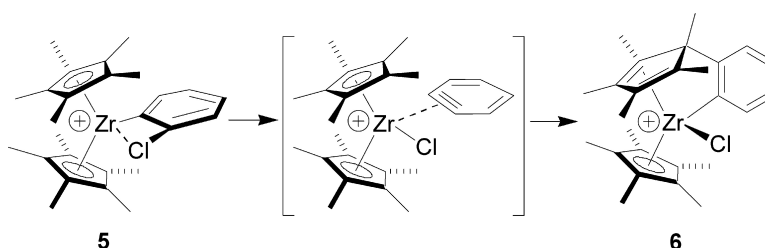


Structures and Reactivity of Zr(IV) Chlorobenzene Complexes

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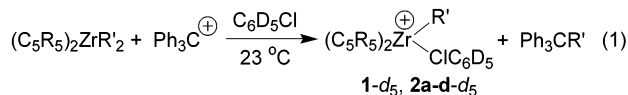
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The structures and reactivity of $L_nM(\eta^1\text{-XR})$ halocarbon complexes of group 6–11 metals have been studied extensively.^{1,2} Several general reactions have been established for these systems, including substitution of the halocarbon by 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 $(C_5R_5)_2ZrR'(CIPh)^+$ 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-d₅**, $R' = CH_2Ph$ and $(C_5R_5)_2 = Cp_2$; **2a-d-d₅**, $R' = Me$ and $(C_5R_5)_2 = rac\text{-}(EBI)$ (**2a**), Cp_2 (**2b**), Cp'_2 (**2c**), Cp^*_2 (**2d**)).^{5,6} **1-d₅** was characterized by X-ray diffraction, while **2a-d-d₅** were characterized by NMR. The cation of **1-d₅** (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-d₅** more electrophilic than that in the CH_3CN complex and resulting in a stronger $Zr\cdots Ph$ interaction.

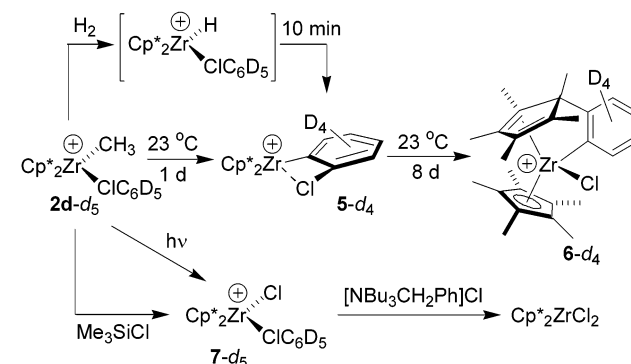


1-d₅ and **2a-c-d₅** are stable for several days at 23 °C in C_6D_5Cl solution, but only if protected from light. Exposure of C_6D_5Cl solutions of **1-d₅** and **2b,c-d₅** to room light for 8 days results in ~20% conversion to dinuclear dicationic complexes $[(C_5R_5)_2Zr(\mu\text{-Cl})_2][B(C_6F_5)_4]_2$ (**4b,c**), which were characterized by X-ray diffraction.¹⁰ The mechanism of this photochemical reaction is under investigation.

Reaction of **2d-d₅** at 23 °C yielded unexpected results (Scheme 1). After 1 day, 70% of **2d-d₅** 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-d₄**) and $[(\eta^4, \eta^1\text{-}C_5\text{-}Me_5C_6D_4)Cp^*ZrCl][B(C_6F_5)_4]$ (**6-d₄**), 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-d₄** grows in with time at the expense of **5-d₄**, and after 8 days, **2d-d₅** is completely

consumed and **6-d₄** is present in 90% yield. A small amount (<10%) of the chloride complex $[Cp^*_2ZrCl(ClC_6D_5)][B(C_6F_5)_4]$ (**7-d₅**) is also formed. Control experiments show that **7-d₅** is formed by a photochemical process. Exposure of **2d-d₅** to a 1000 W Hg–Xe lamp for 1 h yields **7-d₅** in 80% yield, whereas **7-d₅** is not formed when **2d-d₅** is protected from light.

Scheme 1



5-d₄ was prepared independently (100%) from $Cp^*_2ZrH^+$ via the reaction of **2d-d₅** 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 CIPh) 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 $CH_3\text{-}CN$ adduct, $[Cp^*_2Zr(\eta^2\text{-}C, Cl\text{-}2\text{-}Cl\text{-}C_6H_4)(CH_3CN)][B(C_6F_5)_4]$ (**5-CH₃CN**), was generated by addition of CH_3CN to **5**. The structure of **5-CH₃CN**, free of disorder, is shown in Figure 1. The *ortho*-Cl

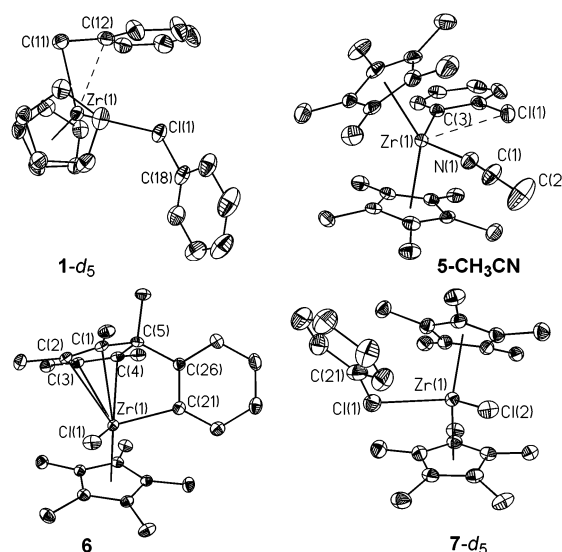


Figure 1. ORTEP views of the cations of **1-d₅**, **5-CH₃CN**, **6**, and **7-d₅**. H/D atoms are omitted.

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-d₅**. The C–Cl distance (1.775(4) Å) is similar to that in free chlorobenzene.

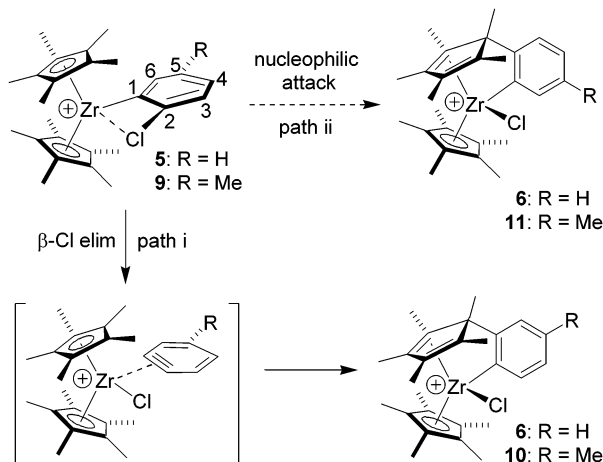
6 was generated quantitatively by reaction of **5** in C₆H₅Cl (6 days, 23 °C). X-ray analysis (Figure 1) shows that **6** contains a cyclopentadiene–phenyl ligand that is η⁴-coordinated through C(1)–C(4) and σ-coordinated through C(21), and formally is derived by insertion of benzyne into a Zr–C_{Cp}* 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 sp³ hybridization of C(5) are all indicative of an η⁴-cyclopentadiene structure. The NMR data for **6** are fully consistent with the solid-state structure.

7-d₅ was prepared independently (100%) by the reaction of **2d-d₅** with Me₃SiCl in C₆D₅Cl (Scheme 1). X-ray analysis (Figure 1) shows that **7-d₅** contains a terminal Zr–Cl ligand and an η¹-ClPh ligand. The Zr–ClPh distance (2.698(1) Å) is similar to that in **1-d₅**, 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-d₅** with [NBu₃CH₂Ph]Cl yields Cp*₂ZrCl₂ quantitatively.

The observation of CH₃D as the major organic product in the formation of **5-d₄** from **2d-d₅**, 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(C₆H₄)⁺ (**8**), followed by benzyne insertion into a Zr–C_{Cp}* bond. Jones showed that thermolysis of Cp*₂Zr(C₆F₅)H to form Cp*₂Zr(*o*-C₆F₄H)F proceeds via a similar benzyne intermediate, Cp*₂ZrHF(C₆F₄), and was able to trap the C₆F₄ 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*₂ZrH₂ with fluoroarenes.^{12b}

Scheme 2



To probe the mechanism of conversion of **5** to **6**, the *p*-Me-substituted complex [Cp*₂Zr(η²-C,Cl-2-Cl-5-Me-C₆H₃)] [B(C₆F₅)₄] (**9**) was generated by the reaction of [Cp*₂ZrMe(*p*-Cl-MeC₆H₄)] [B(C₆F₅)₄] with H₂, and its reactivity was studied (Scheme 2). Complex **9** rearranges to [{η⁴,η¹-C₅Me₅-(4-Me-C₆H₃)]Cp*ZrCl]-

[B(C₆F₅)₄] (**10**) quantitatively (2 days, 23 °C). A ¹H–¹H NOESY correlation between the resonance of the Me group bound to the cyclopentadiene sp³ 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-(C₆H₄)⁺ intermediate in the reaction of **5** were unsuccessful, implying that the benzyne is more strongly bound than that in Cp*₂ZrHF(C₆F₄).^{12a} Stronger benzyne coordination is expected for cationic versus neutral species, and for nonfluorinated versus fluorinated benzyne, since d-π* back-bonding is not possible in these d⁰-metal systems.

These results show that (C₅R₅)₂ZrR'⁺ species can be stabilized by intermolecular (**1**, **2**, and **7**) and intramolecular (**5**, **5-CH₃CN**, and **9**) Zr⋯ClPh coordination. Noncrowded (C₅R₅)₂ZrR'(ClPh)⁺ species are thermally robust but are converted to [(C₅R₅)₂Zr-(μ-Cl)]₂²⁺ 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-d₅**, **5-CH₃CN**, **6**, and **7-d₅** (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 = C₅H₅, Cp' = C₅H₄Me, Cp* = C₅Me₅.
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- (13) The distance between C(12) and the closest C₆D₅Cl *ortho*-D in **1-d₅** is 4.9 Å, and that between Cl(2) and the closest C₆D₅Cl *ortho*-D in **7-d₅** is 2.7 Å.

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