

## LIGAND REDISTRIBUTION REACTIONS OF DICYCLOPENTADIENYLZIRCONIUM(IV) COMPLEXES

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### Summary

The rates of several ligand redistribution reactions of dicyclopentadienylzirconium compounds  $\text{Cp}_2\text{ZrR}_2$ ,  $\text{Cp}_2\text{ZrRX}$  and  $\text{Cp}_2\text{ZrX}_2$  vary as a function of ligand in the order  $\text{F, I} > \text{Cl, Br}$  and  $\text{CH}_3 > \text{Ph}$ . The variation of rate with ligand is considerably larger than for the analogous Ti compounds.

### Introduction

Ligand or substituent exchange reactions provide the basis for a variety of applications of dicyclopentadienylzirconium(IV) complexes in organic synthesis such as Zr-mediated coupling reactions [1] and transmetallation chemistry [2]. Ligand exchange also provides a potential pathway for racemization of chiral zirconium(IV) and titanium(IV) compounds [3]. Puddephatt and Stalteri have studied the ligand redistribution reactions between  $\text{Cp}_2\text{TiX}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $\text{Cp}_2\text{TiR}_2$  (eq. 1) in chloroform [4].



The observed rate profiles were  $\text{I} > \text{Br} > \text{F} > \text{Cl}$  for  $\text{Cp}_2\text{TiMe}_2$  and  $\text{I} > \text{Cl} > \text{Br} > \text{F}$  for  $\text{Cp}_2\text{TiPh}_2$ , although the variation in rate as a function of the ligands X and R was small. Decomposition of  $\text{Cp}_2\text{TiR}_2$  was competitive with ligand exchange.

In the course of other work we had occasion to investigate the redistribution reactions for the analogous Zr compounds. In contrast to the results observed for Ti, the rates of these reaction are quite sensitive to the ligands X and R.

### Results

Mixture of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  and  $\text{Cp}_2\text{ZrX}_2$  in THF at room temperature resulted in nearly complete conversion to  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{X}$  (eq. 2). Approximate half-lives  $t_{1/2}$

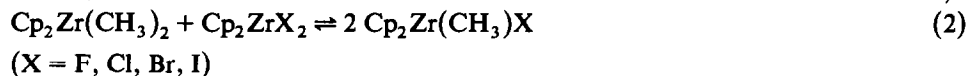


TABLE 1

HALF-LIVES  $t_{1/2}$  AND EQUILIBRIUM CONSTANTS  $K_{eq}$  FOR REDISTRIBUTION REACTIONS OF  $Cp_2Zr(CH_3)_2$  AND  $Cp_2ZrX_2$  (eq. 2) <sup>b</sup>

X	$t_{1/2}$ <sup>a,b</sup>	$K_{eq}$
F	3 h	170 ± 30
Cl	20 d	240 ± 40
Br	8 d	75 ± 25
I	1 h	950 ± 250

<sup>a</sup> Concentration of each reagent ca. 0.1 M. <sup>b</sup> T 25°C.

for approach to equilibrium and equilibrium constants  $K_{eq}$  for eq. 2 were determined by <sup>1</sup>H NMR in sealed tube experiments and are listed in Table 1. The <sup>1</sup>H NMR spectra are tabulated in Table 2. Reaction 2 occurred rapidly for X = F, I but very slowly for X = Cl, Br. The approach to equilibrium by the reverse of eq. 2 was briefly investigated for X = Cl. An equilibrium mixture of  $Cp_2Zr(CH_3)Cl$  [5],  $Cp_2Zr(CH_3)_2$  and  $Cp_2ZrCl_2$  formed after ca. 3 weeks by disproportionation of  $Cp_2Zr(CH_3)_2$  in THF at room temperature. For X = F, Br, and I the reactions were performed on a larger scale and the methyl halide complexes isolated in high yield.

The rate profile F, I > Cl, Br was observed for several other ligand exchange reactions of zirconocene halide complexes. In 1969 Lappert et al. reported that  $Cp_2ZrCl_2$  and  $Cp_2ZrBr_2$  exist in equilibrium with  $Cp_2ZrClBr$  in THF (eq. 3) [6].



$K_{eq}$  for eq. 3 was found to be  $4.3 \pm 0.2$  (approximately the statistical value of 4) and exchange between the 3 species was slow on the NMR time scale [6]. We confirmed these results and also investigated the <sup>1</sup>H NMR spectra of an equilibrium mixture of  $Cp_2ZrCl_2$ ,  $Cp_2ZrBr_2$  and  $Cp_2ZrClBr$  in THF at higher temperatures. No line broadening was observed up to 55°C placing an upper limit of ca.  $30 M^{-1} s^{-1}$  on the second order rate constants for halide exchange between these species at this temperature.

TABLE 2

<sup>1</sup>H NMR SPECTRA OF DICYCLOPENTADIENYLZIRCONIUM COMPOUNDS <sup>a</sup>

Compound	$\delta(C_5H_5)$	$\delta(CH_3)$	$\delta(\text{other})$
$Cp_2Zr(CH_3)_2$	6.08	-0.42	
$Cp_2Zr(CH_3)F$	6.17	0.17	
$Cp_2Zr(CH_3)Cl$	6.23	0.21	
$Cp_2Zr(CH_3)Br$	6.27	0.09	
$Cp_2Zr(CH_3)I$	6.35	-0.23	
$Cp_2ZrF_2$	6.38		
$Cp_2ZrCl_2$	6.48		
$Cp_2ZrBr_2$	6.55		
$Cp_2ZrI_2$	6.67		
$Cp_2Zr(Ph)_2$	6.18		6.93 m (phenyl) 7.23 m

<sup>a</sup> THF-*d*<sub>8</sub>.

We observed a similar equilibrium for  $\text{Cp}_2\text{ZrF}_2$  and  $\text{Cp}_2\text{ZrI}_2$  in THF (eq. 4) for which  $K_{\text{eq}} = 4.4 \pm 0.4$  at  $-40^\circ\text{C}$ . A resonance at  $\delta$  6.58, between those for  $\text{Cp}_2\text{ZrF}_2$  and  $\text{Cp}_2\text{ZrI}_2$ , was assigned to the mixed halide complex  $\text{Cp}_2\text{ZrFI}$ . However, in this

$$\text{Cp}_2\text{ZrF}_2 + \text{Cp}_2\text{ZrI}_2 \rightleftharpoons 2 \text{Cp}_2\text{ZrFI} \quad (4)$$

case ligand exchange between the 3 species was rapid on the NMR time scale. At concentrations of ca. 0.01 *M* the Cp signals for  $\text{Cp}_2\text{ZrF}_2$  and  $\text{Cp}_2\text{ZrFI}$  coalesced at  $20^\circ\text{C}$  from which a second order rate constant  $k(\text{Cp}_2\text{ZrFI}, \text{Cp}_2\text{ZrF}_2) - 2.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  was estimated for this temperature. Ligand exchange involving  $\text{Cp}_2\text{ZrI}_2$  was slower but was manifested by broadening of the Cp peak at  $55^\circ\text{C}$  from which a second order rate constant  $k(\text{Cp}_2\text{ZrI}_2, \text{Cp}_2\text{ZrF}_2/\text{Cp}_2\text{ZrFI}) \approx 340 \text{ M}^{-1} \text{ s}^{-1}$  was estimated for this temperature.

Several additional experiments demonstrate that the greater lability of the F and I complexes versus the Cl and Br complexes is not limited to the dihalides  $\text{Cp}_2\text{ZrX}_2$ . The  $^1\text{H}$  NMR spectrum at  $-40^\circ\text{C}$  of a solution of  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{I}$  and  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$  (each 0.1 *M*) exhibited resolved Cp and  $\text{CH}_3$  peaks for the two compounds, but the peaks broadened as the temperature was raised. From the coalescence of the Me peaks at  $34^\circ\text{C}$  a second order rate constant  $k - 8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  was estimated for ligand exchange. Similarly  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{F}$  and  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Br}$  were found to undergo rapid ligand exchange ( $k - 300 \text{ M}^{-1} \text{ s}^{-1}$  from Me coalescence at  $-0^\circ\text{C}$ ). In contrast ligand exchange between  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$  and  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Br}$  was slow on the NMR time scale. From the lack of significant line broadening in the  $55^\circ\text{C}$   $^1\text{H}$  NMR spectrum of a solution which was  $\sim 0.2 \text{ M}$  in each compound an upper limit of  $30 \text{ M}^{-1} \text{ s}^{-1}$  was estimated for the rate constant for this process at this temperature.

Previously Brubaker and coworkers showed by labeling studies that Cp exchange involving  $\text{Cp}_2\text{ZrCl}_2$  did not occur thermally (refluxing benzene, 72 h) and was slow under photochemical conditions ( $k - 0.01 \text{ M}^{-1} \text{ s}^{-1}$ ) [7]. These results and the fact that the products (e.g.  $\text{Cp}_2\text{ZrClBr}$  from  $\text{Cp}_2\text{ZrCl}_2/\text{Cp}_2\text{ZrBr}_2$ ) and line shape effects (e.g. Me peak coalescence in the  $\text{Cp}_2\text{ZrCH}_3\text{F}/\text{Cp}_2\text{ZrCH}_3\text{I}$  system) observed for many of the exchange reactions studied here can only result from Me and/or X exchange strongly suggest that Cp exchange is unimportant.

In contrast to the facile ligand redistribution reactions of  $\text{Cp}_2\text{ZrMe}_2$ , analogous reactions of  $\text{Cp}_2\text{ZrPh}_2$  were found to be extremely slow. No ligand exchange between  $\text{Cp}_2\text{ZrPh}_2$  and any of the dihalides was observed in sealed tube reactions in THF- $d_8$  even after extended periods at  $55^\circ\text{C}$ . At this temperature there was minor decomposition of  $\text{Cp}_2\text{ZrPh}_2$  to benzene and unidentified Zr products. Also, under similar conditions no ligand redistribution between  $\text{Cp}_2\text{ZrMe}_2$  and  $\text{Cp}_2\text{Zr}(\text{OMe})_2$  was observed.

## Discussion

The rates of ligand redistribution reactions of dicyclopentadienylzirconium(IV) compounds are very sensitive to the nature of the ligands involved. While detailed kinetic studies were not carried out, the experiments discussed above reveal two general trends in the variation of ligand exchange rate as a function of ligand:  $\text{F}, \text{I} > \text{Cl}, \text{Br}$  and  $\text{CH}_3 \gg \text{Ph}$ . The variation of rate with ligand is significantly greater than was observed for the corresponding reactions of the analogous Ti compounds

[4]. For example, the range of half-lives  $t_{1/2}$  observed for the reaction of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  and  $\text{Cp}_2\text{ZrX}_2$  (Table 1) corresponds to a range of rate constants of ca.  $10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) to  $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{X} = \text{F}, \text{I}$ ), a 100 fold variation, whereas the rate constants of the analogous Ti reaction varied only by a factor of 6 [4]. Also, the reactivity of  $\text{Cp}_2\text{ZrPh}_2$  with  $\text{Cp}_2\text{ZrX}_2$  is significantly less than that of  $\text{Cp}_2\text{ZrMe}_2$  whereas little difference in the reactivity of  $\text{Cp}_2\text{TiPh}_2$  and  $\text{Cp}_2\text{TiMe}_2$  was observed [4].

At this point the origin of the trends in ligand redistribution reactivity of dicyclopentadienylzirconium(IV) compounds is obscure. The intriguing rate profile  $\text{F}, \text{I} > \text{Cl}, \text{Br}$  suggests the operation of several mechanisms. The most straightforward mechanism for ligand exchange is one involving an intermediate or transition state with bridging ligands similar to the ground state structures of  $\text{AlR}_n\text{X}_{3-n}$ ,  $[\text{Cp}_2\text{TiX}]_2$  and  $[(\text{C}_5\text{H}_4\text{CH}_3)_2\text{ZrH}(\mu\text{-H})]_2$  [8]. Such a mechanism is presumed to be operative in ligand redistribution reactions of  $\text{BR}_n\text{X}_{3-n}$  compounds [9]. The greater reactivity of the halide complexes  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{X}$  and  $\text{Cp}_2\text{ZrX}_2$  (which can bridge through X non-bonded electron pairs) versus  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  and  $\text{Cp}_2\text{ZrPh}_2$  is consistent with this mechanism. The low reactivity of  $\text{Cp}_2\text{ZrPh}_2$  versus that of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  may be due to steric inhibition of Ph bridging [10] or to the presumably greater strength of the Zr-Ph bond versus the Zr-CH<sub>3</sub> bond [11].

While ligand bridged intermediates are attractive, radical and ionic processes cannot be ruled out. For the titanium redistribution reactions Puddephatt and Stalteri proposed an electron-transfer mechanism involving a radical pair intermediate such as  $[\text{Cp}_2\text{TiR}_2]^+ [\text{Cp}_2\text{TiX}_2]^-$  which undergoes either ligand exchange or loss of RH [4]. Erker et al. have provided evidence that the photochemical disproportionation of  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})(\text{CHCHPh})$  to  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  and  $\text{Cp}_2\text{Zr}(1,4\text{-diphenylbutadiene})$  proceeds by a radical chain mechanism [1].  $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{CHCHPh})$  reacts similarly without photolysis [1]. Ligand redistribution between  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Cp}_2\text{Zr}[\text{Ru}(\text{CO})_2\text{Cp}]_2$  to give  $\text{Cp}_2\text{Zr}(\text{Cl})\text{Ru}(\text{CO})_2\text{Cp}$  seems likely to proceed through an ionic or electron transfer mechanism as  $\text{CpRu}(\text{CO})_2^-$  is expected to be a poor bridging ligand [12].

Alkyldicyclopentadienylzirconium halides  $\text{Cp}_2\text{ZrRX}$  are useful precursors to a variety of interesting mononuclear and dinuclear compounds [4,13].  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$  is commonly prepared by reaction of  $[\text{Cp}_2\text{ZrCl}]_2\text{O}$  with  $\text{AlMe}_3$  [5] but this compound and analogues can also be prepared by treatment of  $\text{Cp}_2\text{ZrX}_2$  with 1 equivalent of the appropriate Li or Grignard reagent [13a,14], or by olefin hydrozirconation [13c]. The redistribution reaction eq. 2 provides an alternate route to the series  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).

### Experimental

All operations were performed using standard Schlenk or vacuum line techniques under an atmosphere of purified N<sub>2</sub> or Ar, or under vacuum. NMR spectra were recorded on JEOL FX-90Q and Nicolet 200 instruments. IR spectra were recorded on a Perkin-Elmer 283 instrument. Mass spectra were recorded on VG-7070 in EI mode. THF-*d*<sub>8</sub> was purified by vacuum transfer from Na/benzophenone.

$\text{Cp}_2\text{ZrCl}_2$  was purchased from Alfa.  $\text{Cp}_2\text{ZrF}_2$  [6],  $\text{Cp}_2\text{ZrBr}_2$  [6],  $\text{Cp}_2\text{ZrI}_2$  [6],  $\text{Cp}_2\text{ZrCH}_3\text{Cl}$  [5],  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  [15] and  $\text{Cp}_2\text{Zr}(\text{Ph})_2$  [15] were prepared by literature methods or as described below. All compounds were purified by recrystallization and/or sublimation prior to use.

*NMR tube experiments.* An NMR tube containing the solid reactants was attached via a valved adapter to a vacuum line and evacuated. THF- $d_8$  (ca. 0.4 ml) was vacuum transferred into the tube which was sealed off with a torch.

Rate constants were calculated from NMR lineshape changes by standard methods [6]. The method of Shanan-Atidi and Bar-Eli was used for the calculation of rate constants from the coalescence of unequal doublets [16b]. The uncertainty in these estimated rate constants is ca.  $\pm 20\%$  and is primarily due to uncertainties in concentrations.

Values for  $K_{eq}$  are averages of 2 or more runs. It was necessary to keep the mole ratio of the reactants approximately 1/1 in order for  $[Cp_2ZrMe_2]$  and  $[Cp_2ZrX_2]$  to be measurable at equilibrium.

*Dicyclopentadienylzirconium difluoride,  $Cp_2ZrF_2$ .*  $HBF_4 \cdot Et_2O$  1.09 ml (8.05 mmol) was added via syringe to a solution of  $Cp_2Zr(CH_3)_2$  (2.02 g, 8.05 mmol) in 50 ml ether at  $-78^\circ C$ . The reaction mixture was warmed to  $0^\circ C$  at which point gas evolution and the formation of a white precipitate occurred. The reaction was further warmed to room temperature for 5 min, then cooled to  $0^\circ C$  and filtered yielding white solid  $Cp_2ZrF_2$  which was washed with cold ether and dried under vacuum. Sublimation at  $150^\circ C$  gave spectroscopically pure product (1.4 g, 67%).

*Dicyclopentadienylmethylzirconium iodide,  $Cp_2Zr(CH_3)I$ .* A solution of 0.51 g (2.0 mmol)  $Cp_2Zr(CH_3)_2$  and 0.97 g (2.0 mmol)  $Cp_2ZrI_2$  in ca. 20 ml THF was stirred at room temperature for 48 h. The solution was filtered and the filtrate evaporated. The residue was recrystallized from toluene/hexane to give yellow crystalline  $Cp_2Zr(CH_3)I$  (1.3 g, 90%).  $^1H$  NMR (THF- $d_8$ ):  $\delta$  6.35 (s, 10H),  $-0.23$  ppm (s, 3H);  $^{13}C$  NMR (THF- $d_8$ ):  $\delta$  113.4 (Cp), 38.5 ppm ( $CH_3$ ,  $J(^{13}C-^1H)$  120 Hz from gated decoupled spectrum); MS:  $m/e$  362 ( $M^+$ ), 347 ( $M^+ - CH_3$ , base peak); IR: (CCl<sub>4</sub>) [17]: 3100 m, br, 2920 s, 2861 m, 2800 vw, 2775 w, 2720 w, 1815 w, br, 1720 w, br, 1625 w, br, 1440 s, 1410 m, 1130 w, 1065 w, 1010 vs, 905 w, 805 vs  $cm^{-1}$ .

*Dicyclopentadienylmethylzirconium bromide,  $Cp_2Zr(Me)Br$*  was prepared in comparable yield by the same procedure as described for  $Cp_2Zr(CH_3)I$  except that the reaction mixture was heated to reflux for 48 h.  $^1H$  NMR (THF- $d_8$ ):  $\delta$  6.27 (s, 10H), 0.87 ppm (s, 3H);  $^{13}C\{^1H\}$  NMR (THF- $d_8$ ):  $\delta$  113.5 (Cp), 34.1 ppm ( $CH_3$ ,  $J(^{13}C-^1H)$  121 Hz from gated decoupled spectrum); MS:  $m/e$  299 ( $M^+ - CH_3$ ); IR: (CCl<sub>4</sub>) [17]: 3100 m, br, 2925 s, 2865 m, 2800 vw, 2781 w, 2720 vw, 1820 w, br, 1720 m, br, 1628 m, br, 1441 s, 1410 m, 1130 w, 1062 w, 1011 vs, 905 w, 805 vs  $cm^{-1}$ .

*Dicyclopentadienylmethylzirconium fluoride  $Cp_2Zr(Me)F$*  was prepared in comparable yield by the same procedure as described for  $Cp_2Zr(CH_3)I$ .  $^1H$  NMR (THF- $d_8$ ):  $\delta$  6.17 (s, 10H), 0.17 ppm (s, 3H);  $^{13}C\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  112.0 (Cp), 24.5 ( $CH_3$ ,  $J(^{13}C-^1H)$  119 Hz from gated decoupled spectrum); MS:  $m/e$  239 ( $M^+ - CH_3$ , base peak); IR: (CCl<sub>4</sub>) [17] 3100 m, br, 2921 s, 2867 s, 2810 vw, 2784 m, 2720 w, 1810 w, br, 1710 w, br, 1610 w, br, 1440 s, 1410 m, 1160 w, 1060 vw, 1010 vs, 800 vs, 561 vs  $cm^{-1}$ .

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- 17 Bands at ca. 2720 and ca. 2800  $\text{cm}^{-1}$  appear to arise from a 1365  $\text{cm}^{-1}$  (Raman s, IR w) overtone and a 1365 plus 1436  $\text{cm}^{-1}$  (Raman s, IR s) combination, respectively. Similar though weaker bands are observed in the IR spectra of  $\text{Cp}_2\text{ZrX}_2$  and  $\text{Cp}_2\text{ZrMe}_2$ . The band at ca. 2780  $\text{cm}^{-1}$  is only observed for the methyl compounds and is attributed to a 1365  $\text{cm}^{-1}$  plus 1410  $\text{cm}^{-1}$  (Raman m, IR m) combination. The intensities of the bands at 2720, 2780 and 2800  $\text{cm}^{-1}$  are insensitive to solvent.