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Preliminary communication

MONOCYCLOPENTADIENYL ZIRCONIUM(IV) COMPLEXES

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Summary

$CpZrCl_3 \cdot DME$ (I, Cp = η^5-C_5H_5, DME = 1,2-dimethoxyethane) has been synthesized by reaction of sublimed $ZrCl_4$ and TlCp in DME in 2:1 mole ratio (sublimation of the $ZrCl_4$ is essential). Alternatively, unsolvated, insoluble and presumably polymeric $CpZrCl_3$ is selectively produced by photolysis of Cp_2ZrCl_2 in Me_3CCl. The crystal structure of compound I shows axial-equatorial coordination of the DME ligand. The latter is easily displaced by tetramethylethylenediamine. In contrast to the above results, $CpTiCl_3$ may be recrystallized from DME with no coordination of solvent to titanium.

Compounds of the early transition elements often display high reactivity towards otherwise unreactive substrates. Our earlier work [1] on deoxygenation (e.g. reductive coupling of ketones to olefins) with reduced titanium species provided evidence that two cyclopentadienyl ligands may have a detrimental effect on metal complex reactivity relative to a single ring. In pursuing this idea, we sought a convenient route to $CpZrCl_3$ (or derivatives thereof) on a synthetically useful scale.* We report here the results of our synthetic explorations, a structural and dynamic study of $CpZrCl_3(MeOC_2H_4OMe)$, and an indication of its Lewis acidity relative to that of $CpTiCl_3$.

Given the general availability of Cp_2ZrCl_2, we sought to convert this to $CpZrCl_3$. The most promising procedure involves "exchange" of one Cp ring with one halogen. While trace yields of $CpZrCl_3$ are detectable upon irradiation of Cp_2ZrCl_2 in neat CH_2Cl_2, $CHCl_3$ and CCl_4, this method suffers from an inability to control the extent of reaction and (in the case of CCl_4) the low sol-

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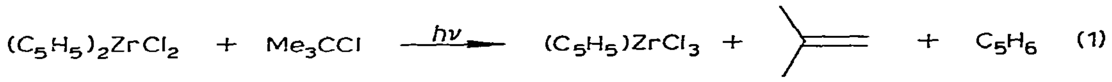
*A previous synthesis, from $MgCp_2$ and $ZrCl_4$ [2], has been reproduced more recently [3]. There is also a patent claim [4] on the use of $Me_3SiC_5H_5$, which has been utilized recently [5].

ubility of Cp_2ZrCl_2 ; the use of more controlled amounts of chlorocarbon in an inert solvent did not materially improve the situation.

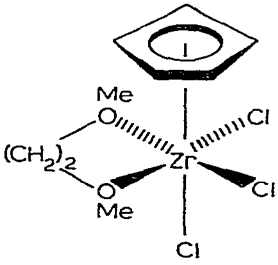
Reasoning that it is necessary to provide for the emerging $C_5H_5^{\cdot}$ radical in this synthetic procedure, we employed t-butyl chloride as an "exchange reagent". Homolysis of t-BuCl produces not only the needed $Cl^{\cdot}$, but also a highly reducing ($H^{\cdot}$ donor) t-butyl radical; C_5H_6 and isobutylene are the expected coproducts (eq. 1).



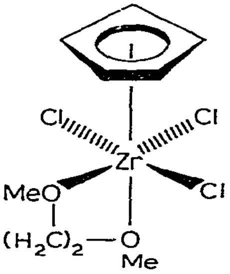
(1)

In fact, this is a rapid and moderately useful procedure for producing $CpZrCl_3$, irradiation being effected by a medium pressure mercury lamp, or even sunlight, through Pyrex. Isobutene is readily detected in the neat t-BuCl reaction medium by proton NMR. The unsolvated $CpZrCl_3$ produced by eq. 1 is insoluble in benzene and chloroform, from which we infer an oligomeric or polymeric structure.

We find the more obvious synthesis of $CpZrCl_3$ from $ZrCl_4$ and limited quantities of NaCp to be disappointing. Even at —78° C, slow addition of one mole of a NaCp solution to two moles of $ZrCl_4$ yields Cp_2ZrCl_2 as the major product; only a small Cp resonance of solvated $CpZrCl_3$ is evident in the reaction solution*. However, reaction of freshly sublimed $ZrCl_4$ with $Tl(C_5H_5)$ (2:1 mole ratio) in 1,2-dimethoxyethane (DME) at 0° C gives $CpZrCl_3(DME)$** free of any Cp_2ZrCl_2. This adduct undergoes substantial decomposition on sublimation at 10^{-5} mmHg and 145° C, but the sublimed material retains one DME ligand per zirconium. Neither of the structural isomers I or II is consistent with the singlet methyl and methylene resonance observed for $CpZrCl_3(DME)$. However, the observation that added free DME exchanges rapidly with coordinated DME (^1H NMR, 25° C, $CDCl_3$ solvent) suggests intermolecular lability. This process, as well as possible intramolecular rearrangements, dictates that ^1H NMR (at 25° C) will not be structurally diagnostic.



(I)



(II)

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*Equally ineffective is attempted comproportionation of Cp_2ZrCl_2 and $ZrCl_4$, at a reflux in DME or even catalyzed by Mg or sodium naphthalide.

**^1H NMR ($CDCl_3$) δ: 6.69 ppm (5H, C_5H_5), 4.17 ppm (4H, CH_2), 3.93 ppm (6H, CH_3).

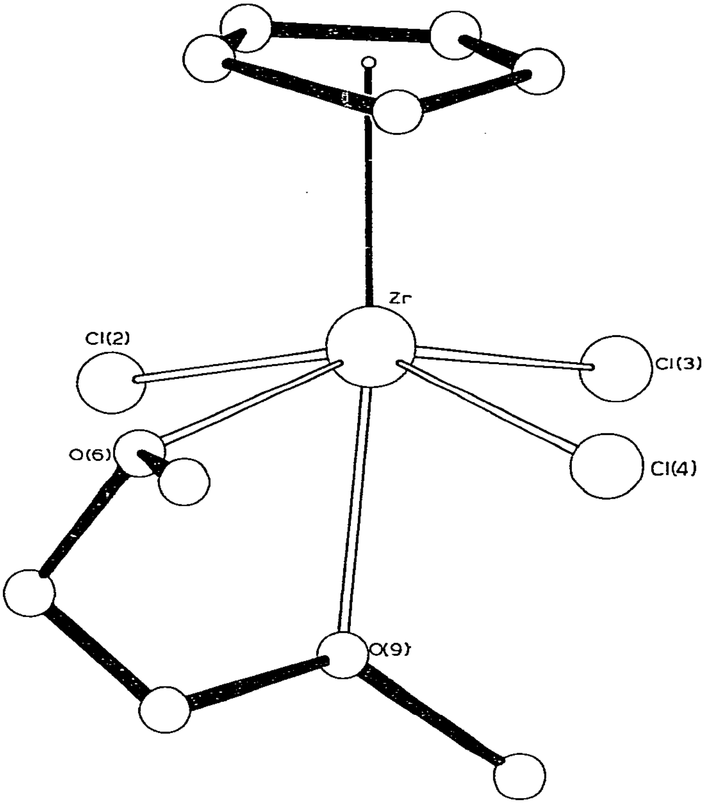

Fig. 1. ORTEP drawing of (η^5-C_5H_5)$ZrCl_3$($MeOC_2H_4OMe$). Selected bond lengths: Zr—Cl(2) = 2.468(3) Å, Zr—Cl(3) = 2.438(3) Å, Zr—Cl(4) = 2.487(3) Å, Zr—O(6) = 2.26(1) Å, Zr—O(9) = 2.37(1) Å, Mean Zr—C(Cp) = 2.55(2) Å.

The crystal structure* of $CpZrCl_3$(DME), Fig. 1, shows that only isomer II is present in the solid state**. The metal is displaced 0.54 Å out of the plane of the three chlorine atoms and the equatorial oxygen, suggesting that isomer II may be preferred for steric reasons (two ether methyl groups interact unfavorably with the Cp ring in I). $CpZrCl_3$(DME) thus exhibits the same isomer preference as that of (C_5H_4Me)UCl_3(THF)$_2$ and also (C_5H_4Me)UCl_3(DME) [6].

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*Crystallographic data (—163°C): a = 13.500(4) Å, b = 7.767(2) Å, c = 13.709(4) Å; β = 114.04(1)°; Z = 4 in space group $P2_1/c$; $R(F)$ = 0.083, $R_w(F)$ = 0.109 for 1859 observed ($F > 3\sigma(F_o)$) reflections using anisotropic thermal parameters for all non-hydrogen atoms. A complete tabulation of crystallographic parameters is available as Molecular Structure Center Report No. 81010, available from the Chemistry Library, Indiana University.

**Anisotropic refinement of the data shows that a small (10°) rotational disorder exists throughout the coordination sphere (three Cl, five Cp carbons, the two oxygens, but not zirconium, which is the effective molecular center of mass). This general rotational disorder, which is more complex than the rotational disorder common with Cp rings, appears to be imposed by a (minimally) two-fold disorder of the Zr(DME) ring and its associated methyl groups. That is, the non-planar five-membered ring adopts several puckered conformations of comparable energy, but the pendant methyl groups of each conformer pack in the crystal in a way which forces a small rotational displacement of the $CpCl_3O_2$ unit. While this precludes any detailed analysis of bond length trends in $CpZrCl_3$(DME), the X-ray work does define the solid state structure unequivocally. We are currently working to prepare another base adduct of $CpZrCl_3$ more suitable for an accurate X-ray study.

Preliminary work shows that tetramethyl ethylenediamine (TMEDA, 4 equivalents) quantitatively displaces DME from $CpZrCl_3(DME)$, even in neat DME. The isolated $CpZrCl_3(TMEDA)$ does not exchange with free TMEDA and is stereochemically rigid (^1H NMR, 25° C); it exists in only one isomeric form (in $CDCl_3$). However, the observation of two methyl resonances and an AA'BB' pattern for the methylene protons is consistent with either structures analogous to I or II. The relative ligand labilities of DME and TMEDA on $CpZrCl_3$ run counter to the usual trend for early transition metals.

In an effort to rank qualitatively the Lewis acidity of $CpTiCl_3$ and $CpZrCl_3$, we have recrystallized the former from neat 1,2-dimethoxyethane. The resulting crystalline material was filtered and allowed to dry at 1 atm N_2 in a glove box. The crystals, which remained transparent after such drying, showed no resonances of DME (free or coordinated) when analyzed by ^1H NMR in $CDCl_3$. This quantitative "rejection" of DME by $CpTiCl_3$ demonstrates the higher acidity of $CpZrCl_3$ and thus the higher utility of the latter for substrate activation and transformation.

Acknowledgment

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