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SYNTHESIS AND PROPERTIES OF NOVEL ORGANOMETALLIC POLYMERS

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ABSTRACT

1,1'-Diruthenocenylnaphthalene has been prepared and its molecular structure has been determined by x-ray diffraction, in order to compare its structure with that of its iron analog. The molecular structure of the half oxidized form of 1,1'-diferocenylnaphthalene has also been determined. Comparison of these structures has made it possible to assign the origins of observed deformations in these substances. Polymeric, face-to-face metallocenes related to the 1,8-dimetallocenylnaphthalenes (M=Fe, Ru) have also been prepared by coupling of 1,1'-bis(chlorozinc)metallocenes with 1,8-diiodonaphthalene. A more general approach to the synthesis of polymeric face-to-face metallocenes incorporating other transition metals has been developed. This involves the sequential replacement of iodo groups in 1,8-diiodonaphthalene with cyclopentadiene and the complexation of these rings with metals. A short synthesis of 4-n-butyl-1,8-diiodonaphthalene has been achieved. The molecular structure of a 2,3-oligomeric face-to-face ferrocene has been determined and shown to have the unexpected *cis* arrangement of naphthalene rings.

Following the synthesis of **1a** and determination of its molecular structure¹, we prepared the corresponding ruthenium compound **1b** in order to assess the origin of structural distortions observed in **1a**². In both of these compounds the metallocene ring planes are rotated through an angle of 45° from a conformation which would place them perpendicular to the naphthalene best plane. This distortion is much larger than that observed in 1,8-diphenylnaphthalene, 5,6-diphenylacenaphthene or in 1,4,5,8-tetraphenylnaphthalene. The origin of this twisting cannot be assigned to steric interactions at C-8 and C-12, since the distance separating these centers is significantly greater in **1b** than in **1a**.

The twist angle is reduced to 30° in the monocation derived from **1a**, and we conclude that the large distortions observed in **1a,b** are mainly the consequence of charge repulsion of the facing cyclopentadienyl rings which is larger in the metallocenes than in a phenyl ring, due to charge separation in these complexes². A number of theoretical analyses show such charge separation in ferrocene.

When the coupling reaction used to prepare **1a,b** is carried out using the dimetallated

metallocene, 1,1'-(chlorozinc)ferrocene or ruthenocene oligomeric and polymeric compounds **2** are formed³. The oligomers (M=Fe or Ru) have been characterized by their NMR and mass spectra, and the electrochemistry of several oligomeric ferrocene have been studied through cyclic voltammetry. A gel permeation chromatographic analysis of the ferrocene polymers shows a weight average molecular weight of 6024 and a number average molecular weight of 3632. These chromatographic plots show a significant amount of polymeric material in the range of 10,000 to 18,000, corresponding to approximately 50 monomeric units. Two probe measurement of the conductivity of a thin film of this polymer, doped with iodine, shows a conductivity of 10^{-4} reciprocal ohms.

A more general synthetic approach to face-to-face metallocenes, which would encompass metals other than iron and ruthenium, has been sought. It has been found that the reaction of $\text{CpCu} \cdot \text{SMe}_2$ with 1,8-diiodonaphthalene results in replacement of each of the iodo groups successively by cyclopentadienyl radicals. These then undergo a [1,5] sigmatropic change, followed by an intramolecular Diels-Alder reaction to give the dicyclopentadienyl bridged naphthalene **3**⁴.

We have more recently observed that the replacement of the first iodo group by cyclopentadienyl takes place at a rate significantly greater than that of the second iodo group. Under controlled conditions it is possible to isolate the iodo-cyclopentadienyl naphthalene derivative **4**. This has been transformed by successive treatment with LDA and ferrous chloride to the ferrocene derivative **5**. Treatment of this substance with cyclopentadienylcopper dimethylsulfide gave **6**, which was then treated with LDA and finally bromomanganese pentacarbonyl to give the first mixed metal face-to-face metallocene triad **7**⁵. An examination of the use of this scheme for the preparation of polymers is in progress, especially those incorporating nickel or cobalt. This methodology may also make it possible to synthesize mixed metal polymers with exactly alternating metal centers.

In order to facilitate the preparation of higher molecular weight polymers, it is necessary to reduce their crystallinity. We have accordingly prepared the n-butyl substituted naphthalene derivative **8** by the simple sequence shown below.

8

In order to provide structural information relevant to the calculation of band structure for polymeric face-to-face metallocenes it was necessary to determine the molecular structure of a polymeric segment. This has now been achieved with the determination of the crystal structure of the 3,2-oligomer **9**⁶. This structure, shown below, is remarkable in that the molecule has adopted the *cis* configuration in the crystal, which places part of each of the two naphthalene rings over one another, rather than the less crowded *trans* configuration.

9

The molecular parameters within the oligomer **9** are very close to those observed in 1,8-diferrocenylnaphthalene, but the distances C(7)-C(13)=3.57; C(7)-C(14)=3.46; C(8)-C(12)=3.34; C(8)-C(11)=3.34 in the oligomer, suggest that there may be π - π interactions of the naphthalene rings which stabilize the *cis* form of oligomer. A projection of a larger oligomeric unit, based on the structure of **9** shows it to have an interesting helical form.

References

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