and the kinetics are consistent with a bridged mechanism involving chelation of Fe^{2+} prior to electron transfer

$$\mathrm{RoL} + \mathrm{Fe}^{2+} \overset{K}{\rightleftharpoons} \mathrm{RoLFe}^{2+} \xrightarrow{k_1} \mathrm{Co}^{\mathrm{II}} + \mathrm{Fe}^{\mathrm{III}}\mathrm{L} \qquad (2)$$

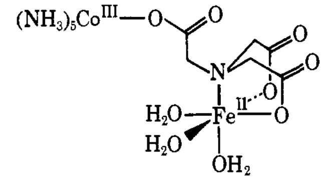
$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Co}^{\mathrm{III}}] = k_1[\mathrm{RoLFe}^{2+}] = \frac{k_2[\mathrm{Fe}^{\mathrm{II}}][\mathrm{Co}^{\mathrm{III}}]}{1 + \{\mathrm{H}^+\}^2/K_{\mathrm{a1}}K_{\mathrm{a2}} + \{\mathrm{H}^+\}/K_{\mathrm{a2}} + K[\mathrm{Fe}^{\mathrm{II}}]} \qquad (3)$$

where

$$k_2 = k_1K \qquad (4)$$

The term "1" in the denominator of eq 3 is negligible under all the conditions used. At low pH, with ferrous ion in moderate (*ca.* 20-fold) excess over cobalt(III), the reaction is pseudo-first order in $[Fe^{II}]$. We observe $k_2 = 1.0 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ at 25°, ionic strength 1.0 M ($NaClO_4$), confirming that the polydentate ligand greatly facilitates electron transfer (*cf.* $L = Cl^-$, $k_2 = 1.35 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$; $L = C_2O_4^{2-}$, $k_2 = 0.43\ M^{-1}\ \mathrm{sec}^{-1}$.[6,7] At higher ferrous concentrations and at the upper end of the pH range the rate approaches a limit, as required by eq 3; whence $K = 1.1 \times 10^6\ M^{-1}$ and $k_1 = 9.4 \times 10^{-2}\ \mathrm{sec}^{-1}$, corresponding to a lifetime of about 10 sec.

The formation constant, K, of the binuclear complex is comparable with that of the N-methyliminodiacetatoiron(II) complex ($4.5 \times 10^6\ M^{-1}$ at 20° in 0.1 M KCl[8]), suggesting the presence of two chelate rings; and the spectrum from 300 to 760 nm shows only the characteristic bands of the pentaamminecobalt(III) and iron(II) chromophores, so that there is little doubt that the oxidation states are as shown. Hence we favor structure I for the predominant form of the intermediate, which could be described as an outer-sphere association complex of cobalt(III) and iron(II), in which the two metal ions also happen to be linked by a "nonconducting" carbon–nitrogen chain. It does not follow, however, that the electron is transferred directly across the intervening space; a carboxyl-bridged transition state (II), formed by rapid elimination of H_2O, is equally consistent with the data.



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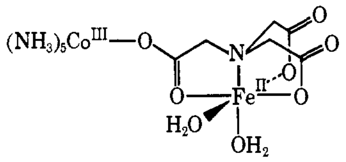

II

Further work on reactions with other divalent metals is in progress.

Acknowledgments. This research was supported by a grant-in-aid from the Royal Society (London). One of us (J. G.) holds an SRC Research Studentship.

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Rapid Interchange of *Monohapto*- and *Pentahapto*cyclopentadienyl Rings in Tetracyclopentadienyltitanium

Sir:

The first molecule containing both an (h^1-C_5H_5) and an (h^5-C_5H_5) group attached to the same metal atom to be studied as a function of temperature by nmr spectroscopy was (h^5-C_5H_5)$Fe(CO)_2$(h^1-C_5H_5).[1] It was shown that the (h^1-C_5H_5) ring is fluxional and all available evidence[2] strongly favors 1,2 shifts as the predominant rearrangement pathway. However, no indication of interchange of the two rings has been seen, even up to temperatures of ~125°, where decomposition becomes rapid.[3] This may be attributed to the fact that no suitable transition state involving two equivalent rings, each having a relationship to the metal atom intermediate between (h^1-C_5H_5) and (h^5-C_5H_5), can be achieved at low activation energy, owing to the lack of available empty orbitals on the iron atom, which has the formal 18-electron configuration. Nor is there any other case in which a genuine (h^1-C_5H_5)–(h^5-C_5H_5) interchange has been observed.[4]

We now wish to report the first such observation with full, though preliminary, documentation.

The three compounds $(C_5H_5)_4M$, M = Ti,[6] Zr,[7] and Hf,[8] have all previously been reported. The Zr and Hf compounds exhibit a single, sharp pmr signal at room temperature and no broadening has been observed at the lowest accessible temperatures[9] (~ −150°), nor have we succeeded in obtaining suitable crystals for X-ray study. Hence the structural and dynamical properties of these molecules remain undefined though there is a strong probability that very rapid interchange of different ring types occurs.

Tetracyclopentadienyltitanium has now been well characterized structurally and dynamically. The compound crystallizes in the hexagonal system, and systematic absences indicate one of the enantiomorphous space groups $P6_122$ or $P6_522$. The unit cell dimensions are: $a = b = 9.214$ and $c = 31.895$ Å. A unit cell

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(1) M. J. Bennett, F. A. Cotton, A. Davidson, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

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(4) The ring interchange in $(C_5H_5)_3MoNO$ is a special case, since two of the rings have a very unusual relationship to the metal[5] quite different from the regular (h^5-C_5H_5)M geometry, and it is easy to believe that this predisposes them toward facile interchange with the h^1-C_5H_5 ring.

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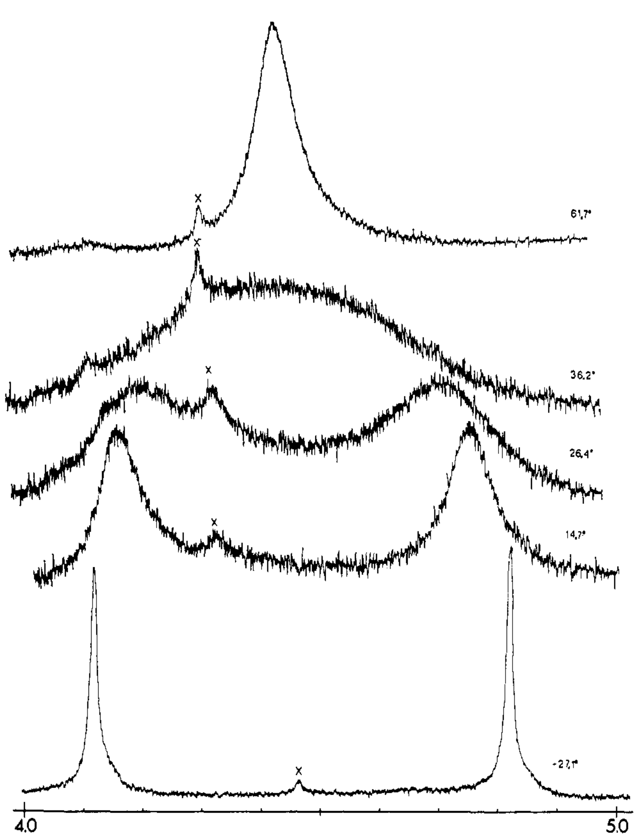
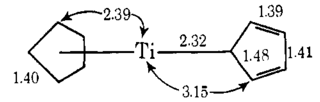


Figure 1. The pmr spectra of $(C_5H_5)_4Ti$ at several temperatures. The intermediate spectra were run at higher gain.

volume of 2345 Å^3 and $Z = 6$ give ρ_{calcd} of 1.31 g/cm^3 (the great reactivity of the compound prevented us from determining the density experimentally). The integrated intensities of 1205 reflections, including 384 Friedel pairs (*i.e.*, 821 Laue-independent reflections), within the sphere $\theta \leq 65°$ were measured on a General Electric XRD-5 manual diffractometer using nickel-filtered copper radiation and a θ–2θ scan technique. The structure was solved by a combination of Patterson, Fourier, and least-squares calculations. At the present stage of refinement, by using isotropic temperature factors and the space group $P6_122$, the conventional R factor is 0.139. Though further refinement is needed for meaningful discussion of the finer details, the structure unambiguously contains $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$ molecules lying on twofold axes. The following average distances (in ångströms with esd's of ~0.02 Å) are pertinent.



The pmr spectra[10] at several temperatures in $C_6D_5CD_3$ solution are shown in Figure 1. The two lines at lower temperatures are due to the fluxional h^1-C_5H_5 rings (τ 4.12) and the h^5-C_5H_5 rings (τ 4.82). Studies at lower temperatures are being conducted in other solvents to examine the h^1-C_5H_5 rearrangement process. As the temperature rises, these two lines collapse and merge, clearly proving that ring interchange occurs. The Arrhenius parameters are $E_a = 16.1 \pm 0.3$ kcal/mol and $\log A = 13.5 \pm 0.5$.

The relatively facile occurrence of $(h^1\text{-}C_5H_5)$–$(h^5\text{-}C_5H_5)$ interchange in this compound may be attributed to the formal 16-electron configuration, which means that the metal atom possesses an empty orbital. This orbital can be employed in binding two rings which are initially $(h^5\text{-}C_5H_5)$ and $(h^1\text{-}C_5H_5)$ in an equivalent fashion, very likely similar to the binding of the two non-$(h^1\text{-}C_5H_5)$ rings in $(C_5H_5)_3MoNO$, thus affording a suitable, low-energy transition state.[11]

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[10] The peak marked X, which has been erroneously attributed[6b] to $(C_5H_5)_4Ti$, is due to $(C_5H_5)_3TiCl$. This molecule, presumably $(h^5\text{-}C_5H_5)_2(h^1\text{-}C_5H_5)TiCl$ is also fluxional, and a broad study of this and other $(C_5H_5)_3TiX$ molecules is in progress.

[11] This work was supported by the National Science Foundation and the Petroleum Research Fund.

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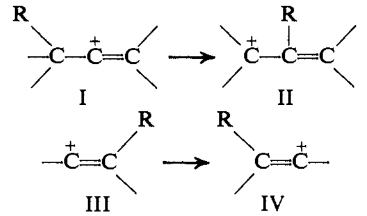
Received April 25, 1970

Rearrangements Involving Simple Vinyl Cations Generated by Solvolysis[1]

Sir:

One of the best indications of the intermediacy of carbonium ions in a reaction is the observation of rearranged products. Although excellent evidence has been presented that the solvolysis of simple alkyl substituted vinyl triflates can in some cases lead to vinyl cations,[2] we wished to confirm this conclusion by studying the behavior of substrates expected to give rise to rearrangement.

Two types of rearrangements involving vinyl cations are possible: (1) *to* the double bond (I → II) and (2) *across* the double bond (III → IV). We present here examples of both types in strain-free systems.[5]



The solvolysis of *t*-butylvinyl triflate (V) in aqueous ethanol was shown to give *t*-butylacetylene as the major product, but 10–15% of 2,3-dimethylbutadiene as well as rearranged alcohols and ethers were also obtained.[3] Similar products are found after acetolysis. Those products were formulated[3] as arising from a vinyl cation rearrangement.[6]

We have now excluded an alternative rearrangement course involving addition–elimination.[7] As indicated

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