Reaction of 3,5,7-Triphenyl-4*H*-1,2-diazepine with Di-iron Nonacarbonyl; the *X*-Ray Crystal and Molecular Structure of a Novel Iron-containing Bicyclo[5,1,1]-system

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Summary Reaction of $Fe_2(CO)_9$ with 3,5,7-triphenyl-4*H*-1,2-diazepine leads to cleavage of the N–N bond and formation of a nitrogen bridged complex which has been shown by *X*-ray crystallography to be a bicyclo[5,1,1]-derivative.

IRON carbonyls react with various compounds containing N–N bonds to give nitrogen-bridged organometallic complexes.[1] These complexes may or may not retain the original N–N bond and in some cases, an extensive rearrangement of the molecule takes place.[2] Our characterization of the $Fe_2(CO)_9$ derivative of 3,5,7-triphenyl-4*H*-1,2-diazepine has revealed that two $Fe(CO)_3$ units have been inserted into the 7-membered heterocyclic ring system, breaking the N–N bond and producing the first example of an unsaturated 8-membered metallocyclic ring system. Only one other example of the reaction of iron carbonyls with a ring system containing an N–N bond has been studied and in this case the N–N bond was retained.[2]

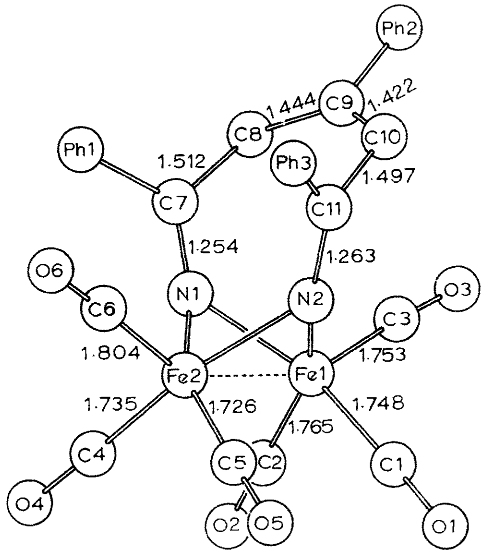

FIGURE. *Atomic numbering and pertinent distances in the* $Fe_2(CO)_6$ *adduct of* 3,5,7-*triphenyl*-4H-1,2-*diazepine. The* Fe(1)–Fe(2) *distance of* 2·392, Fe(1)–N(1) *of* 1·921, Fe(1)–N(2) *of* 1·919, Fe(2)–N(1) *of* 1·960, *and* Fe(2)–N(2) 1·969 Å *are not shown.*

Reaction of 3,5,7-triphenyl-4*H*-1,2-diazepine (L)† with $Fe_2(CO)_6$ at room temperature followed by chromatography on alumina gave a red-brown product (m.p. 137—139°; yield 14·3%). Analysis indicated the formula $Fe_2(CO)_6(C_{23}H_{18}N_2)$. An i.r. spectrum ($C_6H_{14}$) showed carbonyl bands at 2068m, 2031vs, 1998vs, 1986s, 1967m; however, bands due to ν(C=N) and ν(C=C) of the diazepine remained unchanged, ruling out co-ordination of two double bonds of the ring to an $Fe(CO)_3$ unit as found in other diazepine complexes.[3] A 100 MHz ^1H n.m.r. spectrum [τ (C_6D_6) 2·94 (m, phenyl H), 3·50 (s, vinyl H), 3·78 (AB quartet, CH_2, J_{AB} 17 Hz)] compared with the spectrum of the free diazepine[4] suggested retention of the essential features of the diazepine with an increase in both J_{AB} and ring planarity. A Mössbauer spectrum indicated two non-equivalent iron atoms [δ 0·22 mm s^{-1}, Δ 0·93 mm s^{-1}, (Fe_2) and δ 0·35 mm s^{-1}, Δ 1·19 mm s^{-1} (Fe_1)]. The latter values (Fe_1) are similar to those found for iron in quasi-octahedral environments[5] while the former (Fe_2) imply a more regular octahedral configuration. In the mass spectrum peaks at *m/e* corresponding to $Fe_2(CO)_{5-n}$ (n = 1—5) were found but no parent ion peak at *m/e* 602 [$Fe_2(CO)_6L$] could be traced. There was no evidence for L^+ at *m/e* 322, suggesting the absence of an N–N bond in the complex. While the bulk of the evidence favoured a structure similar to that of di-μ-(4,4′-dimethylbenzophenoniminato)bis(tricarbonyliron),[6] the available data did not unequivocally distinguish between $Fe_2(CO)_5L$ and $Fe_2(CO)_6L$, nor explain the observed Mössbauer non-equivalence of the iron atoms. A single-crystal *X*-ray study was therefore carried out.

Crystal data: $(C_{23}H_{18}N_2)Fe_2(CO)_6$, monoclinic crystals, space group $P2_1/c$ (No. 14), a = 14·003 ± 0·006, b = 14·140 ± 0·005, c = 13·349 ± 0·006 Å, β = 90·77 ± 0·04°, U = 2642·9 Å^3, D_m = 1·440 g/cm^3, Z = 4, D_c = 1·512 g/cm^3.

X-ray intensity data were collected on a G.E. automatic diffractometer using the stationary crystal–stationary counter method and Fe-K_α (λ = 1·93597 Å) radiation. A total of 7650 reflections were measured and reduced to a set of 2409 unique reflections of which 2052 were considered observed and used in the refinement. The structure was solved by the heavy-atom technique and refined by least-squares methods using anisotropic thermal parameters to an R value of 0·085.

The molecular geometry and pertinent bond lengths are shown in the Figure. The molecule, which is derived from the parent diazepine by insertion of two $Fe(CO)_3$ units

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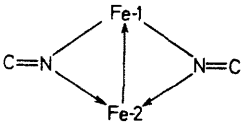
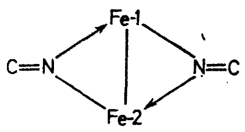
across the N–N bond can be described as a metallo-bicyclo-[5,1,1]-system. The most interesting feature of the 8-membered metallocyclic rings is the near equivalence of the C(8)–C(9) [1·444 (9) Å] and C(9)–C(10) [1·422 (5) Å] bond lengths. While there is no *a priori* reason on symmetry grounds to differentiate C(8) and C(10), the n.m.r. results are consistent with the presence of an isolated CH_2 group. The observed near-equivalence of the bond lengths may therefore result from disorder in the crystal. A similar disorder has been found in other organic [7a] and organometallic compounds.[7b]

The N(1)–N(2) distance of 2·248 (7) Å, the Fe(1)–Fe(2) distance of 2·393 (2) Å and the Fe–N distance [Fe(1)–N average is 1·920 Å and Fe(2)–N average is 1·965 Å] are similar to these found in comparable compounds.[2,6] The N–N distance is much longer than a single bond and is consistent with a rupture of the N–N bond in the parent diazepine. The dihedral angle between the Fe–N–N planes is 98·1°, in agreement with that expected for a long N–N distance.[2] The difference in the Fe–N distances may be a steric effect related to the location of the two phenyl rings, Ph(1) and Ph(3), on the same side of the molecule as Fe(2). The inequality in the Fe–N distances could explain the two different iron atoms observed in the Mössbauer spectrum. A detailed comparison of the Mössbauer parameters with data for other iron carbonyl complexes[5] suggests that the observed magnitude of the non-equivalence of the Fe atoms could also arise as a result of a dative Fe → Fe bond. Therefore, the bonding in the present complex may be better represented by (I) rather than the alternative description (II).



(I)



(II)

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