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Facile Arene C−H Bond Activation and Alkane Dehydrogenation with Anionic $LPt^{II}Me_2^-$ in Hydrocarbon−Water Systems (L = Dimethyldi(2-pyridyl)borate)

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Alkane CH bond activation with Pt^{II} complexes (Shilov chemistry[1]) is a rapidly developing, practically important, and challenging area of current research.[2−5] Despite the fact that the original Shilov systems included water as a solvent,[1] much less coordinating organic solvents[3,5] ranging from neat hydrocarbons[6] to trifluoroethanol (TFE)[7] were used later. Important reasons for this was that formation of Pt^{II} alkane complexes (eq 1-a), suggested key intermediates in C−H bond cleavage,[8] was inhibited dramatically by water[7] and by products of alkane functionalization, such as alcohols or ethers (eq 1-b):[9]

$$\text{(a)}\quad L'Pt^{II}(RH) \xleftarrow[\text{- LG}]{\text{RH}} L'Pt^{II}(LG) \xrightarrow[\text{- LG}]{\text{solv}} L'Pt^{II}(solv) \quad \text{(b)} \qquad (1)$$

$$\text{solv} = H_2O,\ \text{TFE},\ \text{MeOH},\ Me_2O \qquad \text{LG} = \text{solv},\ R'H$$

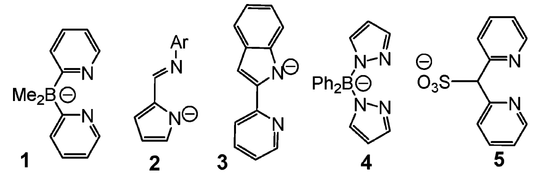
At the same time, subsequent functionalization of organoplatinum intermediates resulting from hydrocarbon activation may require more polar media, including water (solv = H_2O).[1−2,4,10]

A plausible solution to the problem could be the use of relatively *lipophilic* $L'Pt^{II}$ in *biphasic hydrocarbon−water systems* which might favor the RH over H_2O competition by extracting more hydrophobic RH−Pt-derived species into the organic phase[11] and/or to use $L'Pt^{II}(H_2O)$ species prone to more facile dissociation of the aqua ligand. In the course of our studies of anionic dipyridine ligands,[10,11] in order to develop water-tolerant systems for alkane functionalization, we chose to explore Pt complexes of the anionic dimethyl dipyridylborate ligand, dp-BMe_2^-,[12] **1** (Scheme 1). This choice was based, in part, on a number of recent reports[3,5,11,13−15] documenting CH bond activation with $Pt^{II}Me$ complexes supported by other anionic NN donors,[3,5] including **2**,[13] **3**,[14] **4**,[15] and **5**.[11] Some of these systems showed tolerance of few equivalents of water.[8a] An important argument to study lipophilic Pt complexes derived from **1** came from our DFT modeling studies. The calculated standard Gibbs energy of dissociation of the aqua ligand from the plausible $LPt^{II}Me(OH_2)$ intermediate, 13.4 kcal/mol, was lower than 15.3 kcal/mol for *cis*-$PtCl_2(OH_2)_2$, the species responsible for methane activation in neat water in the Shilov system.[1]

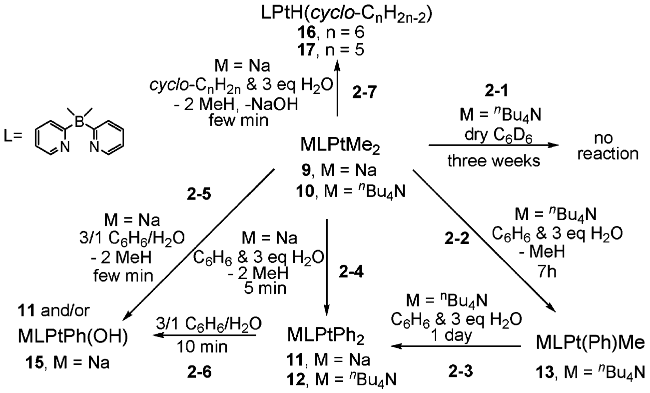
In this paper, we report facile stoichiometric arene and alkane CH bond activation with ionic dipyridylborato Pt^{II} complexes $MLPt^{II}Me_2$ (M = Na, $^nBu_4N$; Scheme 2), which occurs in the mono- and biphasic hydrocarbon−water systems. Interestingly, the sodium cation dramatically accelerated the rate of these reactions.

Anionic ligand **1** in a form of sodium salt NaL, **7**, was prepared by reacting hydrogen dimethyldi(2-pyridyl)borate[12] (**6**) with an excess of sodium hydride in dry THF. Subsequent metathesis of **7** with $^nBuN_4Br$ afforded the tetra-*n*-butylammonium analogue $^nBuN_4L$, **8**. Corresponding dimethylplatinum(II) derivatives $MLPtMe_2$, **9** (M = Na) and **10** (M = $^nBu_4N$), were synthesized using a ligand exchange reaction between **7** or **8** and $Pt_2Me_4(\mu\text{-}SMe_2)_2$ in dry THF and were fully characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Remarkably, when benzene, which was not dried carefully enough, was used instead of THF in the attempted synthesis of **9**, a reaction occurred which produced along with free Me_2S a solid, sparingly soluble in PhH, which turned out to be an analytically pure diphenyl complex $NaLPtPh_2$, **11** (12 h, 88% isolated yield). In contrast, no phenyl complexes formed after 12 h with the same batch of benzene when the $^nBu_4N$ analogue **8** was used instead. The important role of water in this unusually facile cation-dependent "double" CH activation of benzene[14,15] with the anticipated reaction product, complex **9**, was revealed in separate experiments.

Scheme 1



Scheme 2



We found that complex **10** does not react with benzene *dried* over the Na benzophenone adduct even after 3 weeks at room temperature (Scheme 2-1). In contrast, when dry benzene was combined with **10** and 3 equiv of water to produce a biphasic system, a slow reaction occurred leading in 1 day to the diphenyl complex **12** in >90% isolated yield (Scheme 2-2 and 2-3). The identity of **12** was confirmed by X-ray diffraction (Figure 1). Formation of $^nBu_4NLPtPh(Me)$, **13**, in high yield, was evident after the first 7 h of the reaction (Scheme 2-2). Most remarkably, reaction between the sodium analogue, $NaLPtMe_2$, benzene, and 2 equiv of H_2O was complete in less than 5 min to produce **11** (90% isolated yield, Scheme 2-4). Four isotopologues CH_nD_{4-n} ($n = 1-4$) were observed in the 10:8:7:7 ratio when C_6D_6/D_2O was used instead. The effect of the Na^+ cation on the reactivity of $LPtMe_2^-$ was confirmed in experiments with $^nBu_4NLPtMe_2$, wet benzene, and an additive of $NaBAr^F_4$, sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, a good source of "naked" electrophilic Na^+.[17] An initially slow reaction could be brought to completion virtually immediately upon addition of 0.5 equiv of $NaBAr^F_4$. Further experiments showed that the fast reaction between **9**, PhH, and H_2O occurred in the *organic phase*.

Benzene saturated with water reacted with a solution of **9** in PhH instantaneously to cleanly produce complex **11**. Thus, the

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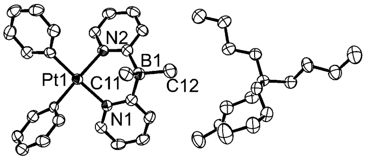


Figure 1. ORTEP drawings (50% probability ellipsoids) of complex **12**. Hydrogen atoms are omitted for clarity.

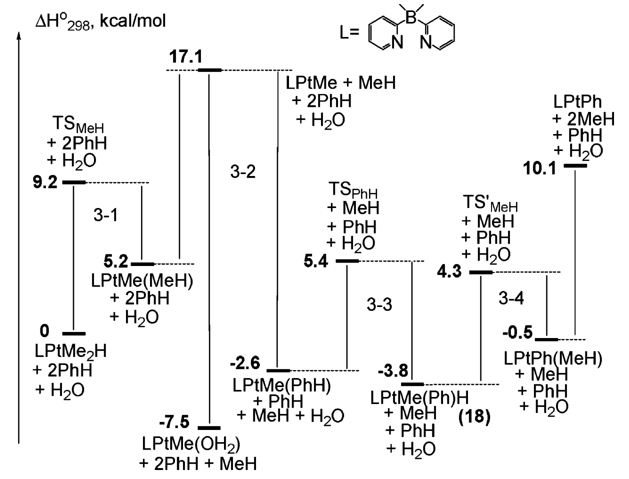
homogeneous reaction between $LPtMe_2^-$ and benzene could be *catalyzed* with even trace amounts of water, whereas the Na^+ ions dramatically enhanced the catalytic effect. Similar to benzene, clean CH bond activation with $NaLPtMe_2$ in the presence of 3 equiv of water to form $NaLPtAr_2$ could be achieved with *para*-difluorobenzene (Ar = 2,5-$F_2C_6H_3$, **14**, 92% isolated yield).

Importantly, $NaLPtMe_2$ was also shown to carry out CH bond activation in the presence of *larger amounts* of H_2O, in biphasic 3/1 benzene/water systems. The reaction was complete in less than 2 min, but upon removal of all volatiles under vacuum, the solid residue was found to be a mixture of diphenyl complex **11** (80% yield) and a hydroxo phenyl complex NaLPtPh(OH), **15** (15%) (Scheme 2-5). Longer reaction times, 10−12 min, led to the disappearance of the *kinetic* product **11** and formation of **15** exclusively (>90%). The intermediacy of **11** was proven by reacting a pure sample of this complex with a 3/1 PhH/H_2O mixture which produced **15** in >90% NMR yield after 10 min (Scheme 2-6). Interestingly, **11** was stable in wet C_6D_6 or in pure D_2O for at least a few days, though showing complete H/D exchange between the PtPh fragments and D_2O in both cases after <15 h.

High reactivity of **9** toward arenes prompted us to test it in alkane CH bond cleavage. When 3 equiv of water was added to a stirred suspension of **9** in cyclohexane, a vigorous gas evolution occurred at the water/cyclohexane interface. After removal of the solvent under vacuum and extraction of the strongly alkaline residue with cyclohexane, hydrido cyclohexene complex LPtH(*cyclo*-C_6H_{10}), **16**, was isolated in 42% yield (Scheme 2-7). Under the same conditions, cyclopentane could be also dehydrogenated to produce LPtH(*cyclo*-C_5H_8), **17**, in 33% isolated yield. We suggest that poor solubility of **9** in alkanes might be responsible for low yields. Finally, in 2:1 alkane:water mixtures, both substrates reacted with **9** to produce LPtH(olefin) complexes in essentially the same yields as with 3 equiv of water. Dehydrogenation of various alkanes with $Pt^{IV}R_2H$ and $Pt^{IV}Me_3$ complexes is well established[18] but, to the best of our knowledge, was never observed in hydrocarbon−water systems.

The mechanism of the reaction between complex **9** and hydrocarbons might involve protonation of anionic $LPt^{II}Me_2^-$ with H_2O to form a very reactive *lipophilic* $LPt^{IV}Me_2H$ which could be efficiently extracted into the organic phase.[11] In water-poor systems, the Na^+ ion could coordinate few equivalents of H_2O, so suppressing hydrolysis of Pt−C bonds, *enhancing acidity* of H_2O, and thus accelerating formation of $LPt^{IV}Me_2H$. According to our DFT calculations,[19] the CH reductive coupling of $LPt^{IV}Me_2H$ is facile (Scheme 3-1). Considering the MeH ligand in the LPtMe(MeH) intermediate as a good leaving group, we suggest that MeH for PhH (Scheme 3-2) and MeH for H_2O substitution has similar activation barriers, so that PhH can win a kinetic competition with H_2O for Pt^{II} in the *organic* phase, where the [PhH]/[H_2O] ratio is high. Subsequent benzene CH bond oxidative cleavage might lead to $LPt^{IV}Ph(Me)H$, **18** (Scheme 3-3). **18** could lose H^+ in a reaction with OH^-, producing $LPtPh(Me)^-$, eliminate methane (Scheme 3-4), or react with the second PhH and form $LPtPh_2^-$ in a similar reaction sequence.[19] Similar energies of TS_{PhH} and TS'_{MeH} are consistent with the observed multiple deuterium incorporation in the methane liberated in reaction between **9** and C_6D_6 and involving **18**. Finally, the Na^+ ion could enhance acidity of water in the organic phase and accelerate formation of $LPtR_2H$ in water-rich biphasic systems, too, since both **9** and **11** are benzene-soluble. The presence of large amounts of water could favor transformation of **11** to the thermodynamic product **15**.

Scheme 3



To the best of our knowledge, a combination of high basicity of the $Pt^{II}Me_2$ fragment,[20] high reactivity of the related Pt^{II} transients toward CH bonds, and tolerance of water is currently the unique feature of the system presented here. In summary, Pt^{II} dipyridine complexes can be electronically tuned for facile alkane and arene CH bond activation in hydrocarbon−water systems.

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Supporting Information Available: Experimental and computational details, additional discussion, and CIF file for **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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