

Generation of Perfluoropolyphenylene Oligomers via Carbon–Fluorine Bond Activation by $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$: A Dual Mechanism Involving a Radical Chain and Release of Tetrafluorobenzene

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Abstract: The thermal decomposition of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in THF results in the slow formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and tetrafluorobenzene. The tetrafluorobenzene is trapped by THF to give several products. The same reaction performed in the presence of durene or furan also results in the formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and the respective Diels–Alder adducts of tetrafluorobenzene. If $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ is heated in the presence of C_6F_6 , linear chains of perfluoroarenes are rapidly generated along with $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ is observed to slow dramatically after 30–80% completion, with the extent of reaction being inversely dependent on the concentration of C_6F_6 . Dual mechanisms involving a rapid radical chain- and a slower tetrafluorobenzene-producing reaction are proposed to account for these observations.

Introduction

Research in the area of C–F bond activation by transition metal complexes has increased significantly in the past decade.¹ Despite this, the activation of C–F bonds by electron-deficient d^0 metal complexes has received less attention than electron-rich late metal compounds. The proposed mechanisms of C–F bond cleavage by early metal complexes is varied. A radical mechanism has been reported by Weydert and co-workers in the reaction of $(\text{C}_5\text{H}_4\text{Me})_3\text{U}(t\text{-Bu})$ with hexafluorobenzene.² An electron-transfer mechanism was proposed by Burk et al. in the reaction of tetrakis(trifluoromethyl)cyclopentadienone with bis-(cyclopentadienyl)-titanacyclobutanes.³ Sigma-bond metathesis and/or β -fluoride elimination has been proposed to account for C–F bond cleavage of vinyl fluoride by Cp^*_2ScH .⁴ Recently, Kiplinger and Richmond have demonstrated that group 4 metallocenes are capable of cleaving the C–F bonds of perfluorocycloalkanes and polyfluoroaromatics using activated Mg or Al as the terminal reductant.⁵ They postulated that low valent “zirconocene” or “titanocene” species were involved as intermediates in the catalytic cycle, possibly cleaving the C–F bond of the polyfluoroaromatics via formal oxidative addition.

An interesting example of intramolecular C–F activation by a lanthanide complex was reported by Deacon and co-workers,⁶

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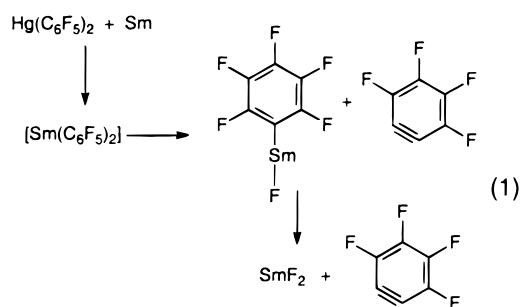
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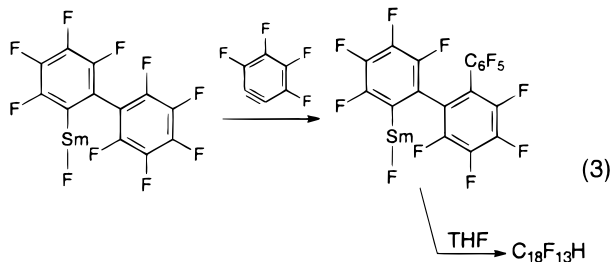
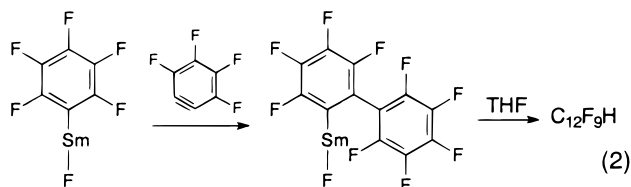
in which the reaction of $\text{Yb}(\text{C}_6\text{F}_5)_2$ with I_2 produces YbI_2 and $\text{C}_6\text{F}_5\text{I}$ in addition to a small amount of $\text{C}_{12}\text{F}_9\text{I}$.^{6b} They proposed the intermediacy of tetrafluorobenzene, which was believed to insert into the $\text{Yb}-\text{C}_6\text{F}_5$ bond, and undergo subsequent reaction with I_2 , ultimately leading to $\text{C}_{12}\text{F}_9\text{I}$.

The same authors also studied the thermal decomposition of $\text{Sm}(\text{C}_6\text{F}_5)_2$.^{6a} The reaction was performed by mixing $\text{Hg}(\text{C}_6\text{F}_5)_2$ with samarium metal at room temperature. Four samarium-containing products were observed: $(\text{C}_6\text{F}_5)\text{SmF}$, SmF_2 , $(\text{C}_6\text{F}_5)\text{-SmF}_2$, and $(\text{C}_{12}\text{F}_9)\text{Sm}$ as well as several polyfluorinated organic products including $\text{C}_{12}\text{F}_9\text{H}$ (three isomers), $\text{C}_{18}\text{F}_{13}\text{H}$, and others. Intramolecular fluoride abstraction and concomitant formation of tetrafluorobenzene was proposed to account for the formation of $(\text{C}_6\text{F}_5)\text{SmF}$, SmF_2 , and $(\text{C}_6\text{F}_5)\text{SmF}_2$ (eq 1).



The organic products $\text{C}_{12}\text{F}_9\text{H}$ and $\text{C}_{18}\text{F}_{13}\text{H}$ were speculated to form by tetrafluorobenzene insertion into polyfluoroarylsamarium bonds followed by hydrogen abstraction from THF (eqs 2–3). The other products were proposed to be formed by an electron-transfer mechanism from samarium(II) species to polyfluoroaryl groups followed by hydrogen abstraction from THF.

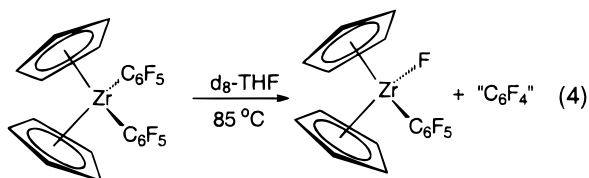
We have recently reported the C–F activation of C_6F_6 by $[\text{Cp}_2\text{ZrH}_2]_2$ to give $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$, Cp_2ZrF_2 , and $\text{C}_6\text{F}_5\text{H}$.⁷ As part of our research on C–F activation of polyfluoroaromatics by



Cp_2Zr complexes, we became interested in studying the thermal decomposition of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in the presence of C_6F_6 . In this paper we demonstrate that the reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 leads to a series of novel linear polyfluoro-polyphenylenes and $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. Our studies indicate that dual mechanisms involving a radical chain process and tetrafluorobenzynes formation are operating.

Results and Discussion

Thermal Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$. A THF- d_8 solution of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ heated at 85 °C in a resealable NMR tube resulted in the slow formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ (eq 4). The rate of



formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ is high during the first 1–2% of reaction but drops substantially after only a few percent conversion (Figure 1). Reaction continues at this slow rate over a period of months. Mass balance would dictate the formation of C_6F_4 , formally tetrafluorobenzynes. When the reaction is performed at 125 °C (or at longer times at 85 °C), several new peaks appear in the ^{19}F NMR spectrum, and a small amount of an orange precipitate is observed to deposit at the bottom of the tube. A GC/MS of the liquid portion of the reaction mixture reveals the presence of compounds whose molecular weight is consistent with the reaction of tetrafluorobenzynes with the THF solvent (see Experimental Section). The reductive elimination product, perfluorobiphenyl, was not observed.

Prior reports indicate that tetrafluorobenzynes (formed by elimination of LiF from LiC_6F_5 at ~ -20 °C) reacts with furan and 2,3,5,6-tetramethylbenzene (durene) to give the Diels–Alder adducts **1**⁸ and **2**,⁹ respectfully. Heating solutions of Cp_2Zr -

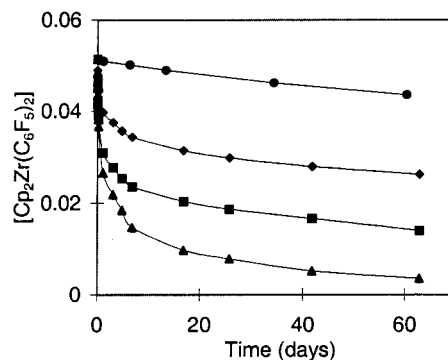
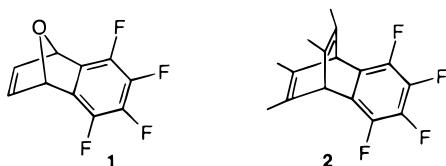
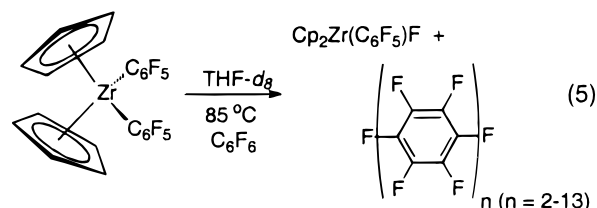


Figure 1. Plot of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (0.051 M) vs time at various concentrations of C_6F_6 : (●) 0 M, (◆) 1.54 M, (■) 0.51 M, (▲) 0.051 M in THF- d_8 . The reaction was performed at 85 °C.

($\text{C}_6\text{F}_5)_2$ at 125 °C in THF- d_8 in the presence of furan or durene also resulted in the formation of **1** and **2** in yields of 50 and 80%, respectively, as well as $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was not affected by the concentration of durene and was comparable to the rate without added durene.

Thermal Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 . A THF- d_8 solution of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and C_6F_6 (1 equiv) was heated at 85 °C in a resealable NMR tube, resulting in the rapid disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and the concomitant formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The rate of this reaction was observed to slow dramatically within a matter of hours after $\sim 50\%$ completion, and a white precipitate deposited on the bottom of the NMR tube (Figure 1). ^1H and ^{19}F NMR spectroscopy of the liquid showed the formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and perfluorobiphenyl as well as higher-molecular-weight linear oligomers of perfluorobenzene (eq 5).¹⁰ GC/MS of the liquid portion revealed



oligomers with up to 5 aryl groups, and LCMS of the white solid displayed oligomers of up to $n = 13$. A similar reaction performed with perfluorobiphenyl as the initial substrate (vs C_6F_6) gave similar results. The complex $\text{Cp}_2\text{Zr}(\text{C}_{12}\text{F}_9)\text{F}$ was not observed.

The rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was monitored with varying concentrations of added C_6F_6 at 85 °C. Figure 1 shows that in each experiment the initial disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was rapid. This rapid reaction was observed to slow dramatically within a matter of hours and remained approximately constant until the $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was depleted. An important observation is that the greater the concentration of C_6F_6 , the less the reaction proceeds before the rate slows. During reaction in the slow regime, the rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ is the same regardless of the concentration of C_6F_6 .

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(10) The oligomers were determined to be a chain of perfluoroaromatics linked together in the *para* position. This was based on comparison to literature ^{19}F NMR spectroscopy of authentically synthesized oligomers up to $n = 5$. See: Maruo, K.; Wada, Y.; Yanagida, S. *Bull. Chem. Soc. Jpn.* **1992**, 65, 3439. In addition, GC/MS showed only a single peak for each mass of oligomer.

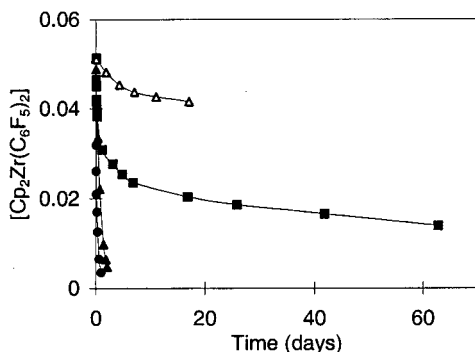


Figure 2. Plot of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (0.051 M) with C_6F_6 (0.51 M) and radical initiators: (■) no radical initiator, (●) Na + naphthalene, (▲) 1,1'-azobis(cyclohexane-carbonitrile) in THF- d_8 , (Δ) radical inhibitor isopropylbenzene, C_6F_6 (0.051 M) in THF- d_8 . The reaction was performed at 85 °C.

During the rapid portion of the reaction, the formation of perfluorobiphenyl and higher-molecular-weight oligomers was observed in all reactions. However, the relative amount of higher-molecular-weight oligomers decreased with increasing C_6F_6 concentration. During the slow portion of the reaction, the formation of perfluorobiphenyl and the higher-molecular-weight oligomers stopped. New products were observed in the ^{19}F NMR spectra consistent with the reaction of tetrafluorobenzene with THF- d_8 solvent (vide supra).

Effect of Radical Initiators and Inhibitors on the Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 . The effect of radical initiators on the rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in the presence of C_6F_6 was monitored. A mixture of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (0.051 M), C_6F_6 (0.51 M), sodium, and naphthalene heated at 85 °C resulted in a moderate initial rate increase compared to the reaction without sodium and naphthalene. In addition, the reaction with added sodium and naphthalene proceeded to completion in approximately 1 day, compared with several months in their absence (Figure 2). (Reduction of C_6F_6 has been reported to give perfluorophenyl radicals.¹¹) The radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (VAZO) had a similar effect.

A THF- d_8 solution of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (0.051 M), C_6F_6 (0.051 M), and the radical trap isopropylbenzene was heated at 85 °C. In this reaction, the initial rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was less than 1/100th that of the reaction without added isopropylbenzene (Figure 2), and the reaction slows after only ~15% completion (compared with 75% completion in the absence of isopropylbenzene).

Alternative Sources of C_6F_4 . The complex $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{-CH}_3$ was heated at 125 °C in THF- d_8 in the presence of durene. The Diels–Alder adduct **2** was formed in ~38% yield. The main zirconium complex formed was $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$. When a THF- d_8 solution of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{CH}_3$ and C_6F_6 was heated at 55 °C, the formation of $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$ was initially rapid and then slowed dramatically as the reaction proceeded. Perfluorobiphenyl and higher oligomers were also observed in the ^{19}F NMR spectrum and by GC/MS. A small amount of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ and $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ were also observed, possibly as a result of con-proportionation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{CH}_3$ and $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$.

Heating $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ with C_6F_6 at 125 °C in THF- d_8 also resulted in the formation of perfluorobiphenyl and perfluoro-terphenyl as well as Cp_2ZrF_2 and products corresponding to the reaction of THF- d_8 with C_6F_4 . A small amount of $\text{C}_6\text{F}_5\text{H}$ was also observed.

Mechanistic Considerations. Several observations lead us to believe that competing mechanisms are operating in the reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 . Most important is the

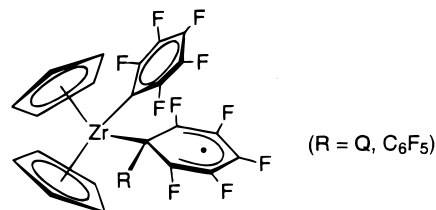


Figure 3. Structure of radical chain carrying intermediate/transition state.

observation that the initial disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ is rapid and then slows dramatically within a matter of hours (Figure 1). Second, radical initiators greatly enhance the rate of the reaction and the dramatic decrease in rate is not observed (Figure 2). Third, the rate of the reaction in the presence of an added radical inhibitor is slow (Figure 2). Fourth, the thermal decomposition of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in the absence of C_6F_6 generates $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ at the same slow rate as the reactions with C_6F_6 at later times (Figure 1). Last, the Diels–Alder adducts **1** and **2** formed slowly during the thermal decomposition of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in the presence of furan or durene, suggesting that tetrafluorobenzene is released in this reaction. These observations are consistent with a radical chain mechanism dominating at early reaction times and a slower reaction involving release of tetrafluorobenzene occurring throughout the course of the reaction. This latter mechanism is observed exclusively at longer reaction times when the radical chain has terminated.

Scheme 1 depicts a plausible radical chain mechanism. The chain is initiated by a trace amount of radical initiator, for example a minor impurity in the starting material, to give the Zr(III) radical species, **3** (step 1). Step 2 involves fluorine atom abstraction from C_6F_6 by **3** to generate $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and $\bullet\text{C}_6\text{F}_5$ radical. This step appears to be approximately thermoneutral based on the reported bond strength of 154 kcal/mol for the C–F bond in C_6F_6 ¹² which is nearly identical to the Zr–F bond strength estimated by Schock and Marks (~154 kcal/mol).¹³ In the third step, the $\bullet\text{C}_6\text{F}_5$ radical combines with $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ resulting in the formation of **3** and perfluorobiphenyl. Ultimately the chains are terminated, and the rate of reaction slows dramatically. As depicted in Figure 1, the rate of chain termination is inversely dependent on the concentration of C_6F_6 , consistent with the idea that C_6F_6 contains some impurity which quenches the radical chain. There is strong evidence that a radical chain mechanism is operating in the autoxidations of dialkylzirconocenes of the type Cp_2ZrR_2 . In these reactions, the radical chain is believed to involve an $\text{S}_{\text{H}}2$ type displacement of an alkyl radical from the metal center by an alkylperoxy radical or di-*tert*-butylnitroxide.¹⁴

Steps 1 and 3 involve a radical attack on the zirconium-bound perfluorophenyl group to give a phenylcyclohexadienyl radical as shown in Figure 3.¹⁵ Facile homolytic cleavage of the Zr–aryl bond results in compound **3** and $\text{C}_6\text{F}_5\text{Q}$ (step 1) or $\text{C}_{12}\text{F}_{10}$ (step 3). Perfluorobiphenyl can now serve as a fluoride atom source (step 2) to generate the $\bullet\text{C}_{12}\text{F}_9$ radical which goes on to form $\text{C}_{18}\text{F}_{14}$ and ultimately the higher-molecular-weight oligomers. Presumably, the stability of the perfluoroarylradicals

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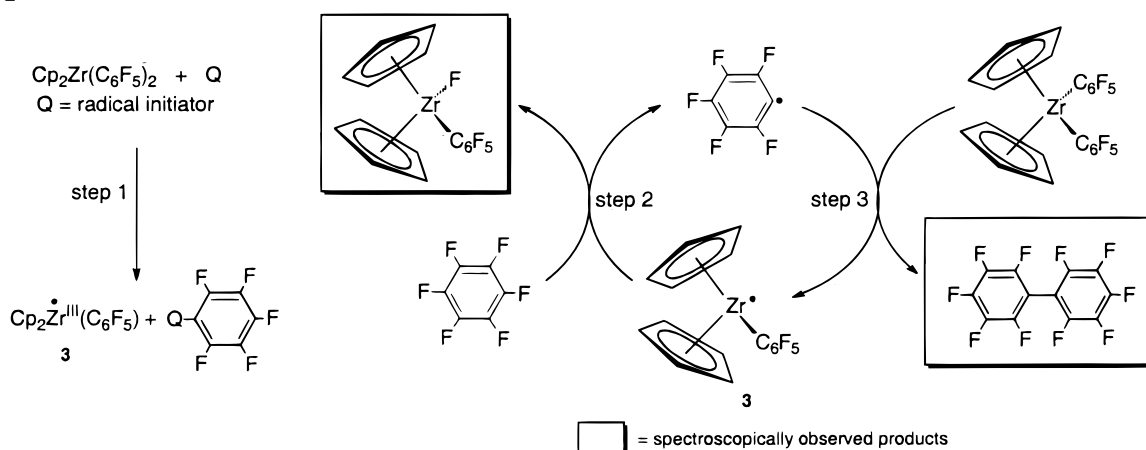
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(14) (a) Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (b) *J. Organomet. Chem.* **1981**, 222, 89.

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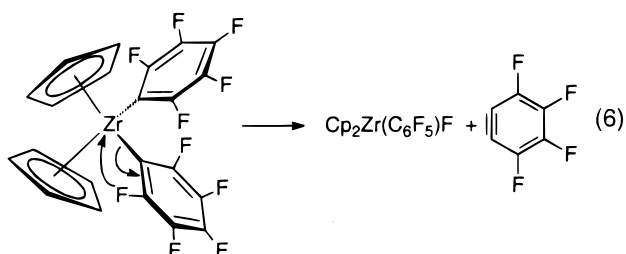
Scheme 1



increases with the number of aryl groups in the chain. Therefore, step 2 would become more facile with higher molecular weight oligomers. This presumption accounts for the observation of the higher-molecular-weight oligomers (and the white precipitate) at early times in the reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with 1 equiv of C_6F_6 and is also consistent with the fact that slightly less than half of the C_6F_6 still remained when $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was depleted. It is also worth noting that reaction of the perfluorophenyl radical with C_6F_6 has been reported to give only traces of perfluorobiphenyl,¹⁶ pointing toward the necessity of having a $\text{Zr}-\text{C}_6\text{F}_5$ bond present to give the observed coupled products.

The perfluoropolyphenylene products in this reaction are potentially interesting materials. Direct synthesis of short oligomers ($n = 2-4$) has been reported,¹⁰ and the preparation of mixtures of meta-linked perfluoropolyphenylenes with high molecular weights has been reported.¹⁷ Interest in the parent protio-polyphenylenes stems from their high thermal and thermo-oxidative stabilities¹⁸ and from their semiconductor properties.¹⁹

Concomitant with the rapid radical chain mechanism is a slower mechanism involving the formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and the release of tetrafluorobenzene (eq 6). Tetrafluorobenzene is



trapped by $\text{THF}-d_8$ solvent to give several of products. Once the radical chains are terminated, this mechanism continues to operate at its much slower pace. The formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and tetrafluorobenzene may result from β fluoride elimination from one of the aryl^F groups on $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$. This type of unimolecular reaction is consistent with the observation that the rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ (at longer times) does not depend on the concentration of C_6F_6 . β -F elimination has been postulated to account for the formation of ethylene and Cp^*_2ScF from Cp^*_2ScH and vinyl fluoride.⁴ There is literature precedent for the formation of $\text{M}-\text{F}$ bonds and tetrafluorobenzene from $\text{M}(\text{C}_6\text{F}_5)_2$ compounds. For example, the pyrolysis of

$\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)_2$ at 150 °C yields small quantities of $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)\text{F}$; however, no mention was made of tetrafluorobenzene.²⁰ As mentioned earlier, the thermal decomposition of $\text{Yb}(\text{C}_6\text{F}_5)_2$ and $\text{Sm}(\text{C}_6\text{F}_5)_2$ reportedly generates tetrafluorobenzene along with the $\text{M}-\text{F}$ compound.⁶ In those reactions, it was reported that the tetrafluorobenzene subsequently inserted into the $\text{M}-\text{aryl}$ bond, although no evidence for this was seen in the reactions described here.

Conclusions

The thermal decomposition of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in THF generates $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and tetrafluorobenzene. Evidence for tetrafluorobenzene formation arises from the formation of $\text{THF}-\text{C}_6\text{F}_4$ insertion products, as well as the formation of Diels-Alder adducts of tetrafluorobenzene when the reaction is performed with furan and durene. When $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ is heated in the presence of C_6F_6 , perfluorobiphenyl and higher-molecular-weight linear oligomers are rapidly produced. However, this reaction slows dramatically with no further formation of the linear polyfluoroarenes. Added radical initiators prevent the slowing of the reaction, while radical inhibitors slow the rate of the reaction. These results are consistent with a rapid radical chain mechanism which leads to the formation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and the linear polyfluoroarenes. The chain is believed to be initiated by an impurity in the $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and is inhibited by an impurity in the C_6F_6 , which accounts for the observed inverse dependence of rate on the concentration of C_6F_6 .

Experimental Section

General Considerations. All manipulations were performed under an N_2 atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation Glovebox. Tetrahydrofuran, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. Alkane solvents were made olefin-free by stirring over H_2SO_4 , washing with aqueous KMnO_4 and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Tetrahydrofuran- d_8 was purchased from Cambridge Isotope Lab. and distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon sealed vacuum line adapters. The preparations of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$,²¹ Cp_2ZrMeF ,²² $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{Me}$,²³ and Cp_2ZrF_2 ²⁴ have been previously reported. Perfluorobenzene, perfluorobiphenyl, and 1,1'-azobis(cyclohexanecarbonitrile) (VAZO) were

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purchased from Aldrich Chemical Co. The liquids were stirred over sieves, freeze-pump-thaw degassed three times, and vacuum distilled prior to use.

All ^1H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer. All ^1H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances (THF- d_8 , δ 1.73). ^{19}F NMR spectra were referenced to external $\text{C}_6\text{H}_5\text{CF}_3$ (δ 0.00 with downfield chemical shifts taken to be positive). GC/MS was conducted on a HP 5890 Series II gas chromatograph fitted with an HP 5970 series mass selective detector. LCMS was conducted on a HP 1100 Series LC/MSD.

Preparation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. A sample of $[\text{Cp}_2\text{ZrH}_2]_2$ (244 mg, 0.546 mmol) was suspended in 8 mL of THF. Perfluorobenzene (13.1 mmol, 1.5 mL) was added at room temperature, and the mixture was heated to 65 °C. Within a few minutes vigorous gas evolution was observed, and the suspension of $[\text{Cp}_2\text{ZrH}_2]_2$ disappeared to give a homogeneous colorless solution. The solvent and excess C_6F_6 , $\text{C}_6\text{F}_5\text{H}$, and H_2 were removed to give a white powder (412 mg). A ^1H NMR spectrum of the sample revealed a 4:1 mixture of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ and Cp_2ZrF_2 . $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ can be separated from Cp_2ZrF_2 by dissolving the mixture in a minimum of THF and layering with hexanes. $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ forms as a white precipitate. ^1H NMR $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ (THF- d_8) δ 6.405 (s, 10 H). ^{19}F NMR $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ (THF- d_8) δ 168.2 (t, $J_{\text{F-F}} = 20.71$ Hz, Zr-F), -49.3 (m, 2 F_{ortho}), -93.8 (t, $J_{\text{F-F}} = 18.83$ Hz, 1 F_{para}), -98.8 (bs, 2 F_{meta}). Calcd for $\text{C}_{16}\text{H}_{10}\text{F}_6\text{Zr}$: C, 47.16; H, 2.47. Found: C, 46.99; H, 2.37.

Thermolysis of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in THF- d_8 . A resealable NMR tube containing THF- d_8 was charged with 16 mg (0.029 mmol, 0.051 M) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and heated at 85 °C in a constant-temperature oil bath (± 0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and NMR spectra were recorded. The disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was monitored by ^{19}F NMR spectroscopy (Figure 1). $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ slowly converted to $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The ^{19}F NMR spectrum and GC/MS of the reaction mixture also revealed the formation of three new compounds, consistent with the reaction of tetrafluorobenzene with THF- d_8 or the Cp ring of the metal complexes. Compound 1 ($\text{C}_6\text{F}_4 + \text{C}_5\text{H}_6$): ^{19}F NMR (THF- d_8) δ -76.2 (m, 2 F), -80.8 (m, 2 F). MS (m/z , %) 215 (M + 1, 12); 214, (M, 100), 213, (M - 1, 95), 195, (M - F, 52), (M - C_2H_2 - H, 89). Compound 2 ($\text{C}_6\text{F}_4 + \text{C}_4\text{D}_8\text{O}$): ^{19}F NMR (THF- d_8) δ -77.2 (m, 2 F), -79.9 (m, 2 F). MS (m/z , %) 228, (M, 68), 226, (M - 2, 15), 196, (M - C_2D_4 , 17), 178, (M - C_3D_7 , 100), 182 (M - C_3D_5 , 37), 166 (M - C_4D_7 , 57). Compound 3 ($\text{C}_6\text{F}_4 + \text{C}_4\text{D}_8\text{O}$): ^{19}F NMR (THF- d_8) δ -76 (m, 2 F), -93.1 (m, 2 F). MS (m/z , %) 224, (M, 82), 206 (M - OD, 100), 192 (M - OD - CD, 72), 173 (M - OD - CD - F, 61).

Thermolysis of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ in the Presence of Furan. A resealable NMR tube containing THF- d_8 was charged with 14 mg (0.025 mmol) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and furan (1.36 mg, 1.4 μL , 0.02 mmol) and heated at 125 °C in an oil bath. After 5 days, ^1H and ^{19}F NMR spectroscopy revealed that approximately three-fourths of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ had been converted to $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The Diels-Alder adduct 1 was also detected by ^1H , ^{19}F , and GC/MS (~50% yield based on ^{19}F NMR spectroscopy). ^1H NMR 1 (THF- d_8) δ 7.13 (t, $J_{\text{H-H}} = 1.0$ Hz, 2 H), 6.08 (t, $J_{\text{H-H}} = 1.0$ Hz, 2 H). ^{19}F NMR 1 (THF- d_8) δ -79.7 (m, 2 F), -94.7 (m, 2 F). MS (m/z) 216 (M^+).

Thermolysis of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{Me}$ in the Presence of Durene. A resealable NMR tube containing THF- d_8 was charged with 13 mg (0.023 mmol) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ and durene (30.8 mg, 0.23 mmol) and heated at 125 °C in an oil bath. After 5 days, ^1H and ^{19}F NMR spectroscopy revealed that approximately two-thirds of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ had been converted to $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$. The Diels-Alder adduct 2 was also detected by ^1H , ^{19}F , and GC/MS (~80% yield based on ^{19}F NMR spectroscopy). ^1H NMR 2 (THF- d_8) δ 4.58 (t, $J_{\text{H-F}} = 1.2$ Hz, 2 H), 1.79 (s, 12 H). ^{19}F NMR 2 (THF- d_8) δ -87.4 (m, 2 F), -99.9 (m, 2 F). MS (m/z) 282 (M^+). A similar reaction with $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{Me}$ and durene gave Cp_2ZrMeF and 2 (~38% yield based on ^{19}F NMR spectroscopy).

Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with Various Concentrations of C_6F_6 . Three NMR tubes were prepared with varying concentrations of C_6F_6 (0.051, 0.51, and 1.53 M) in THF- d_8 . Each tube also contained 16 mg (0.029 mmol, 0.051 M) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$. The NMR tubes were heated at 85 °C in a constant-temperature oil bath (± 0.5 °C). The NMR tubes were removed at various intervals and cooled to room temperature, and NMR spectra were recorded. ^1H and ^{19}F NMR spectroscopy revealed initial rapid conversion of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ to $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$, but within a matter of hours the reaction slowed significantly (Figure 1). In all cases perfluorobiphenyl and higher-molecular-weight oligomers were observed. The ^{19}F NMR spectra were consistent with the formation of only linear oligomers, as judged by a comparison of the spectra with those of authentically synthesized compounds in the literature.¹⁰ A GC/MS of the reaction solution displayed oligomers up to $n = 5$, with only one peak for each mass of oligomer. The relative amount of the higher molecular weight oligomers decreased with increasing concentration of C_6F_6 . The reaction with 0.051 M C_6F_6 also generated a white precipitate within a matter of hours. LCMS (APCI, negative ions) of this solid revealed oligomers with chain lengths from $n = 5$ to $n = 13$ (See Supporting Information).

Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 , Sodium, and Naphthalene. A resealable NMR tube containing THF- d_8 was charged with 16 mg (0.029 mmol, 0.051 M) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$, C_6F_6 (0.51 M), sodium (~5 mg), and naphthalene (~3 mg, 0.023 mmol). The solution had a slight orange tint. The mixture was heated at 85 °C in a constant-temperature oil bath (± 0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and NMR spectra were recorded. ^1H and ^{19}F NMR spectroscopy revealed rapid conversion of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ to $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)\text{F}$ (Figure 2). The ^{19}F NMR spectrum and GC/MS also revealed the presence of perfluorobiphenyl and higher-molecular-weight oligomers. The solution turned deep orange then red as the reaction neared completion.

Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 , and 1,1'-Azobis(cyclohexanecarbonitrile) (VAZO). A resealable NMR tube containing THF- d_8 was charged with 16 mg (0.029 mmol, 0.051 M) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$, C_6F_6 (0.51 M), and the radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (~2 mg, 8.2×10^{-3} mmol) and heated at 85 °C in a constant-temperature oil bath (± 0.5 °C). The NMR tube was removed at various intervals, cooled to room temperature, and a ^{19}F NMR spectrum recorded. The results are similar to those with Na and naphthalene (Figure 2).

In a preparative experiment, 80 mg $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$, 18 μL C_6F_6 , and 20 mg VAZO were dissolved in 3 mL THF in an ampule. The sample was heated to 85 °C for 3 d over which time white solids were observed to precipitate from the faint orange solution. The volatiles were removed under vacuum, leaving 95 mg of solid residue (about 17 mg of which should be perfluoropolyphenylene oligomers). The residue was washed with THF to remove the Zr product, VAZO, and soluble oligomers, leaving 10 mg of insoluble white oligomers of perfluoropolyphenylene. Based on an expected yield of 1 mol benzyne/Zr, the total yield of perfluoropolyphenylene was 80%, with about 47% yield of isolated insoluble oligomers.

Reaction of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ with C_6F_6 and Isopropylbenzene. A resealable NMR tube containing THF- d_8 was charged with 16 mg (0.029 mmol, 0.051 M) of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$, C_6F_6 (0.051 M), and the radical inhibitor isopropylbenzene (0.08 mL, 0.575 mmol, 1.03 M). The tube was heated at 85 °C in a constant-temperature oil bath (± 0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ^{19}F NMR spectrum was recorded. The initial rate of disappearance of $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)_2$ was over 100 times slower than the reaction without added isopropylbenzene. A small amount of perfluorobiphenyl and higher-molecular-weight oligomers was observed by ^{19}F NMR spectroscopy.

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Supporting Information Available: LCMS spectra of the perfluorobenzene oligomers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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