Ring 'Flipping' in Bis(cyclo-octatetraene)titanium(II); an Organometallic Intramolecular Redox Reaction which involves only the Geometrical Deformation of Organic Ligands

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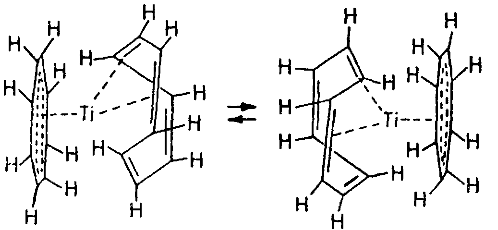
Summary A new type of fluxional process for an organometallic system is described for $(C_8H_8)_2Ti$ in which formal oxidation and reduction occurs for the planar and bent C_8H_8 ligand rings, respectively, solely through reciprocal ring bending and flattening, with an activation energy, at 63°, of $\Delta G^{\ddagger} = 16{\cdot}7 \pm 0{\cdot}2$ kcal/mol.

We report herein the observation of a new type of fluxional process which can occur in complexes of cyclo-octatetraene (C_8H_8). Crystal-structure data indicate non-equivalent metal–ring bonding with one planar and one bent C_8H_8 ring in $(C_8H_8)_2Ti$,[1] (**1**) or in $(C_8H_8)_2Zr(thf)$.[2] Neutral C_8H_8 is bent[3] and $C_8H_8{}^{2-}$ is planar.[4] Formal oxidation states for metal and ligands in complexes of C_8H_8 can therefore be assigned on the basis of this convention for compounds in which the ring geometry is known. For systems such as (**1**), an intramolecular redox reaction can be envisioned, therefore, in which the formal transfer of two electrons from one C_8H_8 ring to the other involves solely the reciprocal flipping of these two rings [see equation (1)]. We have studied the n.m.r. spectrum of (**1**) as a function of temperature, concentration, and other added reagents, and observe therein this redox reaction.

$$(\mathbf{1}) \rightleftarrows (\mathbf{1'})$$

In a typical experiment, (**1**) (deep red crystals) was synthesised[5] from $C_8H_8{}^{2-}$ [prepared in dimethoxyethane (DME)] and $TiCl_4$ in refluxing benzene,† recrystallized from benzene–hexane, washed well with hexane, and dried *in vacuo*. The n.m.r. spectrum of (**1**) was then measured in C_6D_5Cl,† or C_6D_5Cl containing a known amount of C_8H_8 or DME, in n.m.r. tubes sealed *in vacuo*. At −30°, the n.m.r. spectrum‡ showed two sharp singlets, each 0·38 Hz wide, of equal intensity, 50 and 90 Hz upfield from internal benzene standard. At 63°, coalescence occurred and, at 123°, the spectrum displayed only a sharp singlet 70 Hz upfield from the benzene signal. The temperature-dependent line broadening, between −30 and 63°, was the same for both singlets and was reproducible under conditions of increasing or decreasing temperature. The broadening was independent of the concentration of (**1**), added DME, or added C_8H_8. When C_8H_8 was added to a solution of (**1**), a



(1)

(1) (1′)

$C_8H_8{}^{2-}$ C_8H_8 C_8H_8 $C_8H_8{}^{2-}$

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† All solvents were dried by distillation, under argon, from calcium hydride (hydrocarbons) or sodium benzophenone ketyl (DME). All operations were performed under argon with rigorous exclusion of air and moisture.

‡ N.m.r. spectra were recorded at 60 MHz on a Varian A-60A spectrometer equipped with a temperature programming control.

new signal, 4 Hz upfield from the high-field singlet of (**1**) (at −30°) was observed which did not broaden with increasing temperature. Free C_8H_8 is not, therefore, involved in the observed exchange process. The activation energy, $\Delta G^{\ddagger} = 16{\cdot}7 \pm 0{\cdot}2$ kcal/mol,§ for the redox process (at 63°) calculated from the n.m.r. data is comparable with those reported[6] for ring inversion of C_8H_8 and of substituted C_8H_8 derivatives. Because of viscosity and solubility effects, it was not possible to study the n.m.r. spectrum of (**1**) below −30° in pure C_6D_5Cl. We are attempting to freeze out the instantaneous structure of the complex by using mixed solvent systems at low temperatures. We are also studying the temperature dependent n.m.r. spectra of $(C_8H_8)_2$Zr[2,7] and $(C_8H_8)_2$Hf.[8,10]

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§ $\Delta G^{\ddagger}$ at coalescence was calculated from $k_c = (\pi/\sqrt{2})\Delta\nu_{AB}$ and from the Eyring equation. A transmission coefficient, $\kappa = 1$, was assumed. For a discussion of the accuracy of $\Delta G^{\ddagger}$ calculation by this technique, see W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6205.

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