Reactions of [PhI(pyridine)$_2$]$^{2+}$ with Model Pd and Pt II/IV Redox Couples

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S *Supporting Information*

ABSTRACT: The results of the reactions of the dicationic iodine(III) family of oxidants [PhI(pyridine)$_2$]$^{2+}$ with model Pd(II) and Pt(II) complexes are described. Depending on the specific reaction pairs, a variety of outcomes are observed. For palladium, Pd(IV) complexes cannot be observed but are implicated in C−C and C−N bond formation for Pd(II) starting materials based on phenylpyridine and 2,2-bipyridine, respectively. Theoretical comparisons with similar processes for −Cl and −OAc rather than pyridine indicate that these provide greater thermodynamic stability, and our results here show that they also give greater kinetic stability (the failure of MP2 methods for these systems is quite dramatic). In contrast, oxidation and delivery of the pyridine ligands gives dicationic Pt(IV) complexes that may be isolated and structurally characterized.
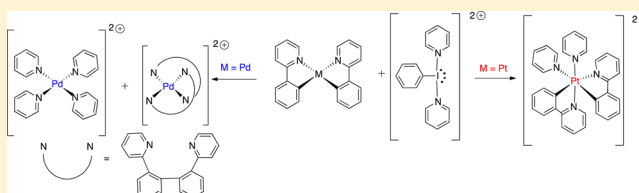
INTRODUCTION

The oxidation of platinum group metals (M = Ni, Pd, Pt) to the +3 or +4 oxidation state from M(II) using iodine(III) reagents is a topic of current interest in inorganic, organometallic, and organic chemistry.[1−5] In particular, the groups of Sanford and Ritter have used this strategy to isolate, access, or implicate Ni, Pd, and Pt in the +4 oxidation state in both catalytic and stoichiometric transformations involving C−C,[6−9] C−Cl,[10−14] C−F,[15−18] C−N,[19,20] and C−O[9,21−29] bond formation. The iodine(III) reagent most commonly has a Ph−I(L)$_2$ motif (L = anionic group or neutral ligand), and in this form I(III) acts both as a two-electron oxidant and as a delivery agent for its ligands or groups. In catalytic systems operating with a +II/+IV redox manifold (+III has also been observed/implicated in some systems),[10,21,30−32] it is typical for the anionic group from the initial PhI(L)$_2$ iodine complex to be incorporated into an organic product by subsequent reductive elimination from the metal. In the reactions of PhCl$_2$ and PhI(OAc)$_2$ with bis(phenylpyridine)palladium(II) (**1Pd**), the Pd(IV) complexes **2Cl** and **2OAc**, respectively, may be isolated and characterized (Scheme 1).[9,14] In these cases, however, the Pd(IV) complex is a kinetic product; exposure to elevated temperatures results in reductive elimination reactions with the formation of C−C or C−X bonds (X = Cl, O).

Our group is particularly interested in the dicationic [PhI(L)$_2$]$^{2+}$ reagents, originally synthesized by Weiss[33] and later reinvestigated by Zhdankin,[34] where L = pyridine (**3H**) or 4-dimethylaminopyridine (**3NMe$_2$**). Previously we structurally characterized these complexes and demonstrated that they can be considered coordination compounds; they are stronger oxidizing agents than the commonly used PhI(OAc)$_2$ reagent, although they are weaker than the nonisolable PhI(OTf)$_2$ precursor.[35,36]
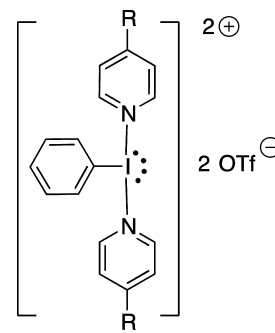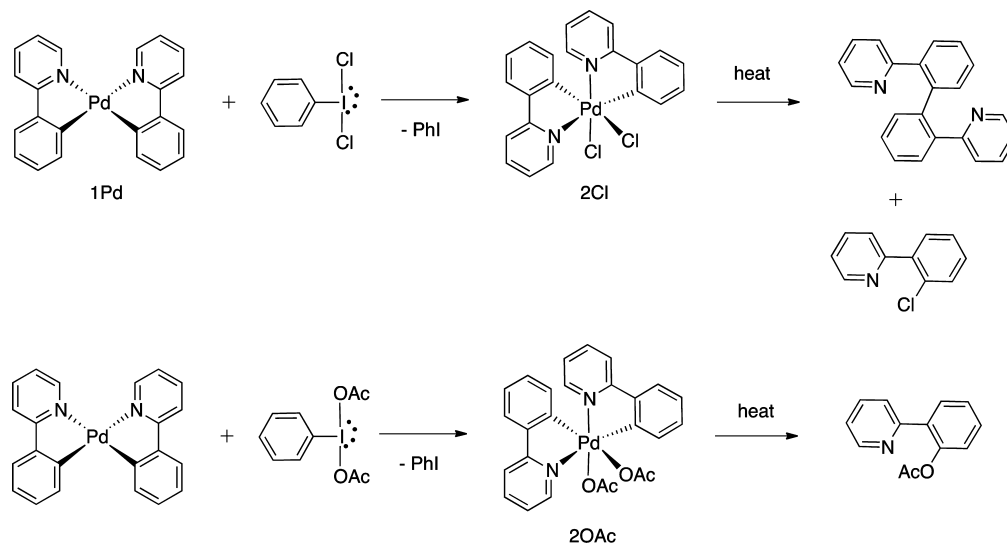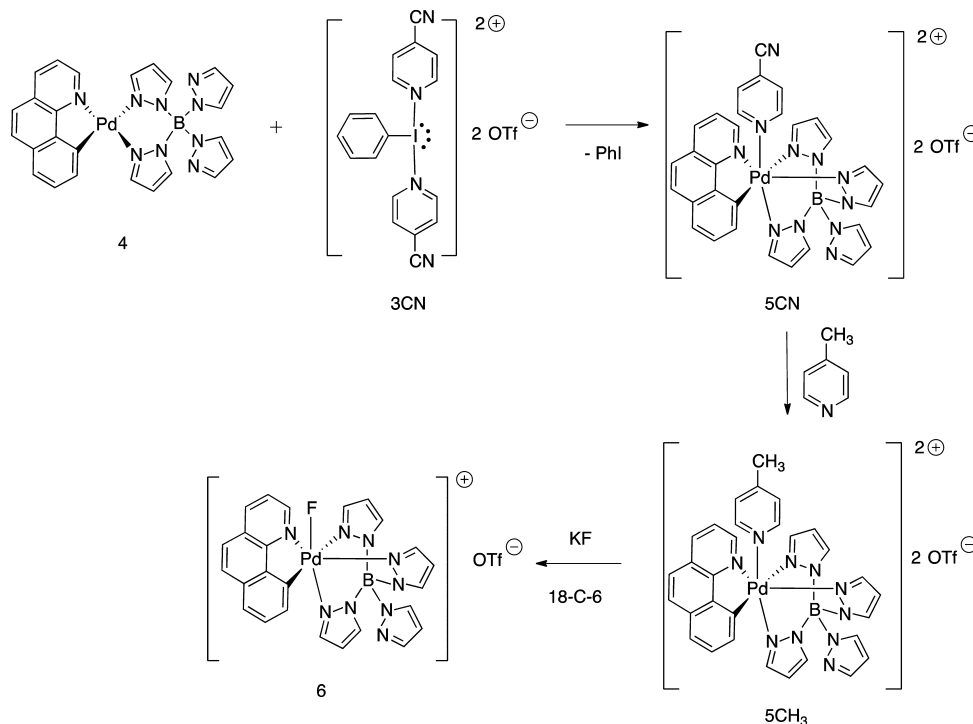
3R; R = H, -NMe$_2$

In a high-profile report, Ritter[16] demonstrated the use of one of these dicationic I(III) reagents, **3CN**, in generating the high-oxidation-state Pd(IV) compound **5CN** from the Pd(II) precursor **4**, where the delivered ligand can be easily displaced by an anionic fragment of interest (Scheme 2). In this case, F$^-$ was used to displace the pyridine ligand from **5CH$_3$** to give **6**, which was followed by a reductive elimination and C−F bond formation to afford a targeted organic compound (using ^{18}F for diagnostic imaging purposes). A subsequent study by Ritter and co-workers found similar functionality using Ni in place of Pd,[17] which suggests that the ability of I(III) reagents to deliver ligands may be more widely applicable.

We became interested in the scope of this strategy and the possibility of using the delivery of neutral ligands to isolate high-oxidation-state dicationic Pd(IV) and Pt(IV) complexes. Here we report the findings from our combined experimental and theoretical study of the oxidations of the model Pd/Pt II/
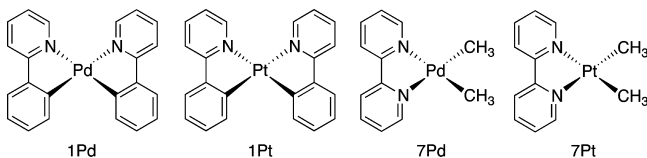
Scheme 1. Synthesis of the Isolable Pd(IV) Compounds 2Cl and 2OAc and Their Organic Thermal Decomposition Products

Scheme 2. Use of 3CN To Generate Pd(IV) Complex 5CN and Ultimate Displacement of the Pyridine Ligand by F⁻ To Give 6

IV redox systems **1M** and **7M** (M = Pd, Pt) with pyridine- and 4-DMAP-ligated I(III) dications **3R** (R = H, NMe₂).

■ RESULTS AND DISCUSSION

Reactions of Ligated I(III) Dications 3R with 1M (M = Pd, Pt). *1Pd*. Compounds **1Pd** and **3NMe₂** were combined in a 1:1 stoichiometric ratio in a CH₃CN solution, and the mixture was allowed to stir for 5 min. The solvent was removed in

vacuo, and the residue was then dissolved in CH_2Cl_2 and precipitated with Et_2O. The solids were separated and dried under vacuum, giving a beige powder. The solid was dissolved in CD_3CN for ¹H NMR analysis, which revealed a relatively clean spectrum containing resonances consistent with compounds containing phenylpyridine and 4-DMAP in a 1:1 ratio. Single crystals were obtained from a concentrated CH_3CN solution of the bulk powder held overnight at −30 °C, and subsequent X-ray diffraction studies revealed the crystals to be a square-planar Pd(II) dication bound by four 4-DMAP ligands (**11NMe₂**). Different single crystals were obtained from the initial solid via vapor diffusion of Et_2O into a CH_3CN solution of the bulk powder at room temperature. X-ray diffraction studies showed that these crystals were a different compound, **10**, wherein four phenylpyridine ligands, linked in pairs through
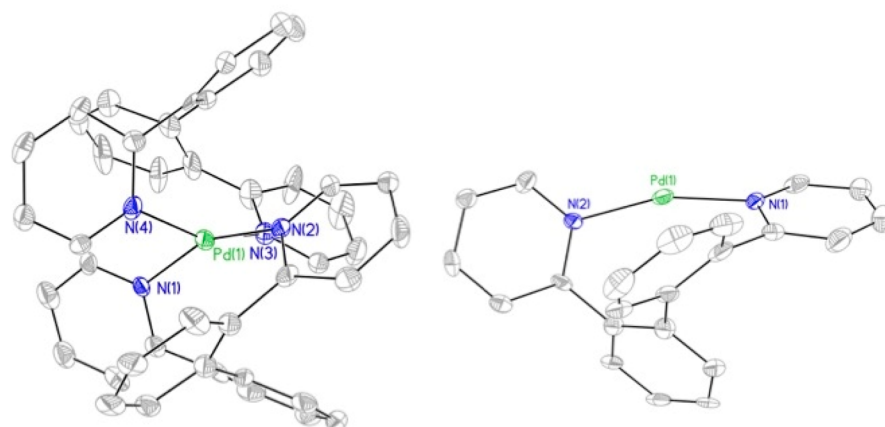
Figure 1. (left) Solid-state structure of the dication in **10**. Ellipsoids are depicted at the 40% probability level, and hydrogen atoms have been removed for clarity. The triflate anions were found to be highly disordered and were removed using the SQUEEZE function in PLATON. (right) Structure showing only one of the C−C-linked bis(phenylpyridine) ligands, highlighting the trans conformation. Selected bond distances (Å) and angles (deg): Pd(1)−N(1) 2.051(7), Pd(1)−N(2) 2.034(7), N(1)−Pd(1)−N(2) 156.8(4).

Scheme 3. Proposed Reaction Pathway to 10 and 11R
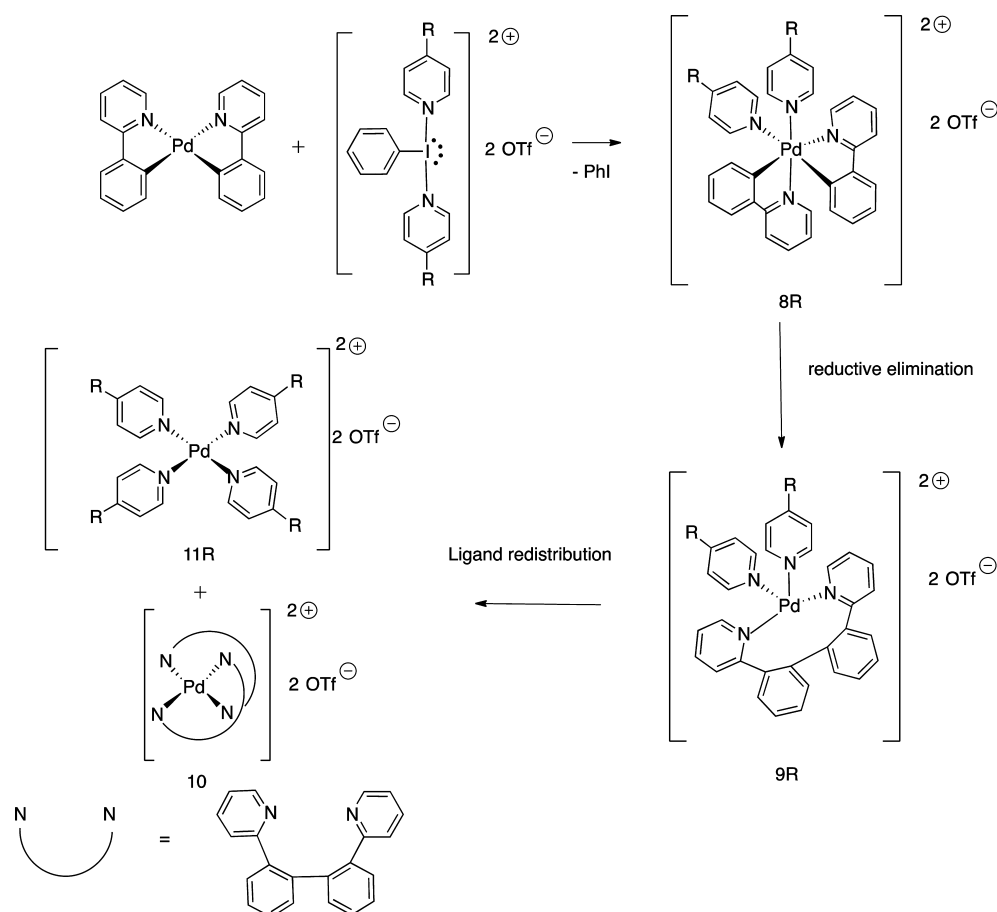
the carbons previously bound to Pd, are coordinated through the nitrogen atoms to a Pd(II) dication (Figure 1). A mass spectral analysis of a CH$_3$CN solution of the solid originally obtained gave several ions and fragments that can be attributed to the two dications observed in the X-ray analysis. We hypothesize that these products are generated as depicted in Scheme 3. Initial oxidation of **1Pd** with **3NMe$_2$** gives Pd(IV) dication **8NMe$_2$**, which undergoes reductive elimination, linking the phenylpyridines via the carbon atoms (**9NMe$_2$**).

This C−C-linked bis(phenylpyridine) has been observed as a reaction product by Sanford in related systems[14] and has remained ligated to ruthenium in another reported case.[37] Compound **9NMe$_2$** then undergoes ligand redistribution to give the two Pd(II) compounds observed, **10** and **11NMe$_2$**.

Density functional theory (DFT) results are consistent with the proposed reaction pathway, with the reductive elimination step predicted to be favorable ($\Delta G = -182$ kJ/mol using M06-2X/def2-TZVP with CH$_3$CN solvent) and the ligand

redistribution reaction also calculated to be exergonic (ΔG = −15 kJ/mol). The trend is consistent across a range of density functionals, which includes empirical dispersion (B3LYP-D3) and solvation effects (SCRF).

In the solid state, the Pd(II) center in **10** is significantly distorted from square-planar. However, the ^{1}H NMR spectrum showed no indication of paramagnetic behavior, indicating that this is likely more of a solid-state effect than a genuine distortion toward a tetrahedral Pd(II) center. The use of the iodine oxidant **3H** bearing pyridine rather than 4-DMAP ligands gave the same product distribution, as inferred from mass spectrometry studies and crystallization of **11H** from the reaction mixture. The chloride salt of **11H** has previously been reported,[38] as has the OH⁻ salt of **11NMe₂**.[39]

1Pt. A 1:1 stoichiometric mixture of **3NMe₂** and **1Pt** in CH₃CN solution was allowed to stir for 5 min. The volatiles were removed under vacuum to afford a brown solid, which was dissolved in CH₂Cl₂. Subsequent addition of Et₂O gave a beige powder. Proton NMR studies of the material dissolved in CDCl₃ revealed a spectrum dominated by two 4-DMAP methyl signals in a 1:1 ratio along with several multiplets in the aromatic region that integrated to 24 protons overall when the 4-DMAP signals were set at a total of 12. Single crystals were grown via vapor diffusion of Et₂O into a CH₂Cl₂ solution of the bulk powder, and X-ray diffraction studies revealed the target Pt(IV) dication **12NMe₂** with two 4-DMAP ligands bound in a cis configuration about an octahedral Pt(IV) center (Figure 2).
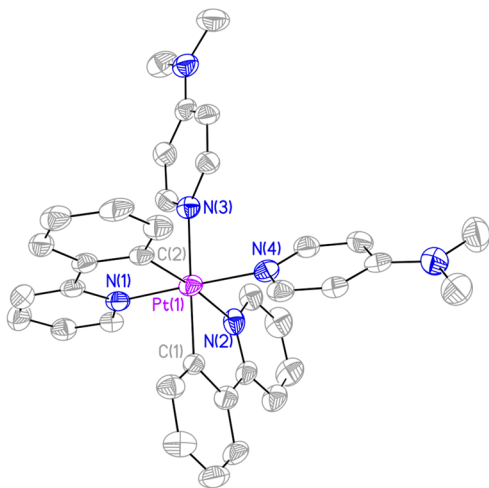

Figure 2. Solid-state structure of **12NMe₂**. Ellipsoids are depicted at the 40% probability level, and hydrogen atoms and triflate counterions have been removed for clarity. Selected bond distances (Å): Pt(1)−C(1) 2.021(7), Pt(1)−N(1) 2.032(6), Pt(1)−C(2) 2.037(6), Pt(1)−N(2) 2.126(5), Pt(1)−N(3) 2.135(6), Pt(1)−N(4) 2.079(5).

One 4-DMAP is trans to a Pt−C phenylpyridine bond and the other 4-DMAP is trans to a Pt−N phenylpyridine bond, accounting for the two different 4-DMAP species in the ^{1}H NMR spectrum. The reaction product (Scheme 4) was isolated in 58% yield. No evidence of the reductive elimination products was observed in the electrospray ionization (ESI) mass spectra of **12NMe₂**.

The DFT results for the Pt analogues of **10** and **11R** demonstrate significant functional dependence. Reductive elimination of the model compound **12H** is calculated to be favorable with M06-2X/def2-TZVP (ΔG = −55 kJ/mol; CH₃CN solvent field), but with B3LYP the reductive

elimination reaction is not favored for Pt (ΔG = +3; gas phase). Inclusion of dispersion (B3LYP-D3BJ/def2-TZVP) yields ΔG = −8 kJ/mol (gas phase). MN12-L gives results equivalent to those with B3LYP (ΔG = +19 kJ/mol with the CH₃CN solvent field), which is consistent with the experimental observations. The CH₃CN solvent effect is −11 kJ/mol with M06-2X/def2-TZVP. A definitive conclusion as to the sign of ΔG for this reaction would require high-level coupled-cluster calculations (see below), which is beyond the scope of this work.

Comparing the Pd and Pt systems, we note that the energetics of the ligand redistribution reactions are very similar for the Pd and Pt systems: ΔG differs by less than 6 kJ/mol for the Pd and Pt systems for all functionals considered. The difference between Pd and Pt arises in the energetics of the reductive elimination: ΔG for the Pt system is calculated to be less exergonic by about 100 kJ/mol (M06-2X/def2-TZVP gas phase, 120 kJ/mol; B3LYP-D3BJ/def2-TZVP gas phase, 93 kJ/mol). The sensitivity to the calculation method for the reductive elimination reaction for Pt makes a definitive assignment of the sign of this reaction difficult. It is concluded that the actual ΔG is small in magnitude, so under the right conditions, reductive elimination may well be observed.

**Reactions of Ligated I(III) Dications 3R with 7M (M = Pd, Pt). 7Pd.** The 1:1 stoichiometric reaction mixture of **3NMe₂** with **7Pd** in C₆D₆ was stirred for 6 h. The dicationic iodine starting material is insoluble in benzene, and therefore, a slurry was observed, which gradually changed in consistency over the course of the reaction and changed in color from beige to yellow. The ^{1}H NMR spectrum of a sample of the supernatant revealed a single set of resonances that could be identified as PhI by comparison with a commercial sample. The solids were isolated, and a sample was dissolved in CD₃CN, revealing signals consistent with the N-methylated pyridinium cation (as compared to a sample separately synthesized from MeI and 4-DMAP) and another set of resonances consistent with bipy, 4-DMAP, and methyl in an approximate 1:1:1 ratio by integration. Reprecipitation of the material using CH₂Cl₂/Et₂O allowed for removal of the pyridinium cation as well as other minor impurities and afforded a light-yellow power. Single crystals were grown via vapor diffusion of Et₂O into a CH₂Cl₂ solution. X-ray diffraction analysis revealed the crystals to be the triflate salt of cation **14NMe₂** containing a cationic square-planar Pd(II) center bearing the bipy ligand, a methyl group, and a 4-DMAP ligand. Related structures (with 4-methylpyridine) have been reported, and the metrical parameters require no specific comments.[40]

The product can be rationalized by an oxidation of **7Pd** to give unobserved Pd(IV) intermediate **13NMe₂**, followed by reductive elimination of the N-methylpyridinium cation (Scheme 5). This reaction represents a relatively rare example of C−N bond formation via reductive elimination from a high-oxidation-state late transition metal.[14,19,20] Use of **3H** as the oxidant gave identical results, and **13H** could be characterized crystallographically, but we were unable to isolate a bulk powder of good purity as observed by ^{1}H NMR analysis.

This Pd system gives a well-defined Pd(IV)/Pd(II) redox couple with clear, unambiguous products, which provides a handle to probe the relative thermodynamic stabilities of Pd(IV) compounds as a function of the ligand. As noted above for the Pd(II/IV) phenylpyridine system, reactions using dicationic pyridine-ligated oxidants give Pd(II) compounds, while the use of PhICl₂ or PhI(OAc)₂ gives isolable Pd(IV)

Scheme 4. Synthesis of Pt(IV) Complex 12NMe$_2$
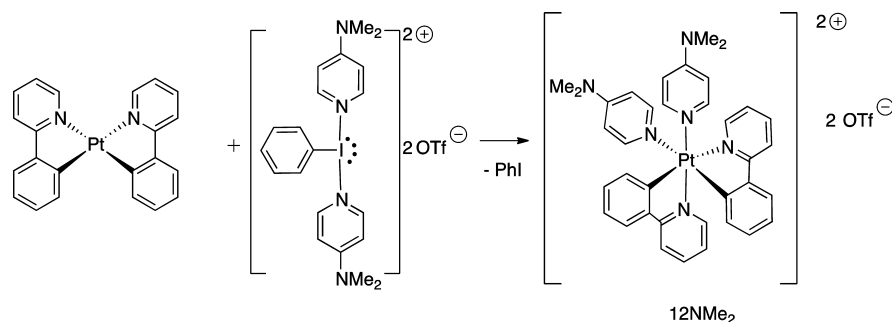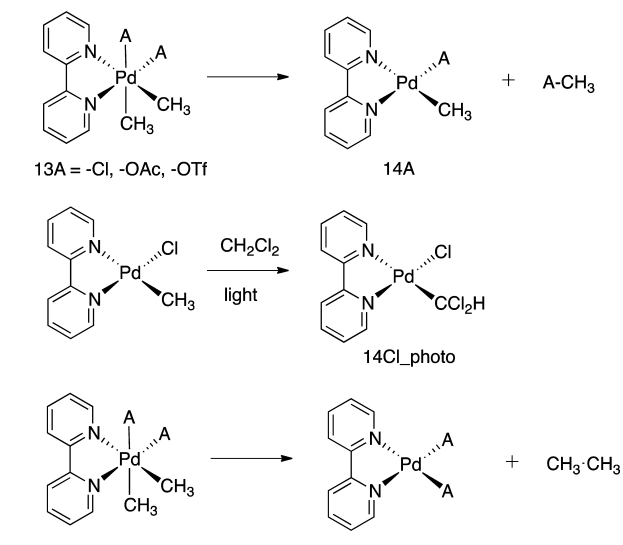

Scheme 5. Reaction of 1Pd with 3R
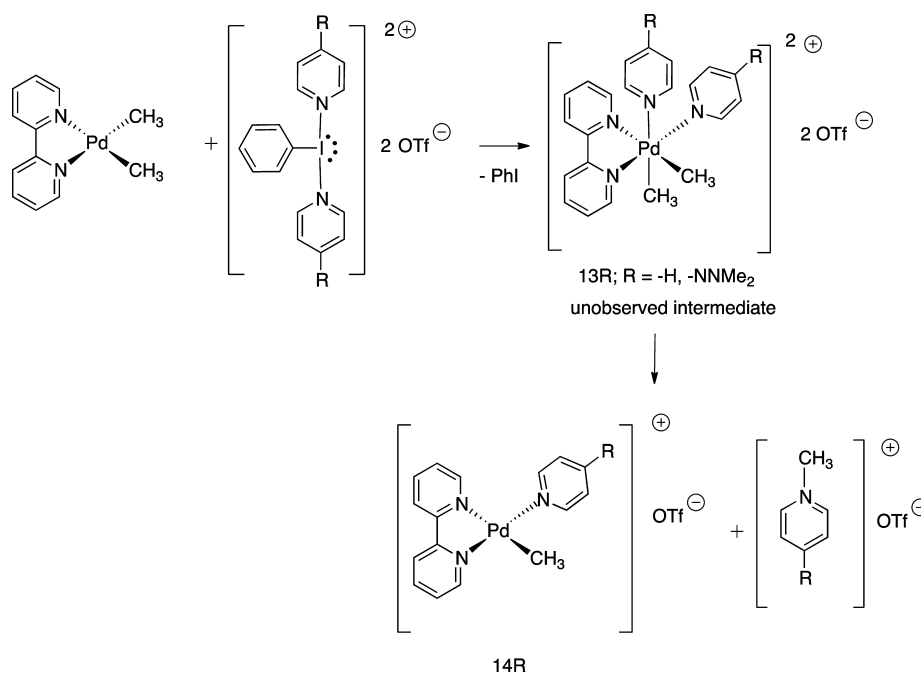
compounds, although they are kinetic rather than thermodynamic products. In the systems reported here, elimination of Me−L is a clear pathway, allowing for direct comparisons of the effect of the ligand on the thermodynamics of Pd(IV)/Pd(II) reductive elimination. Further confirmation of the process was obtained by reacting PhICl$_2$ and PhI(OAc)$_2$ with **7Pd**, which produced CH$_3$Cl and CH$_3$OAc, respectively, as observed by ^{1}H NMR analysis. However, for the reaction with PhI(OTf)$_2$, a complex mixture was observed and MeOTf could not be identified in the products. Nevertheless, the reaction with PhI(OTf)$_2$ is included in the complementary computational study for comparison. The relatively simple Pd system considered here also highlights the versatility of the Pd(IV)/Pd(II) redox couple used in conjunction with I(III) oxidants in that C−Cl, C−O, and C−N bond formation can be achieved with virtually identical reactions. Ethane elimination is a possible competing pathway in these reactions. For PhICl$_2$, no ethane elimination was observed, while for PhI(OAc)$_2$, ethane elimination competed with MeOAc elimination in a ratio of approximately 1:3. A small quantity of (bipy)Pd(OAc)$_2$, the corresponding Pd(II) ethane reductive elimination product, crystallized from a reaction mixture that was allowed to stand, as determined by a unit cell analysis.[41] For the pyridine-ligated dications, some ethane elimination was also observed when the

reaction was carried out in DMSO rather than benzene, but the stoichiometry was difficult to ascertain because of the incomplete solubility of the compounds in the reaction mixture. For the reaction with PhICl$_2$, a large quantity of crystals precipitated from the reaction mixture in CH$_2$Cl$_2$ upon standing, and X-ray studies identified this product as **14Cl_photo**, which is formed photochemically from **14Cl** upon standing in CH$_2$Cl$_2$ in ambient light on the basis of highly related compounds.[42]

DFT calculations of the energetics of these reductive elimination reactions (Scheme 6) were carried out. Here we present B3LYP-D3/def2-TZVP results, including single-point energy solvent corrections in a CH$_3$CN force field, which is important in considering reactions involving cationic species.[43] Results from other functionals (including gas-phase results) are included in the Supporting Information. The most favorable reductive elimination of Me−L is for the cationic pyridine ligands (i.e., generation of **14H** as in Scheme 5) at −139 kJ/mol. The reductive elimination of the anionic ligands from **13A** is in general less favorable, with reaction energies for elimination of Me−Cl, Me−OAc and Me−OTf of −69, −124, and −35 kJ/mol, respectively. The calculated results indicate that from the perspective of isolating Pd(IV) compounds, neutral pyridine ligands are a poor choice from a

Scheme 6. Calculated Reductive Elimination Reactions from Pd(IV) Analogues of 7Pd and Photochemical Reaction of 14Cl with CH₂Cl₂

with def2-TZVP, def2-TZVPP, def2-QZVP are within 1 kJ/mol of each other). Surprisingly, Møller–Plesset methods gave vastly different results than DFT. For example, with L = Cl (def2-TZVP basis set, CH_3CN solvent field) the ΔE values for reductive elimination are +86 kJ/mol (MP2), +421 kJ/mol (MP3), and +500 kJ/mol (MP4)! Clearly, MPn fails dramatically to model the energetics of this observed reaction. A clue to the failure of the MPn methods is evident in the significant effect of spin scaling, with MP2, SCS-MP2, and SOS-MP2 giving values of +86, +50, and +32 kJ/mol, respectively. Analogous gas-phase MP2, CCSD, and CCSD(T) calculations (def2-TZVP basis set) yield ΔE = +50, −47, and −18 kJ/mol, respectively. Here the convergence is toward a more negative value. In particular, the agreement of the B3LYP-D3 results with the CCSD(T) value provides justification for using B3LYP-D3 results in the analysis presented here.

7Pt. Reactions with **7Pt** (Scheme 7) gave a less well-defined distribution of products than those with **7Pd**. The reaction of **7Pt** with one stoichiometric equivalent of **3NMe₂** in C_6H_6 gave a yellow slurry. After 2 h the solvent was removed, and a sample of the powder was dissolved in CD_3CN. ¹H NMR analysis revealed multiple 4-DMAP-containing signals as well as multiple signals associated with Me groups bound to Pt, as ascertained from the presence of ¹⁹⁵Pt satellites. A short workup involving precipitation from CH_2Cl_2/n-hexane gave a solid with a cleaner NMR spectrum containing a single 4-DMAP-containing species as well as a Pt−Me signal with a relative ratio of approximately 6:9 for the methyl signals. Single crystals were grown via vapor diffusion of Et₂O into a concentrated CH_2Cl_2 solution, and X-ray diffraction studies revealed the compound to be the cationic Pt(IV) complex **15NMe₂** with three methyl groups and a 4-DMAP ligand bound to Pt(IV), with 2,2-bipyridine filling an octahedral coordination sphere. A related compound containing the pyridazine ligand rather than 4-DMAP has previously been reported,[45] and the metrical parameters in **15NMe₂** require no special comment.

The same experiment, but using **3H**, gave an apparently similarly complex mixture as judged by the crude proton NMR spectrum, but in this case, workup resulted in the isolation of a relatively pure compound containing only ¹H NMR resonances associated with 2,2-bipyridine and pyridine and no Pt−Me

thermodynamic viewpoint, and our observations in reactions with phenylpyridine-ligated Pd(II) complex **1Pd** indicate that they are less kinetically stable than the Cl and OAc analogues. However, the lessened thermodynamic stability of the dicationic compounds may offer future opportunities to harness increased reactivity, which is apparent in the competitive ethane elimination reactions, which are calculated to be more favorable thermodynamically for the cases involving the anionic ligands, but not for pyridine.[44] For this reaction, the reaction energies for reductive elimination of ethane are calculated to be −229, −209, −213, and −198 kJ/mol for L = pyridine, Cl, OAc, and OTf, respectively, indicating that this reaction is in general more favorable than Me−L elimination. It should be reiterated that these are thermodynamic data only, and ethane elimination was either not observed (Cl) or was a minor product for the reactions involving pyridine and acetate ligands.

Benchmarking DFT calculations indicated that the results are converged with respect to basis set (with M06-2X, the results

Scheme 7. Products of the Reaction of 3R with 7Pt As Identified by X-Ray Crystallography and Mass Spectrometry

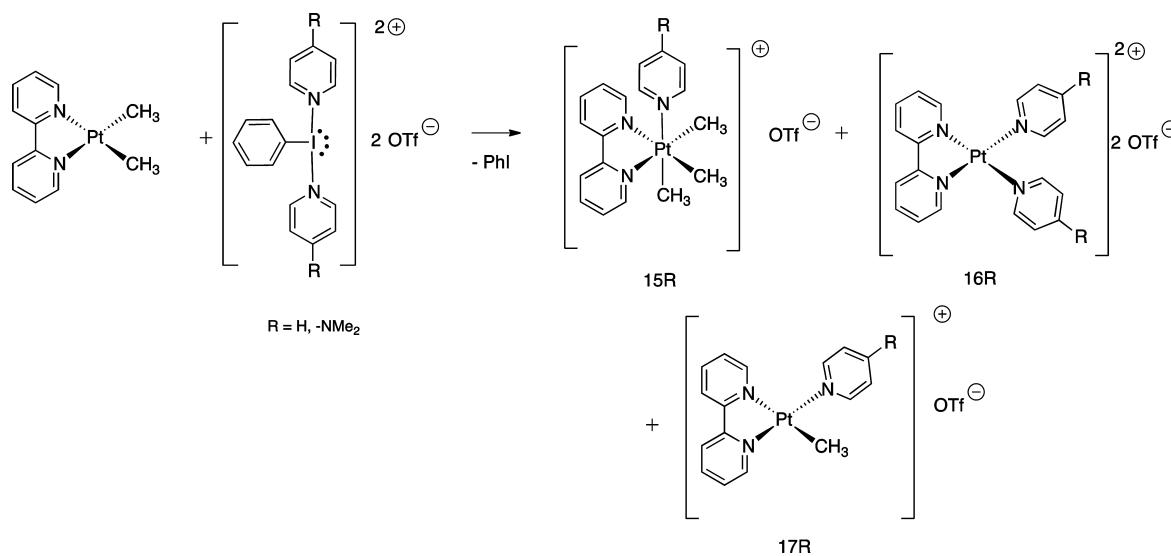**Table 1. X-ray Refinement Details for Single-Crystal X-ray Structural Determinations**

parameter	10	11H	11NMe$_2$	12NMe$_2$	14H
empirical formula	C$_{44}$H$_{32}$N$_4$Pd$_1$^{a}	C$_{22}$H$_{20}$F$_6$N$_4$O$_6$S$_2$Pd$_1$	C$_{18.5}$H$_{26}$F$_3$N$_{5.5}$O$_3$S$_1$Pd$_{0.5}$	C$_{38}$H$_{36}$F$_6$N$_6$O$_6$S$_2$Pt$_1$	C$_{17}$H$_{16}$F$_3$N$_3$O$_3$S$_1$Pd$_1$
FW (g/mol)	723.14	720.94	515.71	1045.94	505.79
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	10.742(2)	17.359(4)	11.136(2)	11.021(2)	8.245(2)
b (Å)	11.593(2)	11.059(2)	11.325(2)	13.311(3)	17.384(4)
c (Å)	18.237(4)	15.135(3)	18.711(4)	14.466(3)	13.412(3)
α (deg)	93.15(3)	90	90	92.57(3)	90
β (deg)	93.05(3)	90.08(3)	93.64(3)	105.87(3)	103.46(3)
γ (deg)	97.94(4)	90	90	104.07(3)	90
V (Å^3)	2241.7(8)	2905(1)	2354.9(8)	1965.9(7)	1869.7(7)
Z	2	4	4	2	4
D_c (mg m^{-3})	1.071	1.648	1.455	1.767	1.797
$R_1 [I > 2\sigma(I)]$	0.1137	0.0317	0.0714	0.0504	0.0582
$wR_2(F^2)$	0.2918	0.0673	0.1965	0.1227	0.1608
GOF (S)	1.070	1.127	1.052	1.097	1.212

parameter	14NMe$_2$	15NMe$_2$	16H	17H	14Cl_photo
empirical formula	C$_{19}$H$_{21}$F$_3$N$_4$O$_3$S$_1$Pd$_1$	C$_{21}$H$_{27}$F$_3$N$_4$O$_3$S$_1$Pt$_1$	C$_{22}$H$_{28}$F$_6$N$_4$O$_6$S$_2$Pt$_1$	C$_{17.25}$H$_{16.25}$Cl$_{0.75}$F$_3$N$_3$O$_3$S$_1$Pt$_1$	C$_{14.66}$H$_{12}$Cl$_4$N$_{2.66}$Pd$_{1.33}$
FW (g/mol)	548.86	667.62	807.61	624.32	509.27
crystal system	monoclinic	monoclinic	triclinic	triclinic	tetragonal
space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P4(2)/n$
a (Å)	30.970(6)	17.882(4)	8.053(2)	13.557(3)	28.064(4)
b (Å)	7.180(1)	20.815(4)	9.087(2)	14.316(3)	28.064(4)
c (Å)	19.112(4)	13.062(2)	19.727(4)	20.976(4)	6.676(1)
α (deg)	90	90	83.45(3)	89.32(3)	90
β (deg)	91.77(3)	91.92(3)	83.30(3)	78.53(3)	90
γ (deg)	90	90	64.52(3)	86.67(3)	90
V (Å^3)	4248(2)	4859(2)	1291.1(4)	3983(1)	5258(2)
Z	8	8	2	8	12
D_c (mg m^{-3})	1.716	1.825	2.077	2.082	1.930
$R_1 [I > 2\sigma(I)]$	0.0357	0.0543	0.0216	0.0522	0.0435
$wR_2(F^2)$	0.0991	0.1202	0.0524	0.1188	0.1023
GOF (S)	1.083	1.177	1.355	1.227	1.091

^{a}Two disordered triflate (CF$_3$SO$_3$$^-$) counterions were removed from the reflection data.

resonance. Single crystals were grown, and X-ray studies showed the compound to be dicationic Pt(II) complex **16H**, which has previously been structurally characterized as a [PF$_6$]$^-$ salt.[46] From the crude material obtained in this reaction, single crystals of compound **17H** were also grown, although this compound could not be isolated in a pure form. Mass spectrometry studies of the crude materials from the reactions of **7Pt** with both **3H** and **3NMe$_2$** gave masses consistent with all three Pt-containing compounds **15R–17R**, allowing us to surmise that the two reactions proceed in the same fashion. We hypothesize that these products arise from oxidative disproportionation of **7Pt** by **3R**, with possible involvement of Pt(III) species, both of which are known in related systems, followed by ligand exchange reactions.[47] Alkyl exchange reactions have also been observed by Puddephatt in other similar high-oxidation-state Pt–Me species.[48] In the context of our study, the important piece of information is that isolation of a well-defined Pt(IV) complex with no scrambling of ligands does not occur in the reaction of **7Pt** with the dicationic iodine oxidants.

CONCLUSIONS

The results presented here show that neutral pyridine ligands provide less stabilization to Pd(IV) centers than do previously reported anionic ligands such as chloride and acetate. While this is a negative in the context of isolating high-oxidation-state Pd complexes, it may be advantageous in increasing the reactivity of these systems. Pyridine delivery and the isolation of dicationic Pt(IV) compounds was found to be possible. We are currently exploring the chemistry of these compounds.

■ EXPERIMENTAL SECTION

General Considerations. All of the reactions involving **3R** were performed in a N$_2$-filled glovebox. Once the reactions were complete, none of the Pt or Pd products formed were found to be air- or moisture-sensitive, and therefore, reaction workups and characterization could be performed on the bench.

Dichloromethane, THF, CH$_3$CN, Et$_2$O, n-pentane, and n-hexane were obtained from Caledon Laboratories and dried using an Innovative Technologies solvent purification system with dual columns packed with solvent-appropriate drying agents. The dried solvents were stored under a N$_2$ atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy (CDCl$_3$ CD$_3$CN, C$_6$D$_6$) were purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH$_2$, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. Reagents were purchased from Alfa Aesar, Aldrich, or Precious Metals Online (Pd/Pt compounds) and used as received. The starting materials cis-(Et$_2$S)$_2$PdCl$_2$,[49] cis-(Et$_2$S)$_2$PtCl$_2$,[50] 2′-bromo-2-phenylpyridine,[28] **1Pd**,[51] **1Pt**,[52] **3R**,[33] **7Pd**,[53] and **7Pt**[54] were prepared using literature procedures.

Synthetic Procedures. *Reaction of 3NMe$_2$ with 1Pd To Give 10 and 11NMe$_2$.* A solution of **3NMe$_2$** (89 mg, 0.12 mmol) in CH$_3$CN

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dx.doi.org/10.1021/ic402836d | *Inorg. Chem.* 2014, 53, 1690–1698

(2 mL) was added to a solution of **1Pd** (48 mg, 0.12 mmol) in CH_3CN (2 mL), giving a pale-yellow solution. The reaction mixture was stirred at room temperature for 5 min, and then the solvent was reduced under vacuum, affording a yellow-brown oil. The yellow-brown oil was dissolved in minimal CH_2Cl_2 (0.5 mL) and added to a stirred vial of Et_2O (10 mL). The resulting pale-yellow precipitate was washed with diethyl ether (2 × 10 mL) and dried under reduced pressure to afford **10** and **11NMe$_2$** (68 mg) as an inseparable pale-yellow solid. See the Supporting Information for the ^1H NMR spectrum of mixture. ESI-MS $[M]^{n+}$: m/z 297.1 $[Pd(DMAP)_4]^{2+}$, 361.1 $[Pd(linked-PhPy)_2]^{2+}$, 621.1 $[Pd(DMAP)_3(OTf)]^+$, 871 $[Pd(linked-PhPy)_2(OTf)]^+$.

Synthesis of 12NMe$_2$. A solution of **3NMe$_2$** (45 mg, 0.06 mmol) in CH_3CN (2 mL) was added to a solution of **1Pt** (30 mg, 0.06 mmol) in CH_3CN (2 mL). The reaction mixture was stirred at room temperature for 5 min, and then the solvent was removed under vacuum, affording a pale-yellow solid. The solid was precipitated from CH_2Cl_2/Et_2O and dried under vacuum to afford **12NMe$_2$** (83 mg, 58%) as a beige powder. Mp: 175−180 °C. ^1H NMR (CDCl$_3$): δ 9.00 (d, J = 4 Hz, 1H), 8.24−7.08 (m, 18H), 6.61 (d, J = 4 Hz, 2H), 6.53 (d, J = 4 Hz, 1H), 6.51 (d, J = 4 Hz, 2H), 3.08 (s, 6H), 3.03 (s, 6H); ESI-MS $[M]^{n+}$: m/z 312.6 $[Pt(phpy)_2(DMAP)]^{2+}$, 373.6 $[Pt(phpy)_2(DMAP)_2]^{2+}$, 775.1 $[Pt(phpy)_2(DMAP)OTf]^+$, 896.2 $[Pt(phpy)_2(DMAP)_2OTf]^+$.

Synthesis of 14NMe$_2$. A solution of **3NMe$_2$** (49 mg, 0.07 mmol) in C_6H_6 (2 mL) was added to a solution of **7Pd** (19 mg, 0.07 mmol) in C_6H_6 (2 mL). The reaction mixture was stirred at room temperature for 6 h, resulting in the formation of a yellow precipitate. The precipitate was washed with C_6D_6 (2 × 5 mL) and dried under vacuum. The solid was then recrystallized from CH_2Cl_2/Et_2O and dried under vacuum to yield **14NMe$_2$** (68 mg, 65%) as a light-yellow powder. Mp: 165−170 °C. ^1H NMR (CD$_3$CN): δ 8.67 (d, J = 8 Hz, 1H), 8.34 (t, J = 7 Hz, 2H), 8.15 (m, 4H), 7.77 (m, 1H), 7.68 (m, 1H), 7.55 (m, 1H), 6.73 (d, J = 7 Hz, 2H), 3.07 (s, 6H), 0.8 (s, 3H). ESI-MS $[M]^+$: m/z 399.0 $[Pd(bipy)(DMAP)(Me)]^+$.

Reactions of 7Pd with PhICl$_2$, PhI(OTf)$_2$, and PhI(OAc)$_2$. A solution of PhICl$_2$, PhI(OTf)$_2$, or PhI(OAc)$_2$ (0.07 mmol) in C_6D_6 (1 mL) was added to a solution of **7Pd** (0.07 mmol) in C_6D_6 (1 mL), and the mixture was allowed to stir for 1 h. The mixture was then centrifuged, and the supernatant was analyzed by ^1H NMR spectroscopy.

Reactions of 7Pt with 3NMe$_2$ and 3H. A solution of **3NMe$_2$** (53 mg, 0.07 mmol) in C_6H_6 (2 mL) was added to a solution of **7Pt** (32 mg, 0.07 mmol) in C_6H_6 (2 mL). The reaction mixture was stirred at room temperature for 2 h, giving a yellow precipitate. The precipitate was washed with C_6H_6 (3 × 5 mL) and recrystallized from CH_2Cl_2/Et_2O, yielding **15NMe$_2$** (15 mg) of approximately 80% purity by ^1H NMR analysis. ^1H NMR (CD$_3$CN): δ 8.43 (t, J = 7 Hz, 2H), 8.05 (t, J = 8 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7 Hz, 2H), 6.93 (b, 2H), 6.11 (b, 2H), 2.80 (s, 6H) 1.42 (t, J_{Pt-H} = 72 Hz, 9H). ESI-MS $[M]^+$: m/z 488.1 $[Pt(bipy)(DMAP)(Me)]^+$, 518.2 $[Pt(bipy)(DMAP)(Me)_3]^+$, 744.1 $([Pt(bipy)(DMAP)(OTf)]^+$.

A solution of **3H** (49 mg, 0.07 mmol) in CH_3CN (2 mL) was added to a solution of **7Pt** (32 mg, 0.07 mmol) in CH_3CN (2 mL), giving a yellow solution. The reaction mixture was stirred at room temperature for 5 min, and then the volume was reduced under vacuum to yield a yellow solid. The solid was washed with Et_2O (2 × 5 mL) and dried under vacuum, giving **16H** as a yellow solid (12 mg). Mp: 195 °C (decomp.). ^1H NMR (CDCl$_3$): δ 8.79 (d, J = 5 Hz, 2H), 8.19 (d, J = 8 Hz, 2H), 8.18 (d, J = 8 Hz, 2H), 7.88 (d, J = 5 Hz, 4H), 7.64 (d, J = 8 Hz, 2H), 7.32 (m, 4H), 7.16 (t, J = 8 Hz, 2H). See the Supporting Information for ESI-MS analysis of the initial reaction solution.

X-ray Crystallography. Single crystals were selected under Paratone-N oil, mounted on nylon loops, and placed into a cold (172 K) stream of N_2 on an Oxford CCD diffractometer using Mo Kα radiation. Structure solution and refinement were performed using the SHELXTL software suite.[55] Structure and refinement information are found in Table 1. For compound **10**, the triflate counterions were found to be disordered to such an extent that no chemically reasonable

positions could be refined. The contribution of these triflates was removed from the reflection data using the SQUEEZE function in the PLATON software suite, as was occluded CH_2Cl_2 in **14Cl_photo**.[56] The crystals from compound **11H** were found to be a pseudomerohedral twin, and the twin law 1 0 0 0 −1 0 0 0 −1 as identified by the TWINROTMAT function in PLATON was applied. The BASF refined to 0.66917.

■ COMPUTATIONAL DETAILS

Unless otherwise noted, calculations were carried out within Gaussian 09.[57] Geometries of all structures were optimized using DFT in the absence of solvent using the B3LYP functional[58−60] with D3[61] and D3BJ[62] dispersion corrections or the M06-2X functional[63] with default convergence criteria. Employing an ultrafine grid changed the energies of reaction by about 1 kJ/mol compared with using a default grid. All of the structures were optimized with the def2-TZVP basis set and associated effective core potential.[64] Optimization with the 6-31G(d) basis set with LANL2DZ core potential yielded equivalent structures for the systems tested. Stationary points were characterized as minima by calculating the Hessian matrix analytically at the same level of theory. Thermodynamic corrections were taken from these calculations (standard state of T = 298.15 K and p = 1 atm). Cartesian coordinates of all optimized structures are included in the Supporting Information. The polarizable continuum model (PCM)[65] self-consistent reaction field (SCRF) was used to model solvent effects at the gas-phase-optimized geometries with a solvent of acetonitrile, consistent with the experimental system. Single-point MP2/def2-TZVP energies (including SCS-MP2[66] and SOS-MP2[67]) were calculated using the M06-2X/def2-TZVP-optimized geometries. Benchmarking calculations were carried out for the reactions in Scheme 6 with Cl using MP2, MP3, MP4(SDQ), CCSD, and CCSD(T). Gas-phase MP2, CCSD, and CCSD(T) calculations were carried out within Molpro.[68]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Cartesian coordinates, electronic energies, and benchmarking tables of calculated species; mass spectral and NMR data for reaction mixtures and isolated products; and X-ray data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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