolved and are listed together.

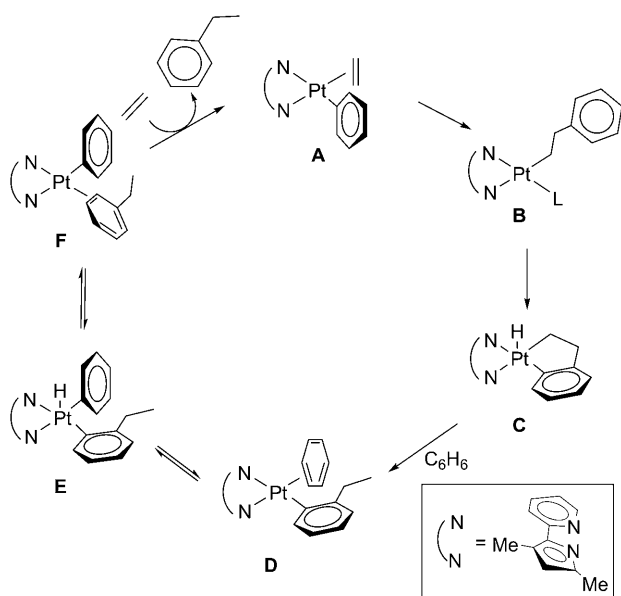
A variety of arene (C₆H₆, C₆H₅CH₃, C₆H₅CF₃) and olefin (C₂H₄, C₃H₆, cyclohexene, norbornene) combinations were examined with **1c** or *trans*-**6** as a precatalyst for hydroarylation. The product distributions were analyzed by GC-MS and GC-FID, and the results are summarized in Table 1 (a more complete listing can be found in Tables S1 and S2 in the Supporting Information).^[11] Hydroarylation of C₂H₄ (390–410 mm initial concentration) in C₆H₆ to form ethylbenzene gave TONs of 26 (**1c**) or 36 (*trans*-**6**); the higher TON for *trans*-**6** compared to **1c** may be due to a more efficient conversion to the active catalyst. Notably, when multiple products are possible, hydroarylation product mixtures contain similar ratios using **1c** or *trans*-**6** as a precatalyst. With C₃H₆, both Markovnikov (*iPr*-Ar) and anti-Markovnikov (*nPr*-Ar) products are observed, with the former favored 5–6:1. The isomeric distribution *meta* > *para* > *ortho* was obtained for reactions with C₃H₆ in C₆H₅CH₃ (*o/m/p* 9:66:25) and C₂H₄ in C₆H₅CF₃ (*o/m/p* 6:62:32). Both the fact that some anti-Markovnikov product is observed and that a preference for *meta* and *para* over *ortho* functionalization is observed suggest that a C–H bond activation pathway is operative.

A small amount of styrenes (0.1–0.7 TON), presumably formed by β-hydride elimination and also some dialkylation products (0.5–1.6 TON) were observed.^[11] Increasing the amount of C₂H₄ from 220 to 390 mm caused a 1.4-fold increase in TON in the hydroarylation of C₆H₆ using **1c** as the precatalyst. The relative amount of dialkylated products also increased from 4% to 9% of the total TON under these conditions.^[11]

Reaction of C₂H₄ with a 1:1 solution of C₆D₆ and C₆H₆ using **1c** as the precatalyst gave [D₀]ethylbenzene through [D₆]ethylbenzene as observed by GC-MS, with the major product being [D₃]ethylbenzene (Supporting Information, Figure S15). This isotopomer distribution suggests rapid scrambling of H or D from the solvent (C₆H₆ or C₆D₆) into ethylbenzene.^[11]

Stoichiometric reactions of *cis*-**5** or *cis*-[D₅]**5** in C₆D₆ with no C₂H₄ present produced PhCH₂CH₃ or PhCH₂CH₂D, respectively, as determined by ¹H NMR spectroscopy.^[11] Thus, whether or not the C2 carbon of ethylbenzene bears one D or only H is dependent upon whether the phenyl group of the 2-phenethyl ligand of *cis*-**5** was deuterated or not.

The mechanism shown in Scheme 2 is consistent with the isotopic labeling results and the regioselectivity described above. A Pt^{II} phenyl ethylene complex, **A**,^[15] formed in situ from **1c** or *trans*-**6**, undergoes migratory insertion of olefin into the Pt–Ph bond. Aryl C–H bond cyclometalation of the phenethyl group of **B** forms **C**. Insertion of an olefin into a Pt^{II}–Ph bond followed by orthometalation of the Ph ring has recently been observed upon thermolysis of [Tp^{Me}₂PtPh-(C₂H₄)] [Tp^{Me}₂ = 3,5-dimethyl-tris(pyrazolyl)borate].^[5] The observation of *cis*-**5** and the results of the stoichiometric reactions of *cis*-**5** and *cis*-[D₅]**5** are consistent with a similar reaction sequence in this system. However, here a five-coordinate cyclometalated hydrido Pt^{IV} species **C** would be formed, and alkyl C–H reductive elimination from five-coordinate Pt^{IV} structures is well precedented.^[4] Coordination of the solvent to the Pt^{II} product of C–H reductive elimi-



Scheme 2. Proposed mechanism for the hydroarylation of C_2H_4 with C_6H_6 . The ligand L in **B** may be an open site, C_2H_4 (complex **5**), or SM_{Et_2} .

nation would produce intermediate **D**, and a rapid equilibrium between arene complexes **D** and **F** would account for the H,D exchange observed in the hydroarylation of C_2H_4 using a 1:1 mixture of C_6H_6 and C_6D_6 . Scrambling of H,D between Pt-bound Ph and arene groups has been previously reported.^[16] Replacement of the bound arene of **F** with an olefin releases the product giving **A**. Displacement of the arene in **D** by the olefin would lead to the formation of dialkylated arene products, and β -hydride elimination from **B** would lead to styrene formation.

In summary, Pt-catalyzed intermolecular hydroarylation of unactivated olefins has been rationally developed. Studies of regioselectivity, relative reactivity of substrates, and deuterium labeling are consistent with a mechanism of olefin insertion into a Pt^{II} -aryl bond and aryl C-H oxidative addition at Pt^{II} center. Modification of both the sterics and the electronics of the (pyridyl)pyrrolide ligand to promote greater selectivity for anti-Markovnikov hydroarylation products and to increase the lifetime of the catalysts are currently under investigation.

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