

C–H Bond Activation by Air-Stable [(diimine)M^{II}(μ₂-OH)]₂²⁺ Dimers (M = Pd, Pt)

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Selective C–H bond functionalization is a potentially valuable approach for synthesis in areas ranging from fuels and commodity chemicals to pharmaceuticals.¹ C–H activation studies in our laboratory have focused on models of the Shilov system,² particularly methylplatinum cations [(diimine)Pt^{II}(Me)(solv)]⁺ (**2**, diimine = ArN=C(Me)–C(Me)=NAr; solv = 2,2,2-trifluoroethanol (TFE), H₂O).³ These cations are able to activate a variety of R–H bonds to form [(diimine)Pt^{II}(R)(solv)]⁺ complexes (**3**), as shown in Scheme 1, because the H can be removed as methane.⁴ Under some conditions double protonolysis of **1a** generates dicationic platinum(II) complex **4a**, which can activate certain C–H bonds: those that are part of a benzylic or allylic system, or can otherwise form a chelate product (illustrated for the allylic case in Scheme 1).⁵

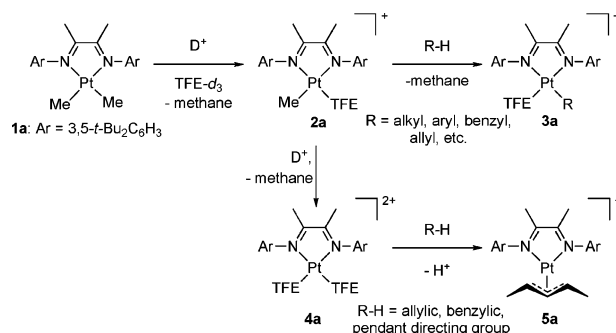
These systems are limited because productive catalytic functionalization, as in the original Shilov system, requires activation by a metal complex that does not include a sacrificial organic group. An alternative, non-organometallic route to complexes of the general form [(diimine)M(solv)₂]²⁺ involves metathesis of [(diimine)MCl₂] complexes with silver salts (in the presence of ~1% water), which leads to the formation of dimeric bis(hydroxo)-bridged complexes for both palladium⁶ and platinum.⁷ No C–H activation reactions have been reported for these species, and in some oxidative functionalization schemes such dimers appear to be the thermodynamic “final resting places”.⁸ As water will usually be a byproduct of oxidative functionalization, aquo- or hydroxo-ligated complexes must not be dead ends.

We here report that the air- and water-tolerant dimeric hydroxy-bridged dimers [(diimine)M(OH)]₂²⁺ (M = Pt, Pd), prepared and used without the intermediacy of any M–Me bond, are not necessarily resting states. In fact, they can effect not only stoichiometric activation of a variety of C–H bonds, but also catalytic conversion of cyclohexene to benzene, using dioxygen as the terminal oxidant, when the metal is palladium.

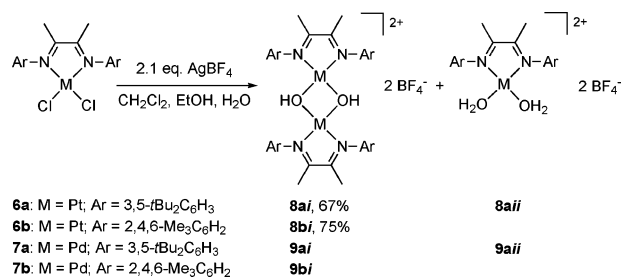
Metathesis reactions of [(diimine)MCl₂] complexes **6** (M = Pt) and **7** (M = Pd) proceed as shown in Scheme 2. For platinum with the diimine ligands Ar = 3,5-*t*-Bu₂C₆H₃ (**6a**) or 2,4,6-Me₃C₆H₂ (**6b**) mixtures of dimeric hydroxo-bridged (*i*) and monomeric bis(aquo) (*ii*) dications are formed initially, but the dimeric forms can be isolated cleanly.⁹ In the case of palladium, the dimers **9a*i*** and **9b*i*** could be cleanly isolated in low yield, while the monomeric bis(aquo)dication **9a*ii*** was synthesized following a literature procedure.⁶ **8a*i*** and **8a*ii*** equilibrate slowly in the presence of added aqueous HBF₄ (Scheme 3), as demonstrated by the dependence of speciation on [H⁺] and temperature (*K*₁ = 1.33(14) × 10³ M^{−1} at 80 °C; Δ*H*° = 17(1) kcal/mol and Δ*S*° = 63(4) eu from 20 to 80 °C).¹⁰

Platinum dimer **8a*i*** reacts with cyclohexene in the presence of acid (delivered as BF₃–TFE-*d*₃, HBF₄ (aq), or **8a*ii***) to yield

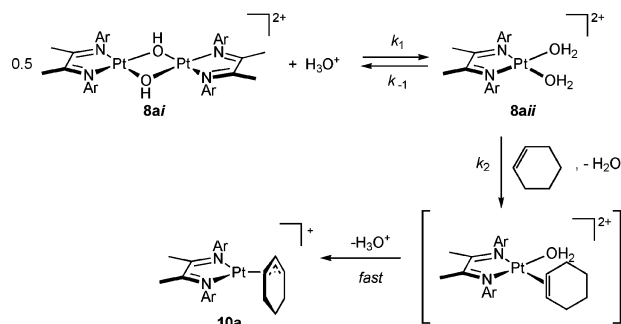
Scheme 1



Scheme 2



Scheme 3



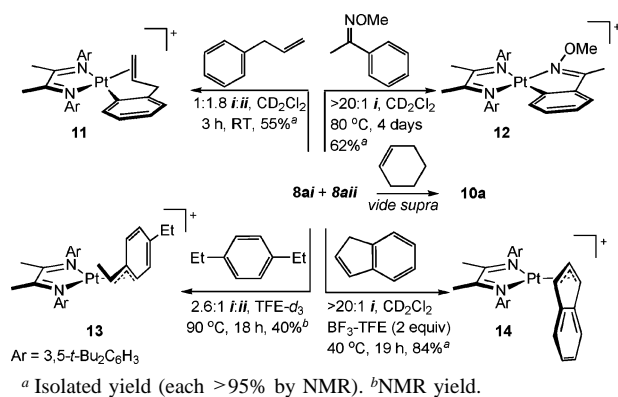
cyclohexenylplatinum(II) complex **10a**;⁹ the reaction is very slow in the absence of added acid. The proposed mechanism for this transformation, involving conversion of **8a*i*** to **8a*ii***, coordination of cyclohexene at a comparable rate, and fast conversion of the cyclohexene adduct to **10a** with the loss of H₃O⁺, is shown in Scheme 3. The kinetic data for a series of reactions with varying [HBF₄] and [cyclohexene] fit the predicted behavior for this system of consecutive (pseudo) first-order reactions, with the first step being first-order in [HBF₄] and the second in [cyclohexene], as expected.¹⁰ Surprisingly, the second step is also first-order in [HBF₄]; this may suggest that general-acid catalysis is needed to facilitate displacement of coordinated water by cyclohexene.¹¹

8a (generally used as a mixture of **8a*i*** and **8a*ii***) activates a variety of C–H bonds, subject to the apparent requirement that a multidentate ligand can be thus produced (Scheme 4). Substrates

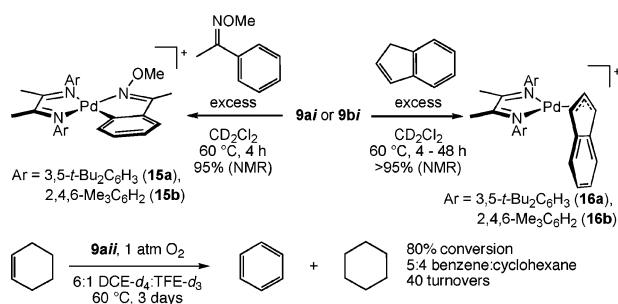
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Scheme 4



Scheme 5



bearing coordinative directing groups undergo cyclometallation, giving the allylbenzene and aryl oxime adducts **11** and **12** in high yield.⁹ Allylic and benzylic C–H bonds are activated to give η^3 platinum species: **10** and **14** are formed quantitatively by NMR, and **13** is formed in 40% yield (NMR). In contrast, neither benzene nor cyclohexene reacts detectably with **8a** in trifluoroethanol-*d*₃ solution after 20 h at 90 °C. The reaction of **8a** with indene to give **14** proceeds smoothly in a variety of solvents, including dichloromethane-*d*₂, trifluoroethanol-*d*₃, or benzene-*d*₆. Although the presence of water retards the rate of reaction, only minimal precautions are needed to exclude air or water: **14** can be formed quantitatively from a dichloromethane-*d*₂ solution prepared in air on the bench top.

The analogous palladium(II) complexes **9a** and **9b** also exhibit C–H activation reactivity: cyclometalates **15a** and **15b** and indenyl complexes **16a** and **16b** are obtained in good yield (Scheme 5).⁹ With palladium catalytic reactions can also be observed: solutions containing a mixture of **9ai** and **9a_{ii}**, clean **9a_{ii}**, or **9bi** all convert cyclohexene to benzene and cyclohexane, with up to forty turnovers (**9a_{ii}**, 6:1 dichloroethane-*d*₄/trifluoroethanol-*d*₃, 1 atm O₂, 60 °C, 3 days).¹⁰ The benzene/cyclohexane ratio is influenced by reaction conditions, particularly oxygen pressure, mixing, and the size and shape of the reaction vessel. Under certain conditions (2 atm O₂ or thorough mixing), cyclohexane formation can be stopped completely.¹⁰ When the reaction is performed under argon, the ratio of benzene to cyclohexane is 1:2, which is consistent with disproportionation being the sole process in the absence of oxygen.

We suggest that in both the presence and absence of oxygen, the reaction involves the C–H activation of cyclohexene by the palladium complex, followed by dehydrogenation; the resulting Pd–H species can be recycled either by hydrogenation of additional cyclohexene (disproportionation) or oxidation by dioxygen. Formation of water is indicated by a broad peak in the ¹H NMR spectrum at δ 1.75 ppm in C₂D₄Cl₂, which corresponds to averaged signals of free and coordinated water (which are in rapid exchange). This signal is greatly diminished and shifted when D₂O is added to the

reaction mixture. Moreover, the consumption of a stoichiometric amount of dioxygen (measured by Toepler pump) corresponding to that needed for catalytic oxidation of cyclohexene to benzene was observed.¹⁰

Disproportionation of cyclohexene effected by simple palladium salts has been previously reported, and proposed to involve heterogeneous catalysis by precipitated metallic palladium(0);¹² there are few examples of homogeneously catalyzed oxidative dehydrogenation.¹³ To confirm that the oxidation described in this work was homogeneous, the filtrate obtained from the reaction mixture (at various stages of the reaction) was found to be catalytically active, whereas the precipitated solid was not; furthermore the reaction was successfully performed in the presence of a drop of elemental mercury.¹⁰

Work toward increasing mechanistic understanding and expanding the scope of these stoichiometric and catalytic C–H activation processes involving bis(aquo) complexes is ongoing.

Acknowledgment. This work was supported by the BP MC² program, the NIH (NRSA fellowship GM075691 to T.J.W.), and Caltech (Switzer fellowship to P.F.O.). We thank V. Rostovtsev, L. Henling, and M. Day for assistance with X-ray crystallography.

Supporting Information Available: Kinetics analysis, van't Hoff data, experimental details, and characterization data of all new compounds (including X-ray information for **8ai** and **12**).¹⁴ This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Experimental details and more extensive discussion are provided in the Supporting Information.
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JA076740Q