t-Butylferrocenylnitroxide, a Stable Ferrocenyl Radical

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Summary The preparation and spectroscopic properties of t-butylferrocenylnitroxide are described, and its structure is related to that of stable α-ferrocenylcarbonium ions.

UNEQUIVOCAL evidence[1] for the existence of neutral ferrocenyl radicals has not hitherto been presented. We describe the preparation, properties, and structure of the first stable radical of this type.

Treatment of ferrocenylmagnesium bromide with 2-methyl-2-nitrosopropane followed by autoxidation of the resulting hydroxylamine yielded the deep-red crystalline t-butylferrocenylnitroxide (I) which was stable for months in the solid state and for weeks in solution. Its structure was based on elemental analysis and i.r. [ν_{max} 1320 (N–O), 1100, 1000, and 800 cm.$^{-1}$], u.v. (λ_{max} 241, 325, 375sh., and 500 nm.) and e.s.r. evidence. Hydrogenation over platinum gave the corresponding hydroxylamine (i.r. absorption >3100 cm.$^{-1}$) but several attempted oxidations with, for example, iodine failed to produce the ferrocenium nitroxide (no absorption in the 600 nm. region). The nitroxide has an a_N value (11·75 G) similar to, but a g-value (2·0149 ± 0·0004) much larger than those of aryl-t-butylnitroxides[2] (about 12·0 G and 2·006, respectively). The smaller coupling (0·8 G) in the spectrum (Figure 1), which almost certainly arises from the 2- and 5-ring protons, is less than half that of the *ortho*-protons in aryl-t-butylnitroxides ($a_{o\text{-H}}$ *ca.* 2·0 G).

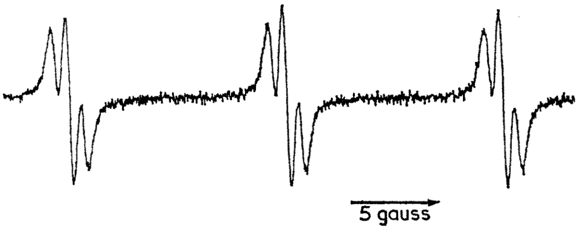


FIGURE 1. *E.s.r. spectrum of t-butylferrocenylnitroxide in* CCl_4 *solution.*

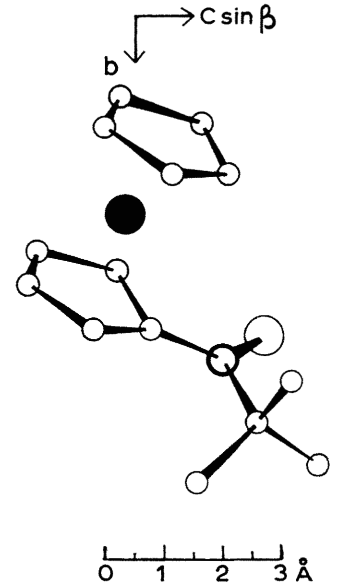
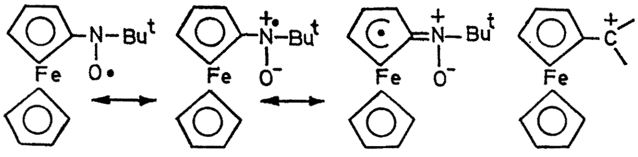


FIGURE 2. a-*Axis projection of t-butylferrocenylnitroxide.*



(Ia) (Ib) (Ic) (II)

Clearly, the unpaired electron is extensively delocalised (Ia ⟷ Ib ⟷ Ic) and there is considerable interaction with the iron atom. This could occur either *via* the metal–ring π-system and/or by direct Fe–N (or O) bonding. By analogy, direct interaction between electron-deficient carbon and iron has frequently been invoked to explain the unusual stability of α-ferrocenylcarbonium ions (II), several models having been suggested.[3] The possibility of direct bonding, in this case, has been examined by crystallographic analysis (Figure 2) which revealed that crystals of the radical were monoclinic, space group $P2_1/c$ with four molecules of $C_{14}H_{18}NOFe$ in a unit cell of dimensions $a = 5{\cdot}91$, $b = 15{\cdot}71$, $c = 14{\cdot}38$ Å and $\beta = 109{\cdot}25°$. The structure was solved by the heavy-atom method using 1284 intensity data estimated visually from Weissenberg films, $0kl$—$5kl$, taken with Cu-K_α radiation. R is at present 0·17 and further refinement is in progress. The iron atom is symmetrically placed between eclipsed cyclopentadienyl rings with an average Fe · · · C distance of 2·06 Å and individual values ranging from 2·03—2·11 Å. The N–O, Fe · · · N, and Fe · · · O distances are 1·20, 3·08, and 3·62 Å, respectively, and the N–O bond makes an angle of only 11·6° with the plane of the cyclopentadienyl ring (*cf.* ref. 4).

These results indicate that direct Fe–N (or O) bonding, if any, must be weak and hence that the radical resembles more closely models of the α-ferrocenylcarbonium ion[5] in which electron delocalisation involving the iron atom occurs mainly *via* the metal–ring π-system.

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