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C−C Bond-Forming Reductive Elimination from a Zirconium(IV) Redox-Active Ligand Complex

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Transition-metal complexes that mediate the formation of carbon−carbon bonds provide an attractive strategy for constructing the basic carbon backbone of both molecules and extended oligomeric and polymeric structures. In particular, the C−C bond-forming reactions of group 4 metallocene complexes have received considerable attention for their direct application to Ziegler−Natta polymerization strategies.[1] Two principal mechanistic pathways for C−C bond-forming reactions are accessible to these group 4 complexes: metathesis and migratory insertion, which operate without requiring redox changes at the metal center. In contrast, mid- and late-transition-metal ions promote a wide array of stoichiometric and catalytic X−Y bond-forming reactions by coupling a reductive elimination pathway to migratory insertion and metathesis pathways. A strategy for enabling a reductive-elimination-type reaction at an early transition-metal center would provide a new mechanistic pathway of group 4 complexes to mediate stoichiometric and catalytic X−Y bond-forming reactions.

One approach to enable redox-based bond-making and bond-breaking reactions for group 4 metals is to incorporate mild redox functionality in an auxiliary ligand set.[2] Recently, we reported a new ligand platform for this purpose in the zirconium(IV) complex $\mathrm{Zr^{IV}(ap)_2(solv)_2}$ (**1a**, solv = THF; **1b**, solv = $\mathrm{Et_2O}$; $\mathrm{ap^{2-}}$ = 2,4-di-*tert*-butyl-6-*tert*-butylamidophenolate).[3] Despite a formal d^0 metal electron configuration, **1a** reacts rapidly with chlorine to afford an oxidative-addition-type product, $\mathrm{Zr^{IV}Cl_2(isq)_2}$ ($\mathrm{isq^-}$ = 2,4-di-*tert*-butyl-6-*tert*-butylimino-semiquinone), in which halogen addition occurs at the metal center with concomitant oxidation of the $\mathrm{ap^{2-}}$ ligands to the imino-semiquinone form, $\mathrm{isq^-}$. Herein we report the complementary C−C bond-forming reaction, proving that a molecular reductive elimination pathway is accessible through the cooperative redox reactivity of a d^0 metal and a redox-active ligand. The new diaryl zirconium complexes, $\mathrm{[Li(OEt_2)]_2[Zr^{IV}R_2(ap)_2]}$ (**3a**, R = Ph; **3b**, R = p-$\mathrm{MeC_6H_4}$), react rapidly upon two-electron oxidation to extrude the biaryl product and form **1a** via a putative diradical intermediate, $\mathrm{Zr^{IV}R_2(isq)_2}$ (**4**). Oxidations of the analogous dimethyl derivative, $\mathrm{[Li(OEt_2)]_2[Zr^{IV}Me_2(ap)_2]}$ (**3c**), do not lead to clean ethane reductive elimination due to competing methyl radical expulsion pathways.

Zirconium(IV) complexes **3a**−**c** were prepared by a one-pot, two-step procedure and isolated as crystalline orange and yellow solids. $\mathrm{ZrCl_4}$ reacted rapidly with 2 equiv of $\mathrm{apLi_2}$ in cold diethyl ether, affording a bright yellow solution of **1b**, which was treated immediately with 2 equiv of PhLi, p-$\mathrm{MeC_6H_4Li}$, or MeLi to afford **3a**, **3b**, or **3c**, respectively. All compounds were isolated as microcrystalline solids in analytically pure form following filtration, solvent removal, and a pentane wash.

X-ray crystallography and NMR spectroscopy were used to probe the molecular structures of **3a** and **3c** (see Figure 1 and Supporting Information). In the solid state, the zirconium centers of **3a** and **3c** adopt a six-coordinate geometry that is distorted only slightly from octahedral due to the small bite angle of the $\mathrm{ap^{2-}}$ ligands (∼76°).[4] The $\mathrm{C_{ipso}{-}Zr{-}C_{ipso}}$ angle for the phenyl ligands of **3a** is 87.30(14)°, whereas the methyl groups of **3c** are set further apart, with a C−Zr−C angle of 92.71(10)°. The lithium cations coordinate to the zirconium complex, interacting with both the $\mathrm{ap^{2-}}$ ligands and either the phenyl (**3a**) or methyl (**3c**) ligands in the solid state (see Supporting Information). In solution, ^{1}H and ^{13}C NMR spectroscopy indicate that the immediate coordination environment about zirconium is preserved. Notably, **3a** shows only one set of ^{1}H NMR resonances for the phenyl ligands (δ 6.79, 6.91, 8.46 ppm), which are shifted downfield relative to free PhLi. The symmetry of the Zr−Ph resonance set indicates that rotation about the $\mathrm{Zr{-}C_{ipso}}$ bond must be fast in solution. In **3c**, the ^{1}H NMR resonances of the methyl ligands shift to higher frequency (δ −0.45 ppm) relative to those of free MeLi (δ −2.02 ppm).

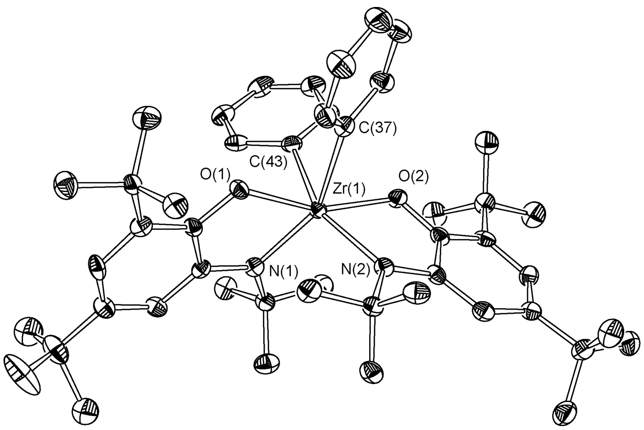

Figure 1. (a) ORTEP of the $\mathrm{[Zr^{IV}Ph_2(ap)_2]^{2-}}$ anion of **3a** with ellipsoids drawn at 50% probability. Hydrogen atoms and two $\mathrm{[Li(OEt_2)_2]^+}$ cations have been omitted for clarity.

According to Scheme 1, oxidation of **3a** in THF produces biphenyl and zirconium complex **1a**. In a typical experiment, **3a** was dissolved in dry, degassed THF and cooled to −78 °C. Solid $\mathrm{[Cp_2Fe][PF_6]}$ (2 equiv) was added to the solution, inducing an immediate color change from the bright orange of **3a** to dark greenish brown. Upon warming, the solution color lightened to orange−yellow, and GC−MS analysis provided a yield of 0.74(4) equiv of biphenyl.[5] The ^{1}H NMR spectrum of the nonvolatile products showed clean formation of ferrocene and zirconium complex **1a**.

The reaction of **3a** with ferrocenium was also monitored by UV−vis absorption spectroscopy. Treatment of a THF solution of **3a** with $\mathrm{[Cp_2Fe][PF_6]}$ at −78 °C resulted in the growth of a broad absorption centered at 740 nm. Upon warming, this absorption disappears to give a spectrum consistent with the products observed by GC−MS and NMR spectroscopy. On the basis of the low-temperature UV−vis spectrum, we propose that $\mathrm{Zr^{IV}Ph_2(isq)_2}$ (**4**), shown in Scheme 1, acts as an intermediate between **3a** and **1a**. Putative intermediate **4** is proposed by analogy to the dihalide

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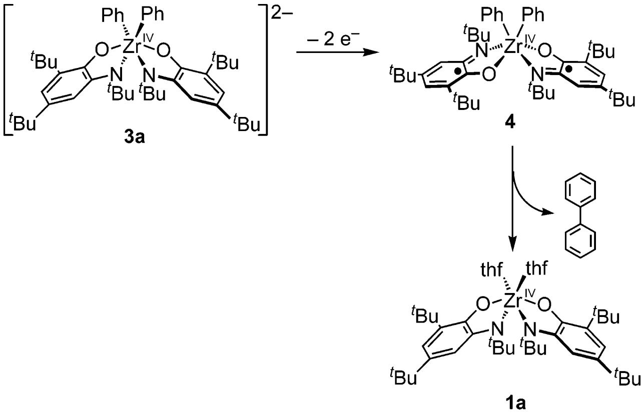
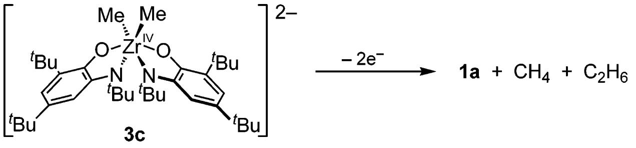
Scheme 1



complex $Zr^{IV}Cl_2(isq)_2$, which we have characterized by X-ray crystallography and UV−vis spectroscopy ($\lambda_{max} = 790$ nm).[3]

Crossover experiments conducted with diphenyl complex **3a** and ditolyl complex **3b** gave exclusive formation of the reductive elimination products. Hence, a 1:1 mixture of **3a**:**3b** reacted with $[Cp_2Fe][PF_6]$ to afford 0.61 equiv of biphenyl, 0.71 equiv of bitolyl, and less than 0.01 equiv of the crossover product PhC_6H_4Me.[5] This result indicates that the primary C−C bond-forming step must occur at a single zirconium center.

Dimethyl zirconium(IV) complex **3c** reacts with ferrocenium in THF to afford low yields of methane and ethane gas. Under the same conditions used for the oxidations of **3a** and **3b**, only 0.23 molar equiv of gas could be isolated. GC analysis showed the mixture to be 21% ethane and 79% methane. For oxidations carried out in THF-d_8, CH_4 was the only observed methane isotopologue; similarly, oxidation of **3c**-d_6 in protio THF produced only CD_3H. These results are consistent with the initial expulsion of a $CH_3^{\bullet}$ radical, followed by hydrogen atom abstraction from a chelating ap^{2-} ligand. Similar $Zr-CH_3$ bond homolysis reactivity has been observed for dimethyl and dibenzyl zirconocene complexes upon oxidation with ferrocenium oxidants.[6]



Authentic carbon−carbon bond-forming reductive elimination reactions are uncommon outside of the platinum group triad. Organometallic complexes of platinum[7] and palladium[8,9] provide key examples of C−C bond-forming reductive elimination reactivity, which is enabled by a two-electron redox change at the metal center. In d^0 transition-metal complexes, oxidatively induced C−C bond-forming reactions have been exploited in alkyne cross-coupling strategies,[10] but radical expulsion rather than reductive elimination appears to be the dominant path leading to cross-coupled products. Oxidation of group 4 metallacyclobutane complexes results in C−C bond formation and cyclopropane elimination, which has been shown to proceed with retention of configuration at the *ipso*-carbon centers.[11] Here the mechanism has been proposed to include the expulsion of a radical cation pair upon one-electron oxidation of the metallacyclobutane complex.[12,13]

To realize an authentic reductive elimination reaction, two-electron valence changes must be enabled at the metal complex. The smooth C−C bond-forming reductive elimination reactivity reported here suggests that the $[Zr^{IV}(ap)_2]$ fragment may accommodate such valence changes via putative intermediate **4**. Conversely, the recent oxidation chemistry of $(Nacnac)Ti^{III}(CH_2{}^tBu)_2$ illustrates a facile one-electron H-atom abstraction pathway in a complex that can accommodate one-electron valence changes.[14] The thermodynamics of the reductive elimination reaction shown in Scheme 1 should be controlled by the relative reduction potentials of the catecholate ligands and the eliminated X−Y product. Along these lines, we are developing the chemistry of amide and alkoxide derivatives of **3a**−**c** and derivatives of the ap^{2-} ligand in order to explore the scope and energetic landscape of this reaction.

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Supporting Information Available: Detailed experimental procedures, GC and GC−MS traces, UV−vis absorption spectra, and X-ray diffraction data for **3a** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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