Journal of Organometallic Chemistry, 49 (1973) C79–C81
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The crystal structure of the product from the reaction of cyclopentadiene with the 2-ferrocenyl-2-propyl cation

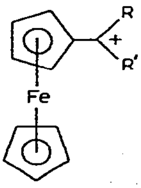
T.S. CAMERON, J.F. MAGUIRE, T.D. TURBITT and W.E. WATTS
School of Physical Sciences, New University of Ulster, Coleraine (Northern Ireland)

(Received January 1st, 1973)

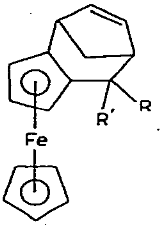
SUMMARY

The crystal structure of the product from the reaction of cyclopentadiene with the 2-ferrocenyl-2-propyl cation has been determined by X-ray diffraction methods.

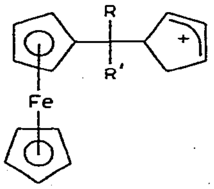
Turbitt and Watts have reported[1] that ferrocenylcarbonium ions (I; R,R′ = H or Me) react stereospecifically with cyclopentadiene to give a single cycloaddition product for which structure (II) was proposed from ^{1}H NMR evidence. In order to confirm the structure of these compounds and to establish their stereochemical features, we have determined the molecular structure of the compound (II) (R = R′ = Me) by X-ray diffraction.



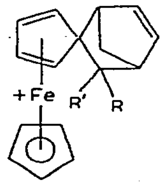
(I)



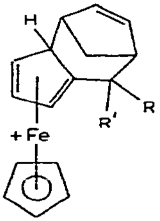
(II)



(III)



(IV)



(V)

Crystal data. $C_{18}H_{20}Fe$, $M = 292.21$, monoclinic, $a = 10.733$, $b = 8.122$, $c = 16.873$ Å, $\beta = 110.95°$, $D_M = 1.414\ g \cdot cm^{-3}$, $Z = 4$, $D_c = 1.412\ g \cdot cm^{-3}$. Space group: $P2_1/c$ (C_{2h}^5 No. 14), Mo–K_α radiation, $\lambda = 0.7107$ Å, $\mu = 10.15\ cm^{-1}$. 924 independent reflections were measured with a Hilger and Watts linear diffractometer.

The thin orange platelet crystals were found to be reflection twins about the (001) plane which was parallel to the face of the plates. It was not possible, therefore, to bisect the crystals and retain a fragment large enough for X-ray intensity measurements.

A twinned crystal was mounted about the unique axis and the intensities of the reflections from one half of the twin were measured. In the few cases where there was a coincidental overlap of reflections from both parts of the twin, the measured intensity was excluded from the list of independent reflections. The structure was determined by the heavy atom method and refined by block-diagonal least squares with anisotropic temperature factors on all non-hydrogen atoms. The residual R is 0.11 and refinement is continuing. The structure is shown in Fig. 1.

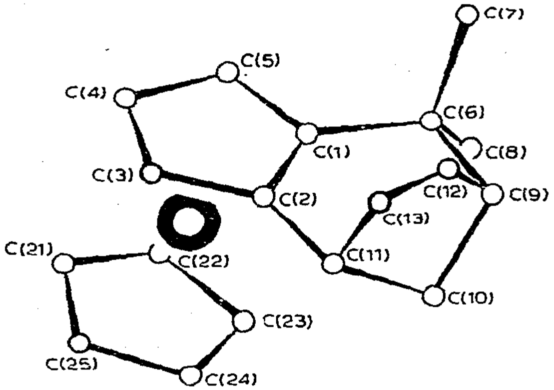


Fig. 1. The molecule (II) (R = R′ = Me) projected perpendicular to the (010) plane.

In the molecule, the carbon atoms in each of the two cyclopentadienyl rings have mean deviations from the least squares best plane of 0.03 Å [C(1)–C(5)] and 0.04 Å [C(21)–C(25)]. These planes are inclined at an angle of 7.0° with the closest interplanar contact between atoms C(4) and C(21). The iron atom is a perpendicular distance of 1.64(1) Å from both planes and the two cyclopentadienyl rings are in the eclipsed conformation, with mean carbon to carbon bond lengths of 1.422(4) [C(1)–C(5)] and 1.420(4) Å [C(21)–C(25)]. These distances are in good agreement with those reported[2] for ferrocene *viz.* C–C, 1.419 Å; (C_5H_5)–Fe, 1.66 Å.

Carbon atoms C(6), C(9), and C(11) are 0.18, 0.21, and 0.05 Å respectively from the least squares best plane through the C(1)–C(5) ring while carbon atom C(10) is 0.70 Å from this plane on the same side (*endo*) as the iron atom. Atoms C(12) and C(13) are 1.46 and 1.41 Å respectively on the opposite side (*exo*). The interatomic distance C(12)–C(13) is 1.32(1) Å and must represent a double bond. The remaining carbon to carbon bond lengths are, within experimental error, those expected for single bonds.

The carbon atom C(10) is 2.97 Å from the best plane through the C(21)–C(25) ring. In the present conformation, one of the hydrogen atoms attached to this carbon atom must approach close to and between the hydrogen atoms bonded to carbon atoms C(23) and C(24). This intramolecular steric interaction is probably responsible for the eclipsed conformation of the cyclopentadienyl rings in the ferrocene unit.

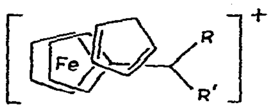


Fig. 2. Stereochemistry of approach of reactants in the cycloaddition of cyclopentadiene to ferrocenylcarbonium ions.

Various mechanisms can be written to account for the formation of compounds of the type (II) from ferrocenylcarbonium ions (I) and cyclopentadiene. For example, electrophilic addition of the cation to the diene would produce a cyclopentenyl cation (III) which could lead to the observed product by an internal electrophilic substitution reaction. Alternatively, a stepwise mechanism can be envisaged involving the initial formation of a spiro-intermediate (IV) leading to product through sigmatropic rearrangement and subsequent proton loss. However, neither of these mechanisms satisfactorily accounts for the formation of a single 1/1 adduct*.

Consequently, we favour a mechanism in which the diene adds to the fulvene ligand** of the cation (I) in a concerted fashion, formally a $(6\pi + 4\pi)$ cycloaddition, to give an intermediate (V), followed by proton elimination. In this case, the molecular geometry of the product*** (Fig. 1) requires that the reactants approach the transition state for cycloaddition with the relative orientation depicted in Fig. 2. Such an arrangement may be stabilised by secondary orbital interactions[6] between the reacting π-systems and correspondingly favoured over the alternative geometry of approach.

ACKNOWLEDGEMENTS

We wish to thank the Oxford University Chemical Crystallography Laboratory for the loan of a diffractometer, and the New University of Ulster Computing Centre for facilities.

REFERENCES

1 T.D. Turbitt and W.E. Watts, *Chem. Commun.*, (1971) 631.
2 J.D. Dunitz and J.A. Ibers, *Perspectives in Structural Chemistry, Vol. I*, Wiley, New York, 1967, p. 4, 9.
3 T.D. Turbitt and W.E. Watts, unpublished research.
4 S. Lupan, M. Kapon, M. Cais and F.H. Herbstein, *Angew. Chem. Internat. Edn.*, 11 (1972) 1025.
5 T.D. Turbitt and W.E. Watts, *J. Organometal. Chem.*, 49 (1973) C30.
6 R.B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970.

---

*Using alternative methods, we have independently synthesized compounds of the type (II) which possess an "inverted" stereochemistry (*i.e.* methylene group *exo*), and shown that molecules of this type are not formed in the cycloaddition reactions of ferrocenylcarbonium ions with cyclopentadiene[3]

**The fulvene ligands of ferrocenylcarbonium ions may be distorted from planarity[4,5].

***The close correspondence between the ^{1}H NMR spectra of the products of all such cycloaddition reactions[1] suggests that they each possess the same stereochemical ligand arrangement.