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Structures and Reactivity of Zr(IV) Chlorobenzene Complexes

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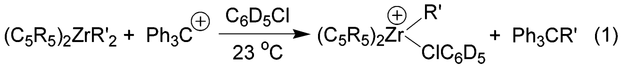
The structures and reactivity of $L_nM(\eta^1\text{-XR})$ halocarbon complexes of group 6−11 metals have been studied extensively.[1,2] Several general reactions have been established for these systems, including substitution of the halocarbon by stronger ligands, C−X oxidative addition, nucleophilic displacement of the activated halide, and X-directed C−H activation.[1,2] It has been appreciated for some time that d^0-metal $L_nMR'^+$ cations, which are active species in olefin polymerization and other reactions, also can be stabilized by halocarbon coordination.[3] However, little is known about the properties of d^0 $L_nMR'(XR)^+$ species.[4] Here, we describe the synthesis, structures, and unusual reactivity of $(C_5R_5)_2ZrR'(ClPh)^+$ chlorobenzene complexes.

The reaction of $(C_5R_5)_2ZrR'_2$ with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_5Cl affords $[(C_5R_5)_2ZrR'(ClC_6D_5)][B(C_6F_5)_4]$ complexes, as shown in eq 1 (**1**-d_5, R′ = CH_2Ph and $(C_5R_5)_2$ = Cp_2; **2a**−**d**-d_5, R′ = Me and $(C_5R_5)_2$ = *rac*-(EBI) (**2a**), Cp_2 (**2b**), Cp'_2 (**2c**), Cp^*_2 (**2d**)).[5,6] **1**-d_5 was characterized by X-ray diffraction, while **2a**−**d**-d_5 were characterized by NMR. The cation of **1**-d_5 (Figure 1) adopts a bent metallocene geometry, and the chlorobenzene ligand is η^1-coordinated via the chlorine. The Zr−ClPh distance (Zr(1)−Cl(1) = 2.746(1) Å) is intermediate between the sums of Zr and Cl covalent radii (2.47 Å) and van der Waal radii (3.23 Å).[7] The C−Cl distance of the coordinated chlorobenzene (1.773(3) Å) is not significantly changed from that in gas-phase chlorobenzene (1.737(5) Å).[8] The Zr(1)−Cl(1)−C(18) angle is 115.0(1)°, and the ClPh ring points away from the benzyl group (C(18)−Cl(1)−Zr(1)−C(12) dihedral angle = 139.1(2)°). The benzyl ligand is strongly η^2-distorted. The Zr(1)−C(11)−C(12) angle is smaller (82.3(2)°), and the Zr(1)−C(12) distance is shorter (2.588(3) Å), compared to the corresponding values in $[Cp_2Zr(CH_2Ph)(CH_3CN)][BPh_4]$ (84.9(4)°, 2.648(6) Å).[9] Chlorobenzene is a weaker donor than CH_3CN, making the Zr(IV) center in **1**-d_5 more electrophilic than that in the CH_3CN complex and resulting in a stronger Zr⋯Ph interaction.



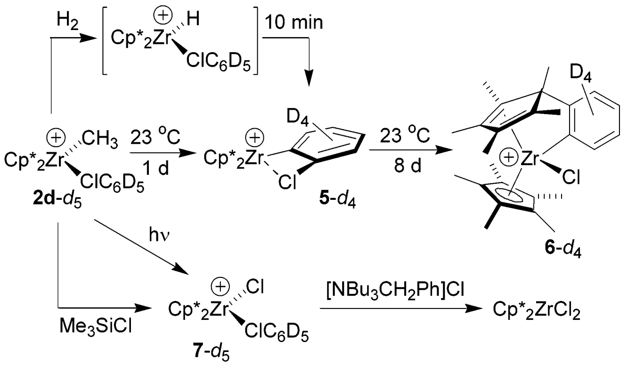
$$(C_5R_5)_2ZrR'_2 + Ph_3C^{\oplus} \xrightarrow[23\ ^{\circ}C]{C_6D_5Cl} (C_5R_5)_2\overset{\oplus}{Zr}(R')(ClC_6D_5) + Ph_3CR' \quad (1)$$

1-d_5, **2a-d**-d_5

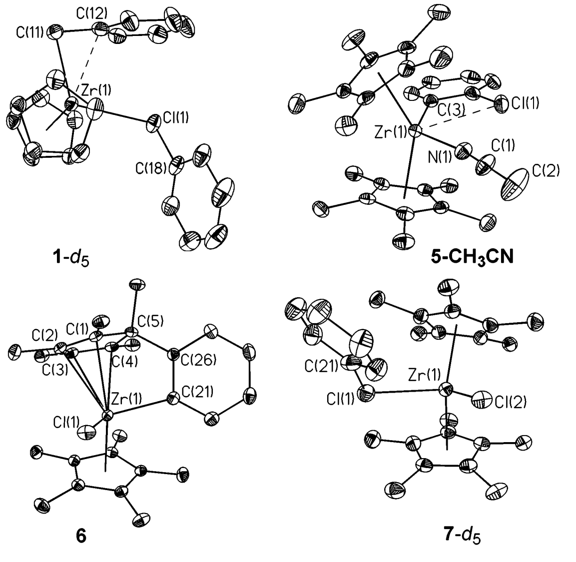
1-d_5 and **2a**−**c**-d_5 are stable for several days at 23 °C in C_6D_5Cl solution, but only if protected from light. Exposure of C_6D_5Cl solutions of **1**-d_5 and **2b**,**c**-d_5 to room light for 8 days results in ∼20% conversion to dinuclear dicationic complexes $[\{(C_5R_5)_2Zr(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ (**4b**,**c**), which were characterized by X-ray diffraction.[10] The mechanism of this photochemical reaction is under investigation.

Reaction of **2d**-d_5 at 23 °C yielded unexpected results (Scheme 1). After 1 day, 70% of **2d**-d_5 is converted to a 4/1 mixture of $[Cp^*_2Zr(\eta^2\text{-}C,Cl\text{-}2\text{-}Cl\text{-}C_6D_4)][B(C_6F_5)_4]$ (**5**-d_4) and $[(\eta^4,\eta^1\text{-}C_5Me_5C_6D_4)Cp^*ZrCl][B(C_6F_5)_4]$ (**6**-d_4), and CH_3D is formed. A small amount of CH_4 is also observed, likely due to a minor Cp* ring methyl C−H activation process.[11] Complex **6**-d_4 grows in with time at the expense of **5**-d_4, and after 8 days, **2d**-d_5 is completely consumed and **6**-d_4 is present in 90% yield. A small amount (<10%) of the chloride complex $[Cp^*_2ZrCl(ClC_6D_5)][B(C_6F_5)_4]$ (**7**-d_5) is also formed. Control experiments show that **7**-d_5 is formed by a photochemical process. Exposure of **2d**-d_5 to a 1000 W Hg−Xe lamp for 1 h yields **7**-d_5 in 80% yield, whereas **7**-d_5 is not formed when **2d**-d_5 is protected from light.

Scheme 1



5-d_4 was prepared independently (100%) from $Cp^*_2ZrH^+$ via the reaction of **2d**-d_5 with 1 atm H_2 in C_6D_5Cl at 23 °C for 10 min (Scheme 1). X-ray structural analysis of **5** (from **2d** and H_2 in ClPh) confirmed the dative coordination of the *ortho*-Cl but was complicated by rotational disorder of the chlorophenyl group. To confirm the identity of **5** and the coordination of *ortho*-Cl, the CH_3CN adduct, $[Cp^*_2Zr(\eta^2\text{-}C,Cl\text{-}2\text{-}Cl\text{-}C_6H_4)(CH_3CN)][B(C_6F_5)_4]$ (**5-CH$_3$CN**), was generated by addition of CH_3CN to **5**. The structure of **5-CH$_3$CN**, free of disorder, is shown in Figure 1. The *ortho*-Cl



1-d_5 **5-CH$_3$CN** **6** **7**-d_5

Figure 1. ORTEP views of the cations of **1**-d_5, **5-CH$_3$CN**, **6**, and **7**-d_5. H/D atoms are omitted.

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is datively bonded to Zr and occupies the central coordination site. The Zr−Cl distance (2.831(1) Å) is longer than the Zr−ClPh distance in **1**-d_5. The C−Cl distance (1.775(4) Å) is similar to that in free chlorobenzene.

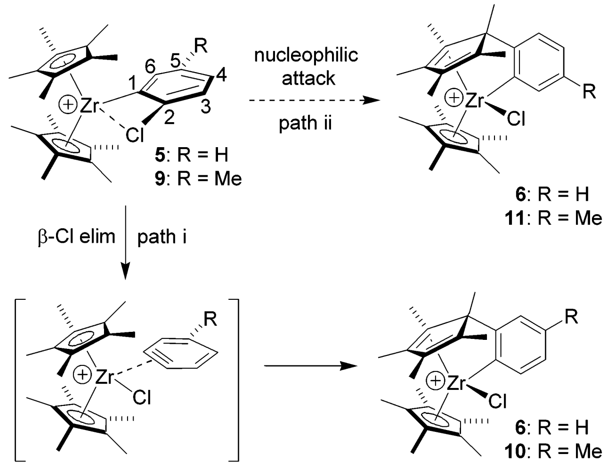
6 was generated quantitatively by reaction of **5** in C_6H_5Cl (6 days, 23 °C). X-ray analysis (Figure 1) shows that **6** contains a cyclopentadiene−phenyl ligand that is η^4-coordinated through C(1)−C(4) and σ-coordinated through C(21), and formally is derived by insertion of benzyne into a Zr−C_{Cp*} bond. The Zr−C(5) distance (2.803(3) Å) is longer than the distances between Zr and C(1)−C(4) (2.638(3)−2.699(3) Å). Bond length alternation in the C(1)−C(5) ring, displacement of C(5) by 0.113(3) Å from the C(1)−C(4) plane, and sp^3 hybridization of C(5) are all indicative of an η^4-cyclopentadiene structure. The NMR data for **6** are fully consistent with the solid-state structure.

7-d_5 was prepared independently (100%) by the reaction of **2d**-d_5 with Me_3SiCl in C_6D_5Cl (Scheme 1). X-ray analysis (Figure 1) shows that **7**-d_5 contains a terminal Zr−Cl ligand and an η^1-ClPh ligand. The Zr−ClPh distance (2.698(1) Å) is similar to that in **1**-d_5, and the Cl−Ph distance (1.784(5) Å) is slightly elongated. The Zr(1)−Cl(1)−C(21) angle is 118.5(1)°, and the ClPh ring points toward the terminal Zr−Cl (C(21)−Cl(1)−Zr(1)−Cl(2) dihedral angle = 43.7(2)°). Reaction of **7**-d_5 with $[NBu_3CH_2Ph]Cl$ yields $Cp*_2ZrCl_2$ quantitatively.

The observation of CH_3D as the major organic product in the formation of **5**-d_4 from **2d**-d_5, and the faster formation of **5** from in situ generated $Cp*_2ZrH^+$ (10 min) than from **2d** itself (>1 day), is consistent with Cl-directed *ortho*-C−H activation via a σ-bond metathesis process.

Two plausible mechanisms for the conversion of **5** to **6** are shown in Scheme 2. Path i involves β-Cl elimination of **5** to form a Zr(IV) benzyne intermediate, $Cp*_2ZrCl(C_6H_4)^+$ (**8**), followed by benzyne insertion into a Zr−C_{Cp*} bond. Jones showed that thermolysis of $Cp*_2Zr(C_6F_5)H$ to form $Cp*_2Zr(o\text{-}C_6F_4H)F$ proceeds via a similar benzyne intermediate, $Cp*_2ZrHF(C_6F_4)$, and was able to trap the C_6F_4 group as the durene adduct.[12a] Path ii involves direct nucleophilic displacement of the activated chloride of **5** by attack of a Zr−C_{Cp*} bond at C2. A related S_NAr2 mechanism was invoked to explain the formation of $Cp*_2ZrHF$ and arene in the reactions of $Cp*_2ZrH_2$ with fluoroarenes.[12b]

Scheme 2



To probe the mechanism of conversion of **5** to **6**, the *p*-Me-substituted complex $[Cp*_2Zr(\eta^2\text{-}C,Cl\text{-}2\text{-}Cl\text{-}5\text{-}Me\text{-}C_6H_3)][B(C_6F_5)_4]$ (**9**) was generated by the reaction of $[Cp*_2ZrMe(p\text{-}Cl\text{-}MeC_6H_4)][B(C_6F_5)_4]$ with H_2, and its reactivity was studied (Scheme 2). Complex **9** rearranges to $[\{\eta^4,\eta^1\text{-}C_5Me_5\text{-}(4\text{-}Me\text{-}C_6H_3)\}Cp*ZrCl][B(C_6F_5)_4]$ (**10**) quantitatively (2 days, 23 °C). A $^1H-^1H$ NOESY correlation between the resonance of the Me group bound to the cyclopentadiene sp^3 carbon and a *singlet* aromatic hydrogen resonance establishes that the aryl−Me group is located at C4, para to Zr. This result is consistent with path i and the exclusive attack of Cp* at the lateral benzyne C≡C carbon without benzyne rotation, but rules out path ii, which would generate the **5**-Me isomer of **10** (i.e., **11**). Attempts to trap benzyne from the proposed $Cp*_2ZrCl(C_6H_4)^+$ intermediate in the reaction of **5** were unsuccessful, implying that the benzyne is more strongly bound than that in $Cp*_2ZrHF(C_6F_4)$.[12a] Stronger benzyne coordination is expected for cationic versus neutral species, and for nonfluorinated versus fluorinated benzynes, since d-π* back-bonding is not possible in these d^0-metal systems.

These results show that $(C_5R_5)_2ZrR'^+$ species can be stabilized by intermolecular (**1**, **2**, and **7**) and intramolecular (**5**, **5-CH$_3$CN**, and **9**) Zr···ClPh coordination. Noncrowded $(C_5R_5)_2ZrR'(ClPh)^+$ species are thermally robust but are converted to $[\{(C_5R_5)_2Zr(\mu\text{-}Cl)\}_2]^{2+}$ species by a photochemical process in ClPh solution. In contrast, $Cp*_2ZrR'(ClPh)^+$ (R′ = Me or H) undergoes facile thermal *ortho*-C−H activation to yield **5**, which rearranges to **6** via β-Cl elimination and benzyne insertion into a Zr−C_{Cp*} bond. The higher thermal reactivity of **2d** versus that of **1** and **2b**,**c** is attributed to steric crowding involving the Cp* ligands, which forces a ClPh *ortho*-hydrogen close to the Zr−Me group in **2d**.[13] Efforts to exploit the Cl-directed C−H activation chemistry in synthetic applications are in progress.

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Supporting Information Available: Experimental procedures and characterization data (PDF). Crystallographic data for **1**-d_5, **5-CH$_3$CN**, **6**, and **7**-d_5 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) EBI = 1,2-ethylene(bis)indenyl, Cp = C_5H_5, Cp′ = C_5H_4Me, Cp* = C_5Me_5.
(6) **2a**−**c**-d_5 are generated within 4 h at 23 °C. In the first few minutes, $[\{(C_5R_5)_2ZrMe\}_2Me][B(C_6F_5)_4]$ (**3a**−**c**) are observed by NMR. However, **2d**-d_5 is formed quantitatively within 10 min at 23 °C, and no intermediate is observed. For μ-Me dinuclear zirconocene cations, see: Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.
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(13) The distance between C(12) and the closest C_6D_5Cl *ortho*-D in **1**-d_5 is 4.9 Å, and that between Cl(2) and the closest C_6D_5Cl *ortho*-D in **7**-d_5 is 2.7 Å.

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