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“Oxidative Addition” to a Zirconium(IV) Redox-Active Ligand Complex

Karen J. Blackmore, Joseph W. Ziller, and Alan F. Heyduk*

Department of Chemistry, 516 Rowland Hall, University of California, Irvine, California 92697

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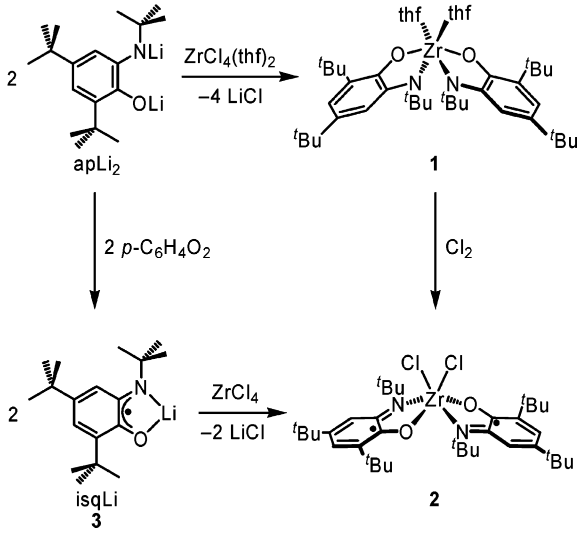
A strategy to enable reactivity analogous to oxidative addition is presented for d^0 transition-metal complexes. The reaction of the redox-active ligand 2,4-di-*tert*-butyl-6-*tert*-butylamidophenolate (ap) with $ZrCl_4(THF)_2$ affords the new complex $Zr^{IV}(ap)_2(THF)_2$. This compound is formally zirconium(IV) and contains no d electrons; however, exposure of $Zr^{IV}(ap)_2(THF)_2$ to chlorine gas results in swift chlorine addition at the zirconium metal center via one-electron oxidation of each ap ligand. The diradical product, $Zr^{IV}Cl_2(isq)_2$ (isq = 2,4-di-*tert*-butyl-6-*tert*-butyliminosemiquinone), has been characterized by X-ray crystallography, electron paramagnetic resonance spectroscopy, and SQUID magnetometery.

Oxidative addition is the fundamental bond-activating step in a variety of catalytic reactions mediated by transition-metal complexes. Despite the importance of this reaction, only a limited subset of transition-metal complexes are capable of oxidative addition reactivity, identified by three simple requirements: two vacant metal coordination sites, electron-poor metal centers (16-electron complexes or less), and a metal ion with readily accessible M^{n+} and $M^{(n+2)+}$ oxidation states.[1] While complexes of metals throughout the transition series satisfy the first two conditions, the last requirement is limiting, most often met by square-planar late-transition-metal complexes. Our research group is interested in developing a redox-based bond-activation pathway analogous to oxidative addition for metals with formal d^0 electron counts. While a conventional oxidative addition reaction may be precluded by such an electron configuration, by harnessing the reducing power of catechol-type ligands, we aim to realize an oxidative addition in which the metal and ligand react in a cooperative manner to effect the bond-activation reaction. This Communication reports the successful design of such an oxidative addition reaction, in which chlorine gas adds to a d^0 zirconium(IV) complex. In this reaction, the metal-centered addition is enabled by the participation of two redox-active *o*-amidophenolate ligands, which provide the necessary reducing equivalents.

Scheme 1



Zirconium(IV) complex **1**, $Zr^{IV}(ap)_2(THF)_2$ (ap = 2,4-di-*tert*-butyl-6-*tert*-butylamidophenolate), was prepared in ether from $ZrCl_4(THF)_2$ and 2 equiv of $apLi_2$ (Scheme 1), which is readily available from 3,5-di-*tert*-butylcatechol and *tert*-butylamine.[2] Compound **1** was obtained in analytically pure form as a bright yellow solid after filtration and solvent removal.

The structure of **1** has been investigated both in solution and in the solid state. X-ray-quality crystals of **1** were obtained from a chilled pentane solution.[3] Compound **1** adopts a six-coordinate trigonal-antiprism geometry that is distorted from octahedral as a result of the small bite angle of the ap ligands (76°; see the Supporting Information). The chelating amidophenolate ligands adopt a ligation mode that places the oxygen atoms in trans-coordination sites and the bulkier *tert*-butylamide groups in cis-coordination sites. Two THF molecules complete the metal coordination sphere. The six-coordinate geometry of **1** is preserved in solution. ^1H NMR spectroscopy reveals one set of resonances for the five

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* To whom correspondence should be addressed. E-mail: aheyduk@uci.edu.

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[2] See the Supporting Information for complete experimental procedures and spectroscopic data.

[3] Crystallographic data for **1**: $C_{44}H_{74}N_2O_4Zr{\cdot}C_5H_{12}$, fw 858.42, monoclinic, $P2_1/c$, $a = 13.3292(17)$ Å, $b = 19.672(2)$ Å, $c = 19.200(2)$ Å, $\beta = 102.262(2)°$, $V = 4919.7(11)$ Å^3, $Z = 4$, $\lambda = 0.710\ 73$ Å, $\rho_{calc} = 1.159$ mg/m^3, $\mu = 0.265$ mm^{-1}, R1 = 0.0914, wR2 = 0.1356, GOF = 1.076.

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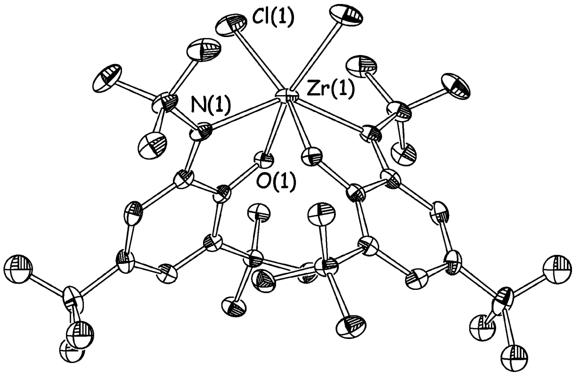


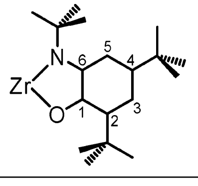
Figure 1. ORTEP of Zr^{IV}Cl$_2$(isq)$_2$ (**2**). Ellipsoids are drawn at 50% probability, and hydrogen atoms are omitted for clarity.

unique protons of the ap ligands. The chirality of the zirconium center, suggested in the X-ray structure, is revealed by a pair of diastereotopic ^{1}H NMR resonances at 3.79 and 4.11 ppm for the α-hydrogen atoms of the coordinated THF molecules.

Zirconium(IV) complex **1** reacts immediately with chlorine, either as a gas or as the chlorine-transfer reagent PhICl$_2$.[4] In a typical experiment maintained at −78 °C, bright yellow ether solutions of **1** turned dark green upon the addition of a slight excess of chlorine gas. A microcrystalline forest-green solid was isolated by filtration of the cold reaction solution. The dark green color results from a very broad absorption centered at 787 nm (ϵ = 2570 M^{-1} cm^{-1}). Such absorptions are characteristic of radical semiquinone and iminosemiquinone ligands,[5−10] suggesting that the green product is a new zirconium(IV) complex, Zr^{IV}Cl$_2$(isq)$_2$ (**2**; isq = 2,4-di-*tert*-butyl-6-*tert*-butyliminosemiquinone), shown in Scheme 1.[11]

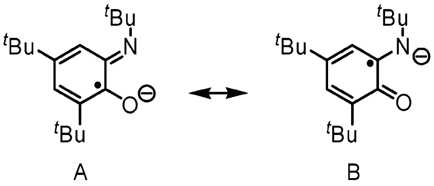
Complex **2** was also prepared from the preoxidized ligand isqLi (**3**), accessible by the reaction of apLi$_2$ and *p*-quinone. Cold ether solutions of iminosemiquinone ligand, **3**, react smoothly with ZrCl$_4$ to afford a green, microcrystalline solid with spectroscopic properties identical with those of complex **2**. X-ray-quality crystals were obtained from ether solutions of this reaction product, and a diffraction experiment confirmed the proposed formula and structure of **2**, presented as an ORTEP in Figure 1.[12] The oxidized complex, Zr^{IV}Cl$_2$(isq)$_2$, adopts a six-coordinate geometry that is between the trigonal-prismatic and antiprismatic conformations, with a dihedral angle between the trigonal faces [defined by Cl(1), O(1), and N(1)] of approximately 25°.[13]

Table 1. Selected Bond Distances (Å) for Zr^{IV}(ap)$_2$(THF)$_2$ (**1**) and Zr^{IV}Cl$_2$(isq)$_2$ (**2**)



	1	**2**
Zr−O	2.057(3)	2.0811(17)
Zr−N	2.126(4)	2.247(2)
O−C(1)	1.358(5)	1.316(3)
N−C(6)	1.413(6)	1.339(3)
C(1)−C(2)	1.400(6)	1.418(3)
C(2)−C(3)	1.394(6)	1.376(4)
C(3)−C(4)	1.387(7)	1.422(4)
C(4)−C(5)	1.394(7)	1.366(4)
C(5)−C(6)	1.396(6)	1.427(4)
C(6)−C(1)	1.424(6)	1.454(3)

Scheme 2



Examination of the bond lengths within the isq ligands of **2** further supports the redox role these ligands play in the oxidative addition reaction of **1** with chlorine. Table 1 presents selected bond distances from the high-resolution X-ray crystal structures of **1** and **2**; a few details warrant comment. First, a significant contraction (−0.074 Å) of the N−C bond distance is observed upon oxidation of **1** to **2**, along with a more subtle contraction of the O−C bond distance. A concurrent elongation of the Zr−N and Zr−O bonds is also observed. Again here the Zr−N distance changes more dramatically (+0.121 Å). Second, localization of the C−C double-bond character is apparent from the short C(2)−C(3) and C(4)−C(5) bond lengths relative to the other C−C bonds in the aromatic ring of **2**. Similar trends in ring bond lengths have been observed for iminosemiquinone and semiquinone complexes of other metals[14−18] and are consistent with the oxidation of each ligand to the radical form.

The relative bond length changes for the coordinating O and N atoms elucidate the relative importance of resonance structures **A** and **B** of Scheme 2. The significant contraction of the N−C bond and elongation of the N−Zr bond upon oxidation of **1** to **2** are consistent with N(1) acting as a

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(11) Compound **1** reacts similarly with F$_2$ (as XeF$_2$), Br$_2$, and I$_2$. The bromine addition product has been characterized by X-ray crystallography and is isostructural with **2**.

(12) Crystallographic data for **2**: C$_{36}$H$_{58}$Cl$_2$N$_2$O$_2$Zr, fw 712.96, monoclinic, *C*2/*c*, a = 21.061(2) Å, b = 9.5915(10) Å, c = 18.717(2) Å, β = 94.929(2)°, V = 3767.0(7) Å^3, Z = 4, λ = 0.710 73 Å, ρ_{calc} = 1.257 mg/m^3, μ = 0.465 mm^{-1}, R1 = 0.0577, wR2 = 0.0928, GOF = 1.097.

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π-donor amide in **1** and as a σ-only-donor imine in **2**. That the Zr−N and N−C bond lengths change by a greater magnitude than the Zr−O and O−C bond lengths upon oxidation suggests that structure **A** of Scheme 2 is the dominant resonance structure in **2**. This preference for iminephenolate resonance structure **A** may play a critical role in the stabilization of **2**, by preventing redox disproportionation to release a two-electron-oxidized iminoquinone ligand.[19,20]

The absorbance spectrum and X-ray crystal structure of **2** suggest that $Zr^{IV}Cl_2(isq)_2$ is a diradical species, with each electron localized on a chelating iminosemiquinone ligand. Temperature-dependent magnetization measurements indicate spin pairing of the electrons to give a singlet ground state. At low temperatures, the effective magnetic moment approaches zero but rises to 1.07 μ_B at room temperature.[21] The room-temperature solution electron paramagnetic resonance (EPR) spectrum of **2** is consistent with thermally accessible uncoupled biradical excited state, displaying a five-line pattern ($g = 2.005$) characteristic of a ligand-localized iminosemiquinone radical.[5]

Through harnessing of the redox properties of a simple redox-active amidophenolate ligand, for the first time a reaction akin to oxidative addition has been enabled for a d^0 zirconium(IV) metal complex. Although this reaction is not a textbook oxidative addition, the cooperative reactivity displayed by the reducing ligand set and Lewis acidic metal center results in the same stoichiometric reaction reiterating the long-standing difficulty associated with separating metal-based and ligand-based redox chemistry.[9,22,23] Because the reducing equivalents utilized in this reaction derive from the π-symmetry highest occupied molecular orbitals of the ap ligands, which interact strongly with empty metal-centered d orbitals, the reaction may be considered a *molecular* oxidative addition reaction. In this case, the reducing electrons provided by the metal complex are housed in a ligand−metal molecular orbital rather than a metal-only d_{z^2} orbital, as is typically observed for square-planar d^8 metal complexes.

The reported addition of chlorine to a zirconium(IV) center is an important proof-of-concept that points to a new strategy for bond-activating reactions at a d^0 metal center. While elimination of the strong oxidant Cl_2 from **2**, a step analogous to reductive elimination, is thermodynamically uphill, making the microscopic reverse of Cl_2 addition unfeasible, examination of a broader substrate scope will provide insight into the potential application of this strategy to stoichiometric and catalytic transformations. Studies aimed at elucidating the electronic configuration of **2** as well as the exact mechanism of its formation are currently in progress.

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Supporting Information Available: X-ray crystallographic data for **1** and **2** (CIF format) and detailed experimental methods and spectral data (PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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