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Platinum and Palladium Complexes Containing Cationic Ligands as Catalysts for Arene H/D Exchange and Oxidation**

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The direct functionalization of C–H bonds has frequently been deemed a “Holy Grail” of organometallic chemistry.[3] A seminal example of this transformation was the demonstration by Shilov and co-workers that platinum(II) salts catalyze the direct oxidation of alkanes into their corresponding alcohols and alkyl halides.[2] Subsequent work in this area has focused on surveying diverse ligands for these reactions in an effort to enhance reactivity and selectivity, slow catalyst decomposition, and replace platinum(IV)-based oxidants with more cost-effective alternatives.[3–5] In a key development, chemists at Catalytica identified [bpymPtCl₂] (bpym = bipyridine) as a pre-catalyst for the oxidation of CH₄ into CH₃OSO₃H in fuming H₂SO₄ (Scheme 1).[5] The reaction medium is believed to play several key roles in this system, including acting as a solvent, oxidant, and catalyst activator. Computational studies suggest that the active catalyst (1-H⁺) is formed by in-situ protonation of the ligand backbone, which limits oxidative catalyst degradation and renders the platinum center highly electrophilic and reactive for C–H bond cleavage.[6]

Despite this initial success, it remains challenging to develop new generations of Group 10 metal catalysts that display higher turnover frequencies and operate in different, less corrosive media.[3, 4] A key goal of our efforts has been to identify ligands that mimic the desirable properties of protonated bipyrimidine but are stable in the absence of strong acids.[7] Herein, we describe the application of dicaticonic-bipyridine-based ligands in platinum- and palladium-catalyzed arene H/D exchange and oxidation reactions.

We considered dicationic ligands of general structure 2 (Scheme 2) for several key reasons. First, they contain electron-withdrawing quaternized nitrogen substituents, which should render coordinated metal centers highly electrophilic.[8] Second, they are bidentate, sp² N-donors, which should allow a direct comparison with other bipyrimidine and bipyridine ligand systems. Third, the quaternized nitrogen atoms are not susceptible to decomposition by dealkylation or deprotonation, which has been problematic in related systems.[5,7] Fourth, substituents can easily be added to the pyridine ring to tune the solubility of these dications. Finally, ligands 2a and 2b are readily available in four steps from commercially available 2,2'-bipyridine (bpy) in 33% and 24% overall yield, respectively (for details, see the Supporting Information).[9]

Platinum(II) complexes of 2a and 2b were synthesized by reaction of these ligands with [(dmso)₂PtCl₂] in methanol at 60°C to afford 3a and 3b in 66% and 52% yield, respectively, after reacrystallization (Scheme 2). The analogous palladium(II) complex 3c was prepared in a similar fashion by the reaction of 2a with [(cod)PdCl₂] in dichloromethane at room temperature (84% yield; Scheme 2). All of these complexes were fully characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy and elemental analysis.

We first evaluated 3a–c as catalysts for H/D exchange[10] between [D₄]acetic acid and benzene using an assay developed in our laboratory.[10a] Under our standard conditions, (2 mol% [M], 4 mol% AgBF₄, 1 equiv C₆H₆ in 25 equiv of [D₄]AcOH, 150°C), these complexes showed very high catalytic activity, with turnover frequencies (TOFs) of 0.1 s⁻¹ (3a,b) and 0.05 s⁻¹ (3c) after 15 minutes at 150°C. For comparison, [dtbpyPtCl₂] (dtbpy = 4,4'-di-tert-butylbipyri...
The catalysts were also compared on the basis of turnover numbers (TONs). Complexes 3a–c achieved the statistical maximum TON of 242 after 24 hours[11,12], which is also superior to the results with [dtbpyPtCl2], [dtbpyPdCl2], and 1 (TON = 144 ± 12, 90 ± 18, and 94 ± 13 under analogous conditions).[10f] Lowering the catalyst loading of 3a to 0.1 mol% resulted in turnovers of 3273 ± 110 after 48 hours at 150 °C, which demonstrates the high activity and stability of this species, even upon prolonged heating at elevated temperatures. Finally, we decreased the reaction temperature to 100 °C. As shown in Figure 1, [dtbpyPtCl2], [dtbpyPdCl2], and 1 promoted very little H/D exchange under these conditions, whilst 3a–c maintained high activity.

There are two possible explanations for the high H/D exchange activity of 3a–c. The first is that the cationic ligands enhance the reactivity of the coordinated metal center towards arene C–H cleavage to generate metal α-aryl intermediates (through an organometallic mechanism). An alternative possibility is that the Lewis acidic metal centers promote proton catalysis through an electrophilic aromatic substitution (Ar–Sx) pathway. To gain insight into the mechanism for H/D exchange, we examined the site-selectivity of D incorporation with catalyst 3a for a variety of substituted arenes at partial (ca. 25%) conversion. Table 1 compares the observed selectivity (as determined by 1H NMR spectroscopy) to the product ratio for electrophilic bromination[13,14]; Table 1, entries 1–3; furthermore, the selectivity of DCl/C6H4D-catalyzed H/D exchange with bromobenzene is shown in entry 4. In all cases, the site selectivity with 3a differed dramatically from that observed in Ar–Sx. This is strongly suggestive of an organometallic pathway for the platinum/palladium-catalyzed H/D exchange reactions.

![Table 1: Comparison of site-selectivity for arene H/D exchange at 25% conversion with site-selectivity obtained in electrophilic aromatic bromination.](image)

![Figure 1. Turnover numbers for H/D exchange between benzene and [D₄]AcOH at 100 °C, catalyzed by 1, 3a–c, [dtbpyPtCl2], and [dtbpyPdCl2] after 2 h (white), 24 h (light gray), and 48 h (dark gray). Conditions: catalyst (2 mol %, 5.00 mmol), benzene (22.3 μL, 0.250 mmol), AgBF₄ (1.9 mg, 10 mol %), [D₄]AcOH (0.37 mL, 6.5 mmol, 25 equiv relative to benzene).](image)

The substrate scope of H/D exchange reactions catalyzed by 3a was also investigated. As summarized in Figure 2, naphthalene, veratrole, 1,2-dichlorobenzene, bromobenzene, ethylbenzoate, (H₃C)₃CCH₂Ph, sec-butylbenzene, cumene, and trifluorotoluene all underwent extensive (48–98%) aromatic H/D exchange with CD₃CO2D. Significant (2–8%) deuteration was also observed at unactivated sp³–C–H sites along the alkyl chains. In an interesting contrast, substrates that do not bear a tethered aromatic group (e.g. cyclooctane, 2,2,3,3-tetramethylbutane, and methane) did not show H/D exchange reactivity with catalyst 3a under analogous conditions. This observation suggests that the arene moiety plays a role in directing the catalyst to the unactivated sp³ sites, likely via cyclometalation[15] or π-coordination[16]. The observation of aliphatic H/D exchange provides further evidence to support an organometallic mechanism, as this side reaction is expected to be negligible under proton catalysis.

The H/D-exchange experiments probed the reactivity of 3a–c in C–H bond cleavage, which is only the first step of a
potentially C–H functionalization process. Thus, it was important to determine whether the high reactivity and stability of these new complexes for arene H/D exchange correlated to catalytic activity in arene oxidation.

To test this, we conducted preliminary studies of the effect of ligand 2a on the Pd(OAc)₂-catalyzed oxidative acetoxylation of arenes with PhI-

Figure 3. Pd(II) catalyzed acetoxylation of benzene. Catalysts [Pd]: (a) Pd(OAc)₂/bpy 2:1; (b) Pd(OAc)₂/bpy 2:1; (c) Pd(OAc)₂/bpy 2:1; (d) Pd(OAc)₂/bpy 2:1. Reaction conditions: 10 equiv. PhI, 1.0 mol % Pd, AcOH/MeCN 1:1, 100 °C.

2a for the oxidation of benzene resulted in a significantly enhanced reaction rate compared to the best catalysts reported to date for this transformation (Pd(OAc)₂)₁₇,₁₈ or Pd(OAc)₂/bpy 2:1₁₈. Similarly enhanced turnover frequencies were obtained in the C–H acetoxylation of naphthalene, 1,2-dichlorobenzene, chlorobenzene, bromobenzene, ethylbenzoate, and α,α,α-trifluorotoluene using Pd(OAc)₂/2a (for full details, see the Supporting Information). These initial results show that ligand 2a can be used to generate robust, highly active palladium C–H oxidation catalysts.

In conclusion, the application of cationic pyridinium substituted ligands of general structure 2 for Group 10 C–H functionalization catalysis has been described. Both platinum and palladium complexes of these ligands display high catalytic activity for arene H/D exchange; furthermore, the combination of Pd(OAc)₂/2a shows enhanced activity for arene acetoxylation, compared with the best previously reported catalysts.¹⁷,₁₈ Further applications of late transition metal complexes of 2a and 2b in C–H functionalization reactions are currently underway in our laboratory.

Received: April 20, 2010
Revised: June 1, 2010
Published online: July 15, 2010

Keywords: C–H activation · H/D exchange · ligand design · oxidation · platinum

[8] For example, the Hammett σₚₚ value for NMe₃⁺ is 0.96.
[11] All reported TONs and TOFs are corrected for the background H/D exchange reaction of AgCl, which is formed as a by-product under the reaction conditions.
[12] For TONs obtained after 2 h and 24 h at 2, 1, 0.5, 0.25, and 0.1 mol % catalyst loading (3a), see the Supporting Information.