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NOVEL IRON COMPLEXES OF [2.2]PARACYCLOPHANE

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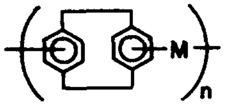
Summary: The synthesis of [2.2]paracyclophane-iron complexes 4 (R=H or Me) is described.

The synthesis of organometallic ptychopolymers,[1] based on through-space conjugated π-complexes, constitutes a synthetic challenge of theoretical and practical significance, and a number of attempts to construct such systems from metallocenes have been recorded.[2] Such polymers derived from [2.2]paracyclophane (1) are of particular interest since these would be expected to exhibit extensive electron delocalization.[3]

Among simple paracyclophane-metal complexes, three general classes may be distinguished (2,3,4), of which those with structure 4 provide the best opportunity for direct metallopolymerization.



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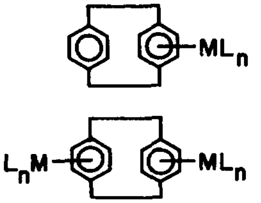

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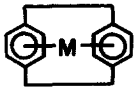

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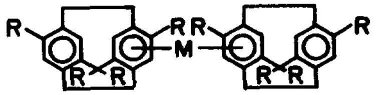

4

A number of complexes of structure 2 are known [ML$_n$ = Cr(CO)$_3$,[4a] Ru^{2+} Arene,[4b] Fe$^+$Cp[4c]], but only a single complex each of structure 3 and 4 (M=Cr, R=H) has been recorded,[5] and the latter was not isolated, but only characterized by its mass spectrum and the ESR spectrum of its cation. We now report the preparation and characterization of an Fe^{2+} complex of structure 4.

The classical method for the synthesis of bis-areneiron (II) complexes, by treatment of the arene with $FeCl_2$ and $AlCl_3$ is not applicable to the preparation of paracyclophane complexes since the hydrocarbon undergoes facile rearrangement in the presence of traces of $HAlCl_4$.[6] However, when 1 mmole of [2.2]paracyclophane is treated with 4 mmoles of $FeCl_2$ in refluxing cyclohexane, in the presence of 3 mmoles of $AlCl_3$ and of $Me_3Al_2Cl_3$ acting as a proton scavenger,[7] and the mixture is subsequently hydrolyzed and treated with NH_4PF_6, an orange solid is obtained (26%). This substance decomposes rapidly in the solid state and in organic solution to give only paracyclophane and $Fe(PF_6)_2$. Analysis of the decompostion product by sublimation of paracyclophane showed that the ratio of these components was 2:1, consistent with structure 4 ($M=Fe^{2+}$, R=H).

The same reaction carried out with 4,7,12,15-tetramethyl-[2.2]paracyclophane[8] gave the bis-tetramethyl[2.2]paracyclophane complex 4 ($M=Fe^{2+}$, R=Me) an orange, air stable solid (78%).[9] This substance is moderately stable in nitromethane solution below 0°, but rapidly decomposes at room temperature. Its proton NMR spectrum (CD_3NO_2, -10°) shows resonance absorption at δ 6.55 (s, 4H, uncomplexed ring protons), 6.15 (s, 4H, complexed ring protons), 3.3-2.5 (m, 16H, CH_2), 2.30 (s, 12H, CH_3) and 2.05 (s, 12H, CH_3).[10]

The preparation of further complexes of this general structure is under investigation as is their polymerization through extended metal complexation.

Acknowledgement

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References

1. From πτυχο (layer). We are indebted to Professor D. J. Stewart, Brandeis University, for suggesting this prefix.
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7. B. B. Snider, Acct. Chem. Res., 13, 426 (1980).
8. D. T. Longone, H. S. Chow, J. Amer. Chem. Soc., 92, 994 (1972).
9. Elemental analysis of the freshly precipitated complex gave: Calcd. for $C_{40}H_{48}FePF_6$: C, 55.79; H, 5.95; Fe, 7.2. Found C, 54.93; H, 5.53; Fe, 6.4. The structure is written with D_2 symmetry, but an isomer of C_s symmetry cannot be excluded.
10. Attempts to obtain a mass spectrum of the complex by either field desorption or fast argon beam techniques were unsuccessful. We are indebted to Dr. Catherine Costello, MIT, for these experiments.

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