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The Mixed Chromocene (Etme$_4$cp)CrCp

FRANK H. KÖHLER*, REN DE CAO† and GISBERT MANLIK

Anorganisch-chemisches Institut, Technische Universität München, D-8046 Garching, F.R.G.

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In asymmetric peralkyl metallocenes (Etme$_4$cp)$_2$M ethyl rotamers are 'frozen out' at room temperature due to steric hindrance, and this has been shown for paramagnetic derivatives by characteristic ethyl ^{1}H and ^{13}C NMR signals [1]. An open question was whether the rotamers are energetically favoured by inter-ring or intra-ring (neighbouring methyl) effects. If the latter effect dominates the two isomers in Fig. 1 can be expected. An approach to this problem is to reduce the transannular repulsion in metallocenes by keeping one ligand peralkylated and replacing the other by unsubstituted Cp. We have tested this for the title compound, *1*.

Experimental*

Successive reaction of CrCl$_2$·THF with ethyltetramethylcyclopentadienyllithium and cyclopentadienylsodium gave cyclopentadienyl(ethyltetramethyl—η^5-cyclopentadienyl) chromium, *1* as a very air sensitive red oil in 38% yield. Elemental analysis and mass spectrum confirm its molecular formula.

The NMR experiments were performed with a Bruker CXP 200 spectrometer. Details of sample

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*Author to whom correspondence should be addressed.

†On leave from the Lanchow Institute of Chemical Physics Academia Sinica, China.

*Preparative details as well as tables of temperature dependent ^{1}H and ^{13}C data have been deposited with the editors. They may be obtained from there or from the authors.

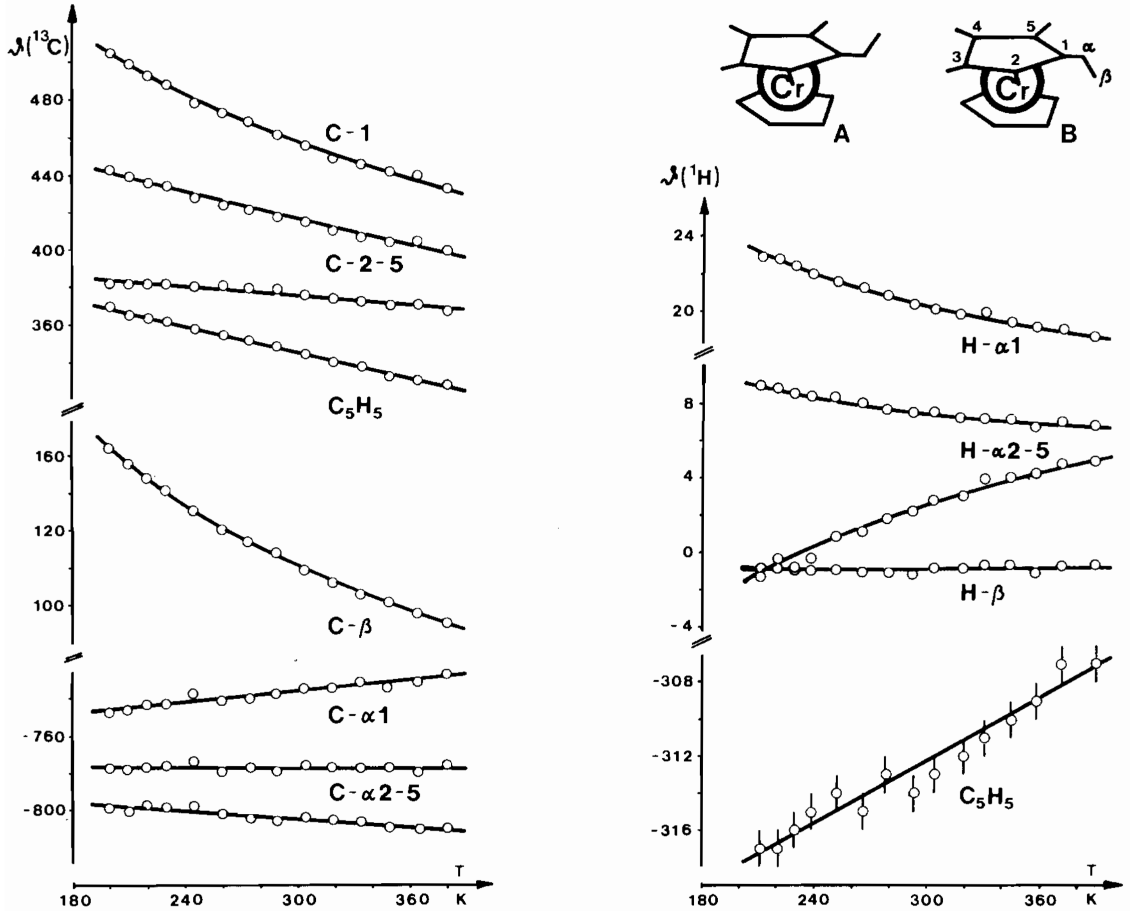

Fig. 1. Temperature dependent paramagnetic ^{1}H and ^{13}C NMR data of a 4.44 mol% solution of (Etme$_4$cp)CrCp in toluene-d$_8$. Paramagnetic low field shifts are negative.

preparation and variable temperature procedure have been given elsewhere [1, 2]. The signals of $(Etme_4cp)_2Fe$ [1] and ferrocene were used as standards for the paramagnetic shifts (at a given temperature), δ_T^{para}, of the two ligands of *1*.

Results and Discussion

Equimolar amounts of $(Etme_4cp)Li$ (or CpLi) and $CrCl_2 \cdot THF$ give a blue reaction mixture which contains more than one intermediate compound; this can be seen from the complex paramagnetic ^1H NMR spectrum. We believe that halogen-bridged chromium half-sandwich compounds are engaged. Such species—although derived from Cr(III)—have been detected by NMR [3], and similar intermediates are known for cobalt [4]. The blue chromium intermediates react with one equivalent of CpLi to give the red chromocene *1*.

The NMR data of *1* (given as δ_{298}^{para}: H–Cp −312, H-α1 20.6, H-α2–5 2.6 and 7.8, H-β −0.8, C-Cp 346, C-1 458, C-2–5 377 and 417, C-α1 −736, C-α2–5 −777 and −804, C-β 101) are only slightly different from those of $(Etme_4cp)_2Cr$, *2* [1] and Cp_2Cr, *3* [5]. Thus, the linewidths permit the detection of impurities of *2* and *3* in ^{13}C and not in ^1H NMR. The important information is that on going from *2* to *1* the H-α-1 and C-β signals hardly move. Since these signals show the predominance of ethyl rotamers *A* and/or *B* in Fig. 1 intra-ring rather than inter-ring repulsion operates. Rotamers *A* and *B* should have different energies ΔG_0. Temperature dependent NMR studies are expected to give a deeper insight if ΔG_0 and the rotational barrier are suitable. The results of our measurements* are summarized in Fig. 1. Since $\nu = \delta_T^{para}$ (T/298) all curves should be parallel to the temperature axis if Curie behavior is present. Deviations in Fig. 1 are pronounced for H-α and C-β as would be expected for a change in population of different ethyl rotamers. However, the slope for C-β is very much the same as for C-1. This indicates a hyperconjugative link between the C-1 and C-β position and favours another origin: a change in population of singly occupied degenerate MOs which are slightly split by substitution. This situation applies for *1* since Cp_2Cr has an $^3E_{2g}$ ground state [6], and the C-1 position suffers from a maximum change in spin density on going from one e-orbital to the other [7]. We conclude that the electronic effect masks small energy differences between rotamers *A* and *B* at a low rotational barrier.

Acknowledgement

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References

1 F. H. Köhler, K. H. Doll and W. Prössdorf, *J. Organomet. Chem., 224,* 341 (1982).
2 F. H. Köhler, P. Hofmann and W. Prössdorf, *J. Am. Chem. Soc., 103,* 4096 (1981).
3 F. H. Köhler, R. Cao, K. Ackermann and J. Sedlmair, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* in press.
4 U. Koelle, F. Sistig and J. Gersdorf, *J. Organomet. Chem., 233,* 253 (1982).
5 F. H. Köhler, *J. Organomet. Chem., 110,* 235 (1976).
6 A. Haaland, *Acc. Chem. Res., 12,* 415 (1979) and cit. Lit.
7 F. H. Köhler and K. H. Doll, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., 37,* 145 (1982).

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