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Diastereoisomeric forms of 1,1′-di-tert-butyl-3,3′-bis(2,2-dimethylpropionyl)ferrocene

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Abstract

The title compound is shown by a combination of ^1H and ^{13}C NMR spectroscopy to exist as diastereoisomeric forms, a racemic form of C_2 symmetry and a *meso* form of C_i symmetry.

Introduction and discussion

We have recently shown [1] that, although the reaction between ferrocene and an equimolar quantity of 2,2-dimethylpropionyl chloride/aluminium chloride (effectively $Me_3CCO^+AlCl_4^-$) gives excellent yields of 2,2-dimethylpropionylferrocene $(C_5H_4COCMe_3)Fe(C_5H_5)$, the use of a large molar excess of the acylation reagent gives multiple products resulting from concurrent acylation (by Me_3CCO^+) and alkylation (by Me_3C^+). Among these products we have identified $[C_5H_3(CMe_3)_2]_2Fe$ (**1**), 1,1′,3-tri-tert-butyl-3′-(2,2-dimethylpropionyl)ferrocene, $[C_5H_3(CMe_3)_2]Fe[C_5H_3(CMe_3)COCMe_3]$ (**2**), and 1,1′-di-tert-butyl-3,3′-bis(2,2-dimethylpropionyl)ferrocene, $[C_5H_3(CMe_3)COCMe_3]_2Fe$ (**3**). Of these products **1** was identified only by GC-MS, but both **2** and **3** were isolated and identified by ^1H and ^{13}C NMR spectroscopy.

For compounds **2** and **3**, the ^1H NMR spectra both show four singlets assignable to four distinguishable tert-butyl groups, and six multiplets readily assigned as two independent AMX systems each with coupling constants characteristic of the protons in a 1,3-disubstituted cyclopentadienyl system. For a rigid conformation of compound **3**, allowing only rotation of the tert-butyl groups, there will be six distinct ring protons, and a total of twenty distinguishable carbon environments.

The ^{13}C NMR spectrum of **3** in chloroform-*d* solution shows nineteen resonances, assignable to four $C(CH_3)_3$ groups, two $-C(CH_3)_3$ and two $-CO-C(CH_3)_3$ groups, six CH ring carbons and both ring $C-COCMe_3$ carbons, (at δ 105.5 and 105.6) but only one ring $C-CMe_3$ resonance at δ 77.3 was resolved: in addition there are two CO resonances. In benzene-d_6 solution however, there are also nineteen ^{13}C resonances which differ from those resolvable in chloroform-*d* only in that while one ring $C-COCMe_3$ resonance is resolvable, now both ring $C-CMe_3$

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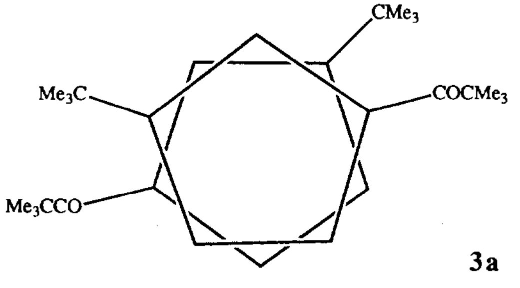
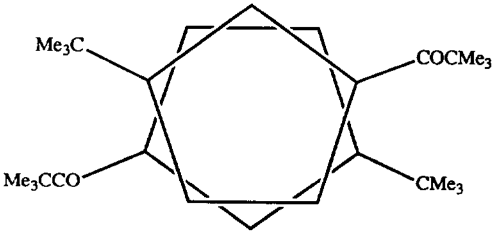


3a



3b

resonances are resolved (at δ 78.6 and 78.8). Hence, taking the two spectra together, all twenty carbon environments expected are observed.

However since the two rings of compound 3 have an identical pattern of substitution, the observation of twenty different carbon resonances, and ten different proton resonances requires a barrier to intramolecular ring rotation markedly larger, at ambient temperature, than is normal in ferrocene and its derivatives [2,3]. Although we originally suggested [1] that these spectra arose from a single molecular species, we now propose an alternative interpretation which requires no assumption of high rotational barriers.

The identical ring substitution patterns allow the existence of two diastereoisomeric forms of compound 3, having respectively C_2 (**3a**) and C_i (**3b**) molecular symmetry at conformation maximising the distance between identical substituents. In **3a** the two [(C_5H_3(CMe$_3$)COCMe$_3$]Fe fragments have the same chirality, while in **3b** the two fragments have opposite chirality: **3a** and **3b** are thus respectively racemic and *meso* forms of 3.

For each of **3a** and **3b** there are ten distinguishable carbon sites and five distinguishable proton sites. Comparison of the ^{13}C NMR spectra of 3 in chloroform-*d* and in benzene-d_6 solution clearly shows unequal intensities where resonances occur in closely corresponding pairs: thus of the *C*O resonances that at δ 210.6 is more intense than that at 208.9; of the ring *C*–COCMe$_3$ resonances that at δ 105.6 is the more intense than that at 105.5, and of the ring *C*–CMe$_3$ resonances that at δ 78.6 is the more intense; of the two –*C*(CH$_3$)$_3$ resonances not involving acyl groups that at δ 30.9 is more intense than that at 30.8. These observations clearly suggest that not all of the ^{13}C resonance arise from single sites in a single molecular species. Confirmation of the presemce of two species is provided by the ^{1}H NMR spectrum. Although accurate integration of the ^{1}H intensities is not possible in chloroform-*d* solution, because of the very close resonances, in benzene-d_6 both the tert-butyl resonances and the ring proton resonances allow accurate integration: the spectrum in benzene-d_6 shows a major isomer with tert-butyl resonances at δ 1.17 and 1.32, and with ring resonances at 4.23, 4.40 and 4.98 and a minor isomer with tert-butyl resonances at δ 1.15 and 1.39, and with ring resonances at 3.99, 4.66, and 5.04. Each component spectrum is consistent with either **3a** and **3b** and the major : minor abundance ratio is ca 1.7 : 1 in benzene-d_6 at 20 °C: it is not possible to identify which individual spectrum arises from which of the individual diastereoisomers **3a** and **3b**.

The ^{1}H resonances of the ring protons give evidence of highly specific solvation by chloroform and benzene. In chloroform the two AMX systems of **3** have chemical shifts δ 4.16, 4.39 and 4.73 for one, and δ 4.43, 4.75 and 4.78 for the other, whereas in benzene the values are 3.99, 4.66 and 5.04; and 4.23, 4.40, and 4.98. Compound **2**, where the two independent AMX systems arise from a single molecular species, likewise shows strong solvent effects on the ring proton resonances, which are at δ 3.78, 3.92, 4.06, 4.38, 4.62 and 4.81 in chloroform, and 3.98, 4.21, 4.25, 4.48, 4.79, and 5.29 in benzene.

Experimental

Compound **3** was isolated [1] from the reaction of ferrocene with a large excess of $Me_3CCOCl/AlCl_3$. NMR spectra were recorded with a Bruker AM-300 spectrometer.

NMR δ_C (C_6D_6): 27.7(q), 28.2(q), 31.5(q), and 31.6(q) [all $C(CH_3)_3$]; 30.8(s) and 30.9(s) [$C-C(CH_3)_3$]; 44.5(s) and 44.6(s) [$C(O)C(CH_3)_3$]; 69.5(d), 70.3(d), 70.6(d), 71.0(2 × d), 71.3(d) (all ring C–H); 77.8(s) (major) and 78.3(s) (minor) [ring $C-C(CH_3)_3$]; 105.5(s) [ring $C-C(O)$]; 208.9(s) (minor) and 209.8(s) (major) (CO). δ_C ($CDCl_3$): 27.8(q), 28.2(q), 31.4(q), and 31.5(q) [all $C(CH_3)_3$]; 30.8(s) and 30.9(s) [$C-C(CH_3)_3$]; 44.4(s) (minor) and 44.6(s) (major) [$C(O)C(CH_3)_3$]; 69.5(d), 70.3(d), 70.4(2 × d), 70.5(d), 71.1(d) (all ring C–H); 77.3(s) [ring $C-C(CH_3)_3$]; 105.5(s) (major) and 105.6(s) minor [ring $C-C(O)$]; 208.9(s) (minor) and 210.6(s) (major) (CO). δ_H (C_6D_6): major isomer; 1.17(s, 18H, CMe_3), 1.32 (s, 18H, CMe_3); 4.23 (m, 2H), 4.40 (m, 2H), 4.98 (m, 2H) (all ring H); minor isomer; 1.15 (s, 18H, CMe_3), 1.39 (s, 18H, CMe_3); 3.99 (m, 2H), 4.66 (m, 2H), 5.04 (m, 2H) (all ring H); ratio major : minor 1.7 : 1. δ_H ($CDCl_3$): 1.23(s), 1.27(s), 1.33(s), 1.34(s) [all $C(CH_3)_3$]; 4.16 (dd, J_1 2.6, J_2 1.7 Hz), 4.39 (dd, J_1 2.6, J_2 1.7 Hz), 4.43 (dd, J_1 2.4, J_2 1.5 Hz), 4.73 (t, J 1.7 Hz), 4.75 (dd, J_1 2.4, J_2 1.5 Hz), 4.78 (t, 1.5 Hz), (all ring C–H).

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