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Formation of Roussin's Methyl Ester from Bis(μ-methylthio)bis(tricarbonyliron)

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Bis(μ-organylthio)-bis(tricarbonyliron) complexes, $(RS)_2Fe_2(CO)_6$ (R = alkyl or aryl) are readily accessible from dodecacarbonyltriiron [1–3]. When R = CH_3 or C_2H_5, two isomers *syn* and *anti* are separable by chromatography, but an equilibrium mixture is rapidly established in solution*: the structure of *anti*-$(EtS)_2Fe_2(CO)_6$ has been established [4] by X-ray analysis. By contrast, the isoelectronic nitrosyl complexes, $(RS)_2Fe_2(NO)_4$, which are usually prepared by the action of nitric oxide on a mixture of RSH and an iron(II) salt [5], appear to exist in only one isomeric form: an X-ray analysis of $(EtS)_2Fe_2(NO)_4$ [6] showed the overall molecular symmetry to be C_{2h} (analogous to *anti*) rather than C_{2v} (analogous to *syn*).

We show here, firstly that the action of nitric oxide on $(MeS)_2Fe_2(CO)_6$ yields $(MeS)_2Fe_2(NO)_4$, despite statements to the contrary in the literature [7], and secondly that irrespective of whether pure *anti* or pure *syn* carbonyl is employed, the product is always the same, presumably C_{2h}, nitrosyl isomer.

Treatment of either isomer in N_2-purged CH_2Cl_2 solution with NO, under dinitrogen at –80 °C, followed by removal of the solvent by freeze-drying, yielded dark-red crystals which were identical (i.r., m.p., mass spectrum) with authentic $(MeS)_2Fe_2(NO)_4$. The products were each homogeneous by t.l.c., and showed only one singlet at δ 2.83 p.p.m. in the ^1H n.m.r. spectrum. When the mixed isomers of $(MeS)_2Fe_2(CO)_6$ (equilibrium composition) were treated with NO, again a single product $(MeS)_2Fe_2(NO)_4$ was obtained, homogeneous by t.l.c. and identical with authentic material.

In $(RS)_2Fe_2(CO)_6$ the equilibrium constants for isomerisation are very similar for R = CH_3 or C_2H_5 [3]; if it is assumed that this is true also for $(RS)_2Fe_2(NO)_4$, then it follows that the single isomer of $(MeS)_2Fe_2(NO)_4$ is the C_{2h} isomer as found for $(EtS)_2Fe_2(NO)_4$ [6]. We note in addition that $(MeS)_2Fe_2(NO)_4$ has an R_f value (silica–40/60 petrol) identical to that of *anti*-$(MeS)_2Fe_2(CO)_4$ whereas that of *syn*-$(MeS)_2Fe_2(CO)_6$ is *ca.* 0.7 that of the *anti* isomer. If *syn*-$(MeS)_2Fe_2(NO)_4$ does in fact yield the C_{2v} isomer of $(MeS)_2Fe_2(NO)_4$ as the primary product at –80 °C, this must be very short lived, as it cannot be detected subsequently at room temperature.

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Formation of an equilibrium mixture from either the *syn* or the *anti* isomer require 2–3 days at 40 °C [3], or 15 minutes in refluxing benzene: for R = CH_3, K = [*anti*]/[*syn*] = 3.2(2) in hexane [3], and K = 1.4(1) in benzene.