Repetitive Intramolecular Substitution (with Inversion) at Carbon: a New Type of Fluxional Process for an Organometallic Complex

By KERRIE I GELL, GREGORY M WILLIAMS, and JEFFREY SCHWARTZ*
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08544)

Summary $Cp_2(Cl)Zr_AOC(1)HRZr_B(Cl)Cp_2$ (Cp = cyclopentadienyl) undergoes a fluxional process which exchanges the O– and C–bonds to Zr_A and Zr_B, respectively, and proceeds by an inversion at C(1)

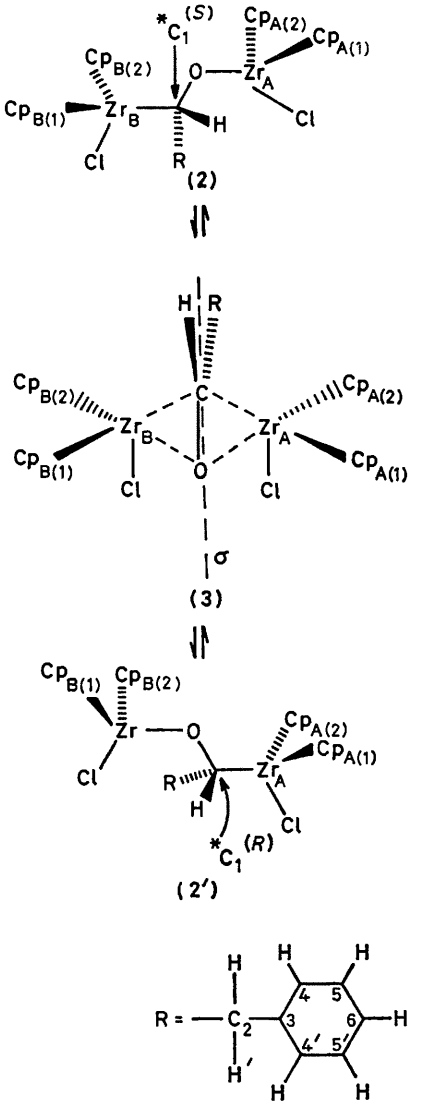
IN conjunction with model studies for the reduction of CO by organometallic complexes, we recently reported[1] reduction of the acylzirconium(IV) complex (**1**) by Cp_2ZrHCl (Cp = cyclopentadienyl) to give the binuclear species (**2**) N m r

$$Cp_2Zr(COR)Cl + Cp_2Zr(H)Cl \rightarrow Cp_2(Cl)Zr(OCHR)Zr(Cl)Cp_2$$
(**1**) (**2**)

$$R = \overbrace{CH_2[CH_2]_4CHCH_2}-$$

spectral studies revealed that (**2**) underwent a fluxional process in which the mode of bonding of the organic ligand (through oxygen or through carbon) to the two different metal centres is exchanged Whereas a similar observation had been reported for $Cp_2Zr(Cl)OCH_2Zr(Cl)Cp_2$,[2] the

presence of the chiral centre in (**2**) has permitted the elucidation of this fluxional pathway. The exchange occurs by a repetitive formal inversion at the chiral carbon centre and represents a new type of fluxional process for an organometallic system.



SCHEME

The pairs of ligands $Cp_{A(1)}$, $Cp_{A(2)}$ and $Cp_{B(1)}$, $Cp_{B(2)}$ (Scheme) are diastereotopic because of the chiral centre at C(1) of the alkoxy-group. At low temperature four sharp singlets for these ligands are thus seen in both the ^1H (Figure 1) and $^{13}C\{^1H\}$ n.m.r. spectra of (**2**). The downfield pair of singlets in the ^1H n.m.r. spectrum (δ 6·12, 6·04; $Cp_{A(1)}$, $Cp_{A(2)}$) are assigned to the Cp ligands on the Zr bound to oxygen, and the upfield pair (δ 5·76, 5·73; $Cp_{B(1)}$, $Cp_{B(2)}$) are assigned to the Cp ligands on the Zr bound to carbon. These assignments are based on numerous observations that, in aromatic solvents, Cp ligands in $Cp_2Zr(OR)Cl$ complexes (R = alkyl) have chemical shifts δ *ca.* 6·0,[3] whereas $Cp_2Zr(R')Cl$ complexes (R′ = alkyl) have Cp chemical shifts of *ca.* 5·75—5·8.[4] These signals for the Cp ligands coalesce at *ca.* 15 °C ($\Delta G_c^{\ddagger}$ = *ca.* 14·7 kcal mol^{-1}) and in the high-temperature limit appear as two sharp singlets (Cp′, Cp″) centred on δ 5·94 (6 Hz separation). Because the signals for $Cp_{A(1)}$ and $Cp_{B(1)}$ collapse to Cp′, and those for $Cp_{A(2)}$ and $Cp_{B(2)}$ collapse to Cp″, the fluxional process in (**2**) must cause the two Zr centres (Zr_A, Zr_B) to become equivalent (see Scheme). As well, the process must be stereospecific at each Zr centre and at the chiral centre C(1). Non-stereospecific displacement at either C(1) or at Zr would cause all of the Cp ligands of (**2**) to become equivalent, an effect not observed even at temperatures up to 80 °C.

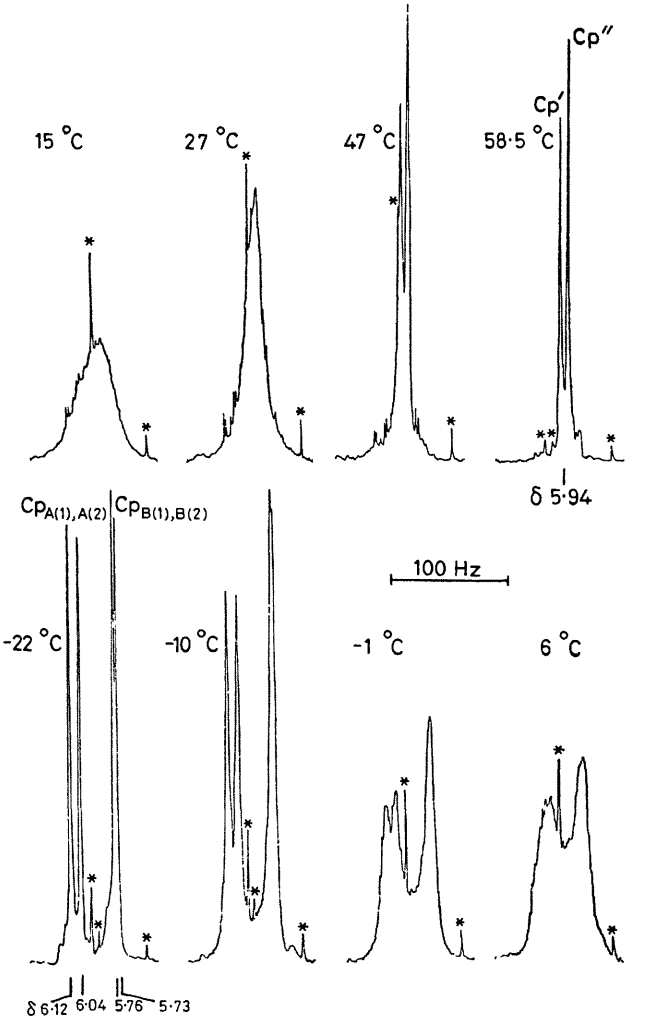


FIGURE 2

Although several combinations of stereospecific displacements are possible, evidence exists for a mechanism which proceeds with inversion at C(1) *and* retention at Zr_A and Zr_B. Such a mechanism is illustrated (Scheme) for (**2**) in a conformation (*cis*-chlorides) in which the steric interaction of the cyclohexanemethyl group with the Cp ligands is minimal.

Although the ^1H n.m.r. resonances of the diastereotopic protons 2-H and 2′-H are obscured by the protons of the

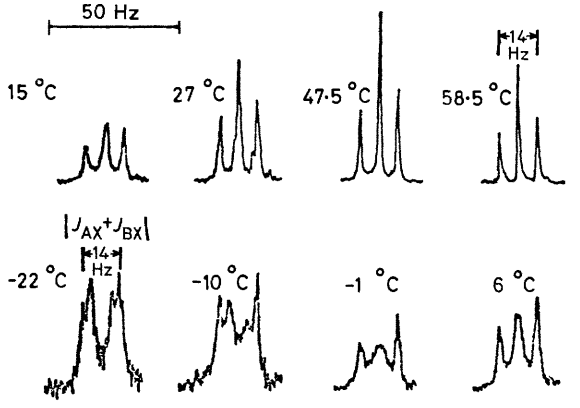


FIGURE 3

cyclohexyl group, their temperature-dependent behaviour can be inferred from the temperature dependence of the ^{1}H n m r signal for 1-H In the low-temperature limit, the resonance for 1-H is a broadened doublet forming the X-portion of an ABX system (2-H, 2′-H = A,B) (Figure 2) This doublet collapses to a simple 1 : 2 . 1 triplet in the high temperature limiting spectrum Throughout this process the average value of the vicinal coupling constant (J_{obs} = $\frac{1}{2}$ | J_{AX} + J_{BX} | = 7 Hz) does not change, implying that rotational averaging is not responsible for the collapse of the signal for 1-H to a triplet Inversion at C(1), however, accomplishes this collapse by causing 2-H and 2′-H to become equivalent (ABX → A_2X)

^{13}C N m r data provide additional support for this 'equivalencing' mechanism In the low-temperature limit, the diastereotopic carbons C(4) and C(4′) of the cyclohexyl ring appear as two singlets† which coalesce at high temperature These carbons are caused to become equivalent by inversion at C(1) Variable-temperature ^{13}C n m r studies revealed a coalescence temperature of 22 °C ($\Delta G_C^{\ddagger}$ = *ca* 14 6 kcal mol^{-1}) Thus, only one process appears to be responsible for the interconversion of the Cp ligands and of the ring carbons The intermediate in this fluxional process (**3**) has a single mirror plane which contains the chiral carbon centre Since the fluxional process involves passage of this carbon centre through the mirror plane, a formal inversion of configuration at carbon occurs We suggest that the bonding pattern in (**3**) resembles that of the η^2-carbonyl unit in monomeric acylzirconium(IV) complexes[5] and can also be compared with the bonding of the ethylene unit in [{$Cp_2(Et_3AlCl)Zr$}$_2$-μ-(CH_2CH_2)] [6]

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† C(5) and C(5′) are also diastereotopic It is of no consequence to the argument whether the two observably different singlets are assigned to C(5), C(5′) or to C(4), C(4′) However, C(4) and C(4′) are closer to the asymmetric centre C(1) than are C(5), C(5′) and may be expected to differ more markedly in chemical shift

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