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π-COMPLEXES OF 1*H*-1,2-DIAZEPINES. SYNTHESIS AND CHARACTERIZATION OF TRICARBONYLIRON AND -RUTHENIUM DERIVATIVES

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SUMMARY

The synthesis of a number of tricarbonyliron and -ruthenium derivatives of 1*H*-1,2-diazepines are described. The complexes have been characterised by infrared, mass, Mössbauer and nuclear magnetic resonance spectra. The 7-membered heterocycles are coordinated to the metal atoms via two olefinic double bonds in typical diene fashion. A complete analysis of NMR chemical shifts and coupling constants in (1-acetyl-1*H*-1,2-diazepine)$Fe(CO)_3$ has been carried out with the aid of a computer simulated spectrum.

INTRODUCTION

Although the synthesis and characterisation of a number of 1*H*-1,2-diazepines (I) have recently been described[1,2] the chemistry of transition metal derivatives of these interesting heterocycles remains largely unexplored. Streith and co-workers[2] have briefly described $Fe(CO)_3$ adducts (VIa), (VIb) and (Xa) and alluded to an unpublished X-ray structure of (1-ethoxycarbonyl-1*H*-1,2-diazepine)$Fe(CO)_3$ (Xa) confirming diene type coordination of the diazepine to the iron tricarbonyl residue. A communication concerning the X-ray structure of (1-isopropoxycarbonyl-1*H*-1,2-diazepine)$Fe(CO)_3$ (Xb) has recently appeared[3]. By contrast 3,5,7-triphenyl-4*H*-1,2-diazepine (III) reacts with $Fe_2(CO)_9$ via cleavage of the N–N bond and formation of a metallobicyclo(5.1.1) system[4]. The same ligand yields $Rh(CO)_2Cl$(Diaz) (Diaz= 3,5,7-triphenyl-4*H*-1,2-diazepine) with $[Rh(CO)_2Cl]_2$ in which coordination occurs via σ lone pair donation from one nitrogen atom of the heterocycle[5].

As part of a study designed to investigate the chemistry of the coordinated 1*H*-1,2-diazepine ring system we have prepared $Fe(CO)_3$ derivatives [(IIa)–(IIc)] and an $Ru(CO)_3$ derivative (VII). Furthermore, unlike (III), the reaction of (IV) with $Fe_2(CO)_9$ gave only an $Fe(CO)_3$ adduct (V). This paper describes in detail the characterisation, mass spectra and Mössbauer spectra of these compounds. Detailed analyses

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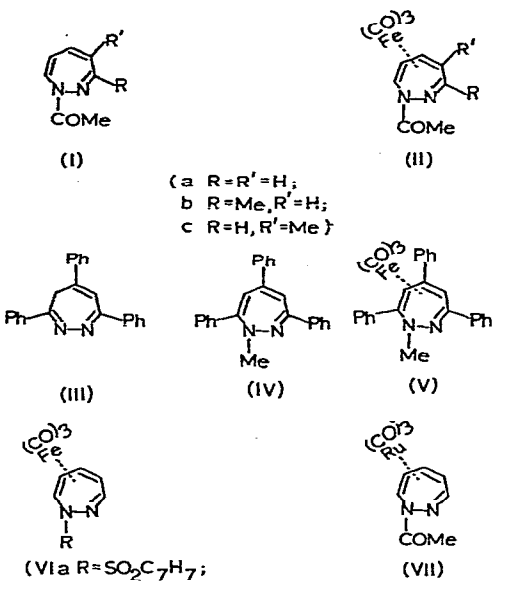
of the NMR spectra of these derivatives, including computer simulation of the spectrum of (1-acetyl-1*H*-1,2-diazepine)$Fe(CO)_3$ (IIa), have also been carried out. Finally, mass spectral and Mössbauer data are included for two of the iron tricarbonyl complexes (VIa, VIb) described earlier by Streith and co-workers[2].



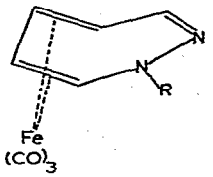
RESULTS AND DISCUSSION

The compounds described herein are all of the type $LM(CO)_3$ (M = Fe, Ru; L = 1*H*-1,2-diazepine). Spectroscopic measurements (*vide infra*) unambiguously favour diene coordination of the diazepine ring to the iron tricarbonyl residue in these derivatives*. In accord with current theories of chemical bonding[9], two models (a) and (b), representing extremes in valence bond terminology depict the interaction of the diene fragment with the metal. While (a) and (b) are probably, in reality, of conceptual value only they serve as a useful framework for the discussion of NMR and Mössbauer results. In the following sections we refer in particular to (b) since we believe that the *gross* structural changes in the heterocycle which accompany complexation are analogous to those expected for 1,4-cycloaddition of a dienophile to the diene chromophore of the diazepine. There is ample evidence from X-ray[3,10,11] data to justify this approach.

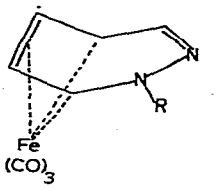
Infrared spectra

Diene–iron tricarbonyl complexes usually exhibit three band infrared spectra in the $\nu(C{\equiv}O)$ region under high resolution consisting of a strong band above 2045 cm^{-1} and an intense doublet[12] near 2000 cm^{-1}. In polar solvents or in situations where

* But see the discussion of NMR results for (V).



(a)



(b)

the molecular symmetry approaches C_{3v} the latter may appear as a broad singlet[13]. The spectra recorded in Table 1 are consistent with coordination of the diazepines via two olefinic bonds to the $Fe(CO)_3$ or $Ru(CO)_3$ entities. Moreover, examination of free ligand and complex spectra in the ν(C=N) and ν(C=C) region indicates that coordination results in a lowering of 150–200 cm^{-1} in the frequency of at least one

TABLE 1

INFRARED SPECTRA OF DIAZEPINES AND THEIR COMPLEXES[a]

Complex	Free ligand spectra[b] (1800–1300 cm^{-1})	Spectra of complexes[b] (1800–1300 cm^{-1})	ν(C≡O)[c] (cm^{-1})
(IIa)	1670 vs, *1628 s*, 1610 s, 1576 m, 1478 w, 1430 m, 1420 m, 1368 vs, 1328 vs, 1310 s	1680 s, 1603 m, *1447 m*, 1426 m, 1376 m, 1370 s, 1300 s	2063 s, 2004 s, 1993 s
(IIb)	1661 s, 1636 m, 1583 w, 1434 m, 1386 s, 1371 (sh), 1336 s	1680 s, 1623 m, 1470 (sh), 1449 m, 1379 s, 1302 s	2062 s, 2002 s, 1991 s
(IIc)	1667 s, *1641 m*, 1621 m, 1451 w, 1442 w, 1382 s, 1339 s, 1322 m	1690 (sh), 1679 s, 1605 m, 1520 w, 1504 w, *1457 s*, 1430 (sh), 1370 s	2058 s, 1998 s, 1987 s
(V)	*1625 s*, 1593 s, 1570 s, 1496 s, 1471 m, 1448 s, 1375 m, 1328 s, 1305 m	1599 m, 1581 m, 1551 w, 1483 s, *1455 s*, 1419 w, 1352 m, 1310 m	2041 s, 1980 s, 1974 s, 1956 m
(VIa)	*1628 m*, 1615 m, 1598 m, 1574 w, 1497 w, 1441 w, 1401 w, 1360 s, 1308 m	1596 m, 1496 w, *1448 s*, 1403 w, 1368 s, 1308 w	2080 s, 2020 s, 1999 s
(VIb)	1651 s, *1635 (sh)*, 1611 s, 1579 m, 1519 w, 1497 w, 1447 m, 1432 m, 1348 s, 1312 m	1670 s, 1604 s, 1582 m, 1497 w, *1450 s*, 1438 (sh)	2064 s, 2003 s, 1994 s
(VII)		1685 s, 1600 s, *1460 s*, 1430 m, 1410 m, 1380 m, 1361 s	2078 s, 2018 s, 2010 s

[a] Frequencies in italics refer to tentative assignments of ν(C=C) of the 7 membered ring. [b] Chloroform solution. [c] n-Hexane solution.

band of the ligand. This is particularly evident for (VIa) where the 1628 cm^{-1} band disappears with the simultaneous appearance of a strong absorption at 1448 cm^{-1}. Shifts of similar magnitude have been reported for ν(C=C) in $(C_4H_6)Fe(CO)_3$[14], $(C_8H_8)Fe_2(CO)_6$[15] and related diene complexes. While the above observations do not eliminate a structure based on π coordination of the >C=C–C=N– chromophore, the poorer coordinating ability of >C=N– compared to >C=C<[16] favours the diene formulation. This assumption is fully justified when viewed in the light of the X-ray structural studies of (1-isopropoxycarbonyl-1*H*-1,2-diazepine)$Fe(CO)_3$[3] (Xb) and (1-methoxycarbonyl-1*H*-1-azepine)$Fe(CO)_3$[10] (IXc), both of which contain coordinated diene residues.

One further feature of interest is a shift of ν(C≡O) of the –COR group to higher frequency on coordination. This reflects a rather weaker N–CO bond and consequently a higher C–O force constant in the complex.

Mass spectra★

The major ion fragments in the mass monoisotopic spectra of the complexes are shown in Table 2. Suggested fragmentation processes are given in Fig. 1

TABLE 2

MAJOR FRAGMENT IONS IN THE MASS SPECTRA OF DIAZEPINE COMPLEXES

Compound	*m/e* [abundance (%)]
(IIa)	276(8), 248(58), 220(68), 192(20), 165(35), 164(26), 151(15), 150(20), 149(45), 138(26), 137(92), 135(33), 123(60), 122(71), 111(27), 98(23), 97(48), 96(52), 95(52), 94(38), 93(13), 85(63), 84(51), 83(39), 82(79), 81(38), 80(50), 71(37), 70(14), 69(22), 68(13), 67(39), 57(42), 56(100), 54(35), 52(25), 43(70).
(IIb)	290(15), 262(86), 234(95), 206(22), 205(20), 191(39), 178(70), 163(100), 151(48), 147(41), 137(97), 135(54), 123(44), 122(79), 109(45), 97(66), 96(41), 95(44), 94(25), 93(44), 84(51), 83(34), 82(32), 81(66), 71(39), 56(85), 43(53).
(IIc)	290(3), 262(45), 234(100), 206(25), 191(8), 179(19), 178(16), 165(16), 164(23), 163(30), 151(95), 149(34), 137(34), 136(35), 135(50), 110(10), 109(15), 97(10), 95(24), 93(17), 84(15), 83(15), 82(8), 81(15), 80(20), 57(11), 56(42), 53(11), 43(16).
(V)	476(1), 448(19), 420(20), 392(20), 377(47), 363(54), 350(29), 307(100), 289(10), 274(6), 273(6), 246(5), 233(60), 230(17), 218(7), 217(7), 202(7),196(8), 192(5), 191(12), 189(6), 104(9), 103(32), 102(7), 77(10), 76(19), 57(10), 56(8), 50(6), 43(11).
(VIa)	446(40)[a], 388(3), 360(40), 332(100), 277(65), 240(57), 213(96), 186(75), 173(20), 171(21), 161(16), 149(45), 148(16), 147(45), 135(16), 134(27),131(15), 130(45), 129(31), 128(27), 124(50), 123(31), 122(50), 121(40), 115(21), 104(18), 96(40), 95(44), 94(26), 93(18), 92(37), 91(70), 89(20), 84(30), 83(25), 82(20), 81(23), 79(60), 78(44), 77(32), 76(20), 67(21), 65(40), 63(21), 56(66), 52(44), 51(42), 50(30).
(VIb)	338(1), 310(22), 282(100), 254(36), 227(23), 226(23), 199(98), 172(56), 169(13), 159(12), 143(81), 133(19), 122(21), 116(12), 115(10), 105(72), 103(71), 94(12), 84(9), 79(62), 78(47), 77(64), 76(36), 56(57), 52(40), 51(37), 50(32).
(VII)	322(2), 294(16), 266(8), 238(9), 224(4), 211(7), 195(13), 183(19), 181(16), 169(19) 168(19), 167(25), 166(18), 141(24), 140(17), 139(21), 138(10), 136(22), 115(7), 114(13), 113(8), 102(14), 94(92), 80(14), 79(86), 78(30), 69(6), 68(23), 67(91), 53(13), 52(76), 51(50), 50(40), 43(100).

[a] Similar peaks at $m/e > m/e$ of the parent ion have been found for other compounds with $-SO_2C_7H_7$ substituents, *cf.* ref. 19, Ch. 19.

★ For a recent review of mass spectra of (diene)$Fe(CO)_3$ derivatives, see ref. 17.

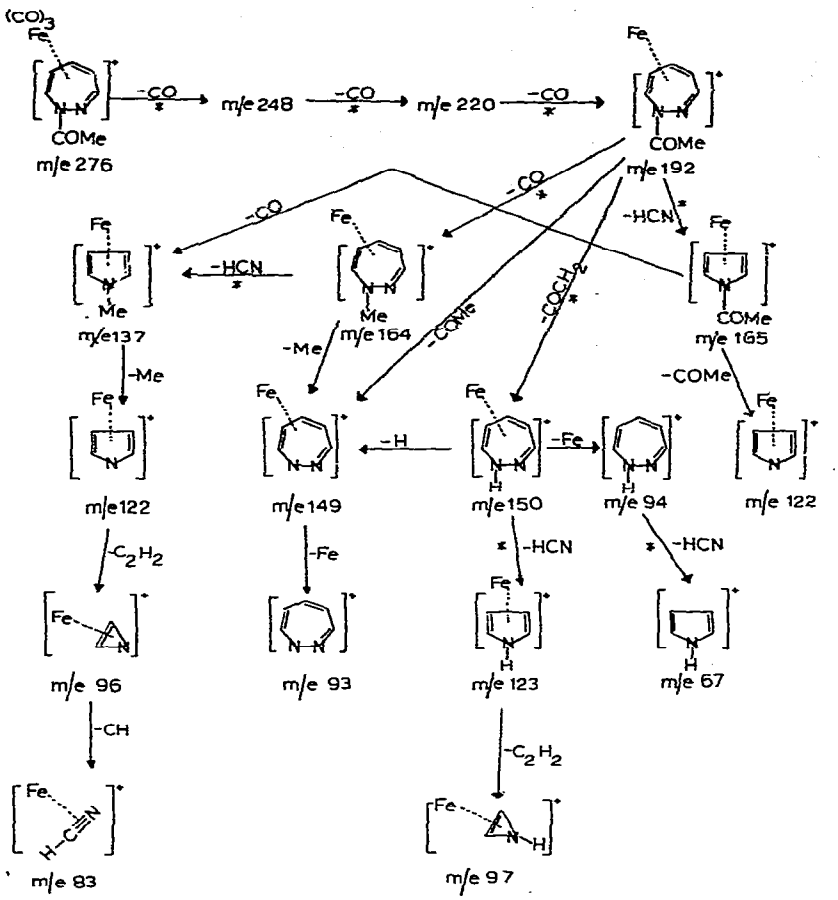


Fig. 1. Suggested electron impact fragmentation scheme for (IIa). * Represents a process for which a metastable ion was observed.

and 2 for (IIa) and (V). All of the complexes prepared exhibit parent ion peaks. In each case fragmentation of the parent ion occurs via consecutive loss of three carbonyl groups yielding the ions LFe^+ (L=1*H*-1,2-diazepine) as major fragments. Fragmentation of FeL^+ in compounds (IIa)–(IIc) occurs by similar mechanisms involving loss of CO ($FeL^+ - 28$) followed by HCN ($FeL^+ - 55$). The alternative process with elimination of HCN preceding CO loss is also important for (IIa) and (IIc) but not (IIb). Elimination of CH_3 from $(FeL-CO)^+$ gives an ion of *m/e* 163 in 100% abundance for (IIb). Similar processes occur for (IIa) and (IIc). It is of interest that Sasaki and co-workers[18] have found the dominant primary fragmentation steps in the mass spectral decomposition of substituted 1-ethoxycarbonyl-1*H*-1,2-diazepines [(I), R=R'=H, $COOC_2H_5$ for $COCH_3$] to be loss of $-NCO_2C_2H_4$ and $-CO_2C_2H_4$. For the iron carbonyl adducts (IIa)–(IIc) elimination of $-COCH_2$ appears to be of lesser importance. The ruthenium derivative (VII) exhibits stepwise loss of 3 CO groups yielding RuL^+ in 9% abundance. The fragmentation of this ion is significantly different from the iron analogue. Thus a high percentage of ion current is carried

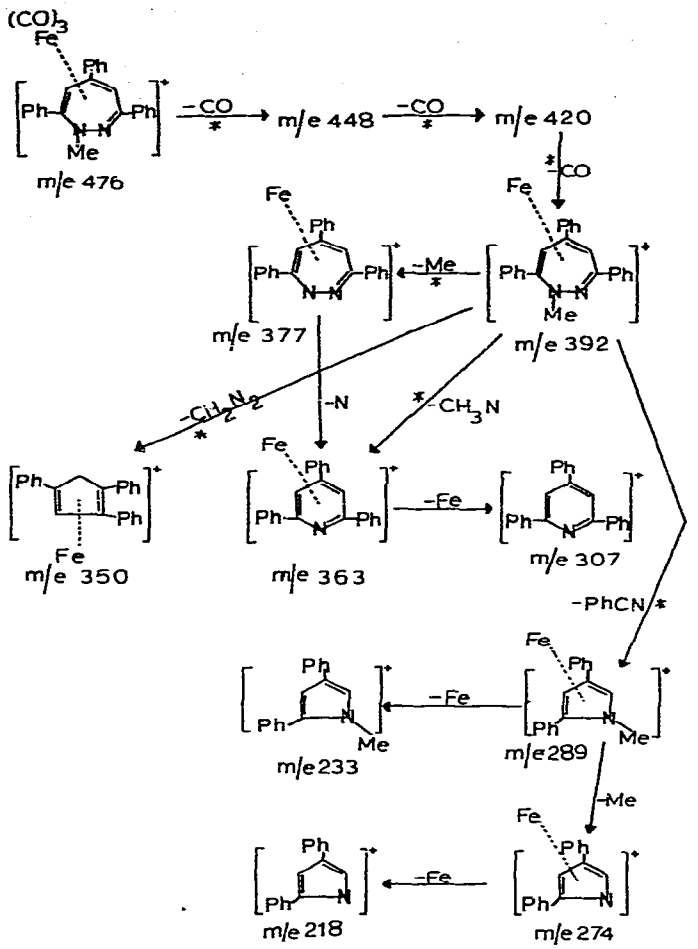


Fig. 2. Suggested electron impact fragmentation scheme for (V). * Represents a process for which a metastable ion was observed.

by an ion of *m/e* 94. This arises from RuL^+ via successive loss of Ru and $COCH_2$. Both processes were confirmed by the presence of appropriate metastable peaks. The most likely structure for the ion of *m/e* 94 is (1*H*-1,2-diazepine)$^+$. This may suggest the use of a ruthenium complex such as (VII) to generate the parent 1*H*-1,2-diazepine which has so far defied synthesis.

The fragmentation pattern for (V) (Fig. 2) shows that although ions $FeL^+ - 15$, $FeL^+ - 42$, $FeL^+ - 103$ occur in reasonable abundance, the major decomposition pathway is via loss of CH_3N from FeL^+ followed by loss of Fe to give the 2,4,6-triphenylpyridine molecule in 100% abundance. This process is not unexpected since 2,4,6-triphenylpyridine is a by-product in the reactions of both 1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine (IV) and 3,5,7-triphenyl-4*H*-1,2-diazepine (III) with $Fe_2(CO)_9$ as well as the major product in the thermolysis of the free diazepine (IV)[6]. The mass spectrum of (3,5,7-triphenyl-4*H*-1,2-diazepine)$Fe_2(CO)_6$ likewise has the 2,4,6-triphenylpyridine molecule ion as the base peak.

For compound (VIa) primary fragmentation of FeL^+ (*m/e* 304) involves successive elimination of HCN, C_7H_7 and Fe or alternatively loss of SO_2, HCN and Fe. The ion of *m/e* 240 $(FeL–SO_2)^+$ may also decompose via loss of C_7H_7 and Fe or C_7H_7 and HCN. The benzoyl complex (VIb) shows a similar fragmentation pattern to the *N*-acetyl derivative (IIa) with loss of CO and HCN or HCN and CO from FeL^+ being the dominant mechanisms.

With one exception (V) the lower mass regions of all complexes show molecule ions due to pyridine and pyrrole derivatives resulting from N and RCN losses from the bare diazepine. In contrast to the 1-ethoxycarbonyl-1*H*-1,2-diazepines[18], the fragmentation of these complexes to cyclopentadiene derivatives by loss of N_2 from *m/e* 93 are never observed. Further fragmentation of pyridine and pyrrole ions occur as predicted[19].

Mössbauer spectra

^{57}Fe Mössbauer parameters of the compounds prepared are collected in Table 3. Only one quadrupole split line was observed in each case consistent with the presence of a single non-cubic iron environment. Both isomer shift δ and quadrupole splitting ΔE_q parameters are virtually invariant throughout the series, testifying to the similarity in structure of all the compounds. The isomer shifts are of the same magnitude as those observed for a variety of organoiron compounds having π bonded diene moieties[20]. Comparison with $(C_8H_8)Fe_2(CO)_6$ (δ 0.26 mm/sec)[21], $(C_8H_8)Fe(CO)_3$ (δ 0.31 mm/sec)[21] and $(C_4H_6)Fe(CO)_3$ (δ 0.29 mm/sec)[22] suggests no significant differences in the *s* electron density at the ^{57}Fe nucleus in these diene complexes compared with the diazepine compounds. Indeed it is remarkable that in the diazepine series the nature and position of the ring substituents has little effect on the isomer shifts. Only in the 1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine derivative (V) is there a marginally lower s electron density at the ^{57}Fe nucleus. The weaker donor characteristics of a diene system having phenyl substituents or a steric effect from phenyl groups in the 5 and 7 positions of the ring may be responsible for the higher isomer shift.

The magnitudes of the quadrupole splittings are again comparable [*cf.* $(C_8H_8)Fe_2(CO)_6$ (ΔE_q 1.32 mm/sec); $(C_8H_8)Fe(CO)_3$, (ΔE_q 1.23 mm/sec); $(C_4H_6)Fe(CO)_3$, (ΔE_q 1.46 mm/sec)] with values obtained for diene complexes[20,21,22]. Although formally only five electron pairs are donated from three carbonyl groups and two olefinic double bonds, the quadrupole splittings observed are much smaller than values (usually >2.00 mm/sec) normally associated with five coordinate complexes[23] but larger than those found for ^{57}Fe in distorted octahedral environments ($\leqslant 1.0$ mm/sec)[24]. The Mössbauer results are therefore best interpreted in terms of a quasi-octahedral configuration for iron involving 2σ bonds and one μ bond from the diene system to the iron atom. In valence bond terms this represents a contribution to the bonding from (*b*). The NMR parameters (*vide infra*) as well as recent Mössbauer results for related compounds[25] favour this interpretation.

Finally it is worth noting that in the complexes (3,5,7-triphenyl-4*H*-1,2-diazepine)$Fe_2(CO)_6$[4] and (3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine)$Fe_2(CO)_6$[26] the two iron atoms are nonequivalent and give 3 or 4 line Mössbauer spectra (Table 3). Comparison of Mössbauer parameters for these nitrogen bridged species with the data for (diazepine)$Fe(CO)_3$ adducts confirms that diene type coordination can be

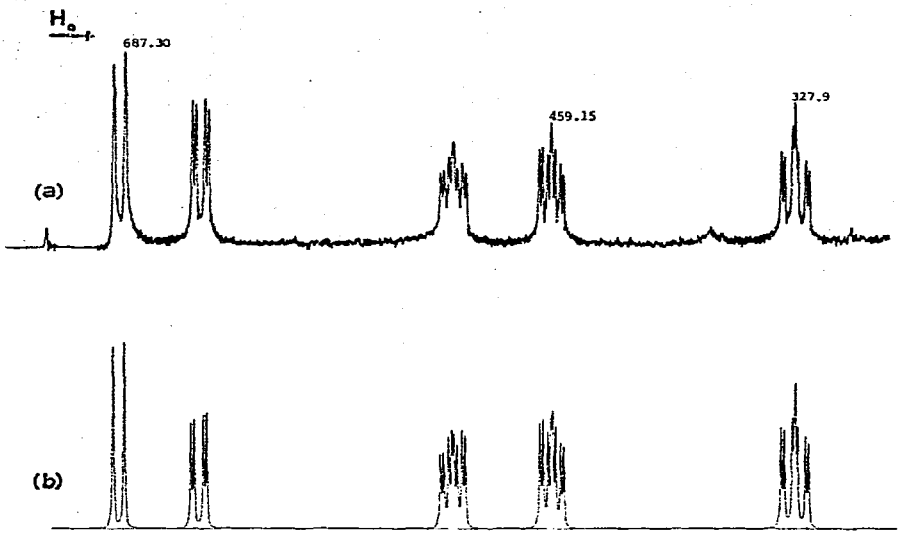


Fig. 3. Experimental (a) and calculated (b) 100 MHz spectrum of the ring protons of (IIa) in $CDCl_3$. Line positions in Hz refer to internal tetramethylsilane at 0.0 Hz.

readily recognised from an analysis of the Mössbauer spectrum.

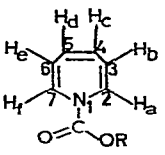
NMR Spectra

Although a larger number of transition metal complexes of cyclic π-systems are now known[27], relatively few of these contain nitrogen heteroatoms as part of the ring framework*. Clearly NMR spectroscopy has yielded important structural information concerning these complexes[27] but, as has been pointed out[29], there has been very little precise data for H,H′ coupling constants in this class of compounds. In this regard, a (1-ethoxycarbonylazepine)iron tricarbonyl complex (VIIIa) has been partially analyzed[30,31] and a first-order analysis of (1-ethoxycarbonyl-1*H*-1,2-diazepine)iron tricarbonyl complex (Xa) has been reported[2,32]. We undertook a detailed analysis of the NMR spectrum of (IIa) in order to gain insight into the nature of the bonding and the geometry in this system. A timely report[3] dealing with the X-ray analysis of (Xb) also presents an opportunity for comparison of data with NMR parameters.

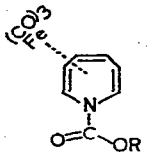
The spectrum of (IIa) recorded at 100 MHz consists of a five-spin system of the ABCDE type with each set of peaks separated in chemical shift for convenient first-order analysis (Fig. 3). The observed spin–spin interactions lead to a unique assignment of resonance frequencies for the structure. The best parameters obtained by iterative computer calculation with a modified LAOCOON II program[33] are given in Table 4. The calculated and observed line positions agreed to better than 0.05 Hz. A zero value was assumed for the coupling constants $J_{be}=J_{eb}$ and $J_{bf}=J_{fb}$. Positive signs of coupling constants were assumed according to currently accepted theory[34].

The known effect of the metal carbonyl group on proton chemical shifts in diene complexes[27] is clearly evident from the comparison of spectra of the free ligand

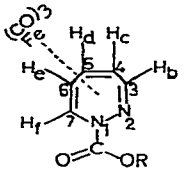
*For recent examples other than those discussed herein, see ref. 28.



(VIII)

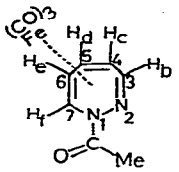


(IX)



(X)

a, R = Et
b, R = iPr
c, R = Me



(IIa)

TABLE 3

MÖSSBAUER DATA FOR DIAZEPINE COMPLEXES[a]

Compound	δ (mm/sec)	ΔE_q (mm/sec)
(IIa)	0.31	1.24
(IIb)	0.31	1.26
(IIc)	0.32	1.31
(V)	0.34	1.25
(VIa)	0.31	1.27
(VIb)	0.30	1.25
$(C_{23}H_{18}N_2)Fe_2(CO)_6$	0.22	0.93
	0.35	1.19
$(C_{23}H_{20}N_2)Fe_2(CO)_6$	0.19	0.77
	0.31	1.49

[a] Relative to sodium nitroprusside.

TABLE 4

CALCULATED NMR SPECTRUM OF (1-ACETYL-1*H*-1,2-DIAZEPINE)$Fe(CO)_3$ COMPLEX (IIa)

Chemical shifts τ values

H_b	3.067	3.127						
H_c	6.647	6.663	6.707	6.719	6.722	6.734	6.778	6.795
H_d	4.818	4.835	4.861	4.878	4.889	4.906	4.932	4.948
H_e	5.345	5.362	5.389	5.405	5.412	5.429	5.456	5.472
H_f	3.486	3.503	3.553	3.571				

Coupling constants (Hz)

$J_{bc}=J_{cb}$	$J_{bd}=J_{db}$	$J_{cd}=J_{dc}$	$J_{ce}=J_{ec}$	$J_{de}=J_{ed}$	$J_{df}=J_{fd}$	$J_{ef}=J_{fe}$
5.99	0.30	7.12	1.61	4.30	1.67	6.73

TABLE 5

NMR SPECTRA OF 1*H*-AZEPINE AND 1*H*-1,2-DIAZEPINE DERIVATIVES AND THEIR $Fe(CO)_3$ COMPLEXES

Proton	Chemical shift, τ		Δ Chemical shift[c]
	(IXa)[a]	(VIIIc)[b]	
H_a	3.5	4.1	−0.6
H_b	4.94	4.5	+0.44
H_c	6.46	3.9	+2.56
H_d	4.94	3.9	+1.04
H_e	5.53	4.5	+1.03
H_f	3.93	4.1	−0.17
	(IIa)	(Ia)[d]	
H_b	3.08	2.64	+0.42
H_c	6.72	3.8	+2.92
H_d	4.89	3.46	+1.43
H_e	5.41	4.23	+1.17
H_f	3.53	3.61	−0.08

[a] Data from ref. 30 determined at ca. 0° (no fluxional character). [b] Data from ref. 31. [c] τ(complex)–τ(ligand). Positive value represents an upfield shift and negative value a downfield shift relative to TMS. [d] Prepared as described in ref. 1b. Assignments based on first-order analysis only. Computer-simulated analysis of this and related diazepines is in progress.

(Ia) and its complex (IIa) (Table 5). The upfield shift of all protons except H_f in (IIa) and (IXa) may be explained by the change in π-electron density at the carbon atoms bound to metal but, as has been previously noted[29], shielding effects due to C≡O and C–metal bonds must also be considered although the nature and the magnitude of these effects are not presently understood. Interestingly, comparison of the reported NMR spectra of 1-methoxycarbonylazepine (VIIIc)[31] with the $Fe(CO)_3$ adduct IXa[30,31] shows very similar changes in chemical shifts upon complexation as those observed in our case [(Ia) to (IIa)] (Table 5). The rather small upfield shift of H_b for both systems upon complexation to (IXa) and (IIa) may be explained by the normal deshielding mechanism associated with the nitrogen atom[35] [N_1 in (IXa), N_2 in (IIa)]

TABLE 6

SELECTED COUPLING CONSTANTS OF 1*H*-AZEPINE AND 1*H*-1,2-DIAZEPINE $Fe(CO)_3$ COMPLEXES AND TCNE ADDUCTS

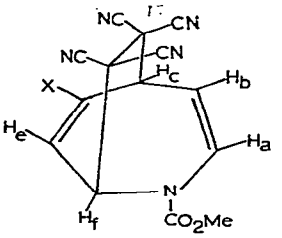
Compound	Coupling constants (Hz)								Ref.
	J_{ab}	J_{bc}	J_{bd}	J_{cd}	J_{ce}	J_{de}	J_{df}	J_{ef}	
(XIb)	8.8	8.8		8.1	1.3	8.1		7.5	37
(IXa)	9	7.8		7.8				6.8	30
(XII)		6		8		8	1.5	7	18
(IIa)		6		7	1.6	4.3	1.7	6.7	[a]
(VIIIa)		5.43	0.65	11.44	0.65	5.43			36
(Ia)		3.5	1	11	1.5	5.5		7.5	[b]

[a] This work. [b] See footnote *d*, Table 5.

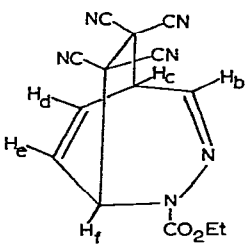
whose effect largely offsets the change due to more sp^3 character at C_3. The marginal downfield shift of H_f for both heterocycles upon complex formation may be a manifestation of the higher sp^3 character at C_7 (which otherwise would have produced a normal upfield shift for H_f) being dominated by a deshielding mechanism due to carbonyl oxygen in the preferred N_1–C=O conformations as indicated in the structural formulas. The X-ray structure supports the N–C=O conformation (Xb) as written for the diazepine derivative[3] and the NMR data shows the preference for conformation (IXa) for the azepine complex at low temperatures [$\Delta G(-58°)$ ca. 0.4 kcal/mole][30]. Similar effects due to N–C=O rotational changes may be operating in the diazepines (II) although here the associated energy barriers must be very low (*vide infra*). In agreement with this conclusion, our infrared data for (IIa) and the X-ray analysis[3] of (Xb) point to very little N–CO double bond character in these structures.

It is more instructive to compare the coupling constants for certain protons in the azepine and diazepine $Fe(CO)_3$ complexes (IXa)[30] and (IIa) respectively (Table 6). The relative magnitude of coupling constants $J_{cd} > J_{de}$ and $J_{ef} > J_{de}$ in both compounds are in agreement with those observed for other diene–metal carbonyl complexes[27].

The close similarity of selected coupling constants for the two compounds offers evidence that they exist in similar conformations. Comparison of the recent X-ray study of (Xb)[3] with that of (IXc)[10] is in agreement with this assertion. Table 6 also presents a comparison of coupling constants for (VIIIa) and (Ia) which demonstrates the existence of gross conformational similarities in the bare azepine and diazepine systems.



(XIa, X=Br;
XIb, X=H_d)



(XII)

Johnson and Paul also compared the X-ray structure of (IXc) with that of the azepine–tetracyanoethylene (TCNE) 1,4-cycloaddition product (XIa) and noted the striking similarities in the bond lengths and bond angles, *i.e.* in the overall geometry, of the two structures[10]. Consideration of the NMR spectra of (IXa) and a close relative of (XIa), (XIb), shows that the same conclusion could also be reached on the basis of comparison of spin–spin interactions (Table 6). It is seen that certain coupling constants in the adduct (XIb)[37] are almost identical to those in the $Fe(CO)_3$ complex (IXa). If now comparison is made of the corresponding coupling constants in the reported diazepine–TCNE adduct (XII)[18] with those of our $Fe(CO)_3$ complex (IIa), a similar pattern is observed with the exception of one coupling constant, J_{de}. The rather large difference of J_{de} in (XII) and (IIa) may be rationalized by considering that in (XII) a pure sp^2-hybridised double bond bearing H_d and H_e is involved whereas

the butadiene bond H_d–C–C–H_e in (IIa) has somewhat less sp^2 character. A comparison of carbon–carbon (H_d–C=C–H_e) bond distances in the analogous azepine–TCNE adduct (XIa) (1.35 Å)[11] and the $Fe(CO)_3$ complex (IXc) (1.40 Å)[10] and knowledge that the same bond distance in (Xb) is 1.38 Å[3] gives confidence to this conclusion. The X-ray picture of (Xb) also indicates that there is substantial sp^3-character at C_4 and C_7. Comparison of the spin–spin interactions J_{cd} and J_{ef} in the Diels–Alder adduct (XII) and our complex (IIa) implies that the dihedral angles associated with these protons must be similar in both compounds and leads to the same conclusion.

It has been noted that the NMR results point to similar conformations for the azepine (VIIIa) and the diazepine (Ia) derivatives (Table 6). In view of this spectral correlation and the fact that an azepine derivative has been shown to possess a tub-shaped conformation by X-ray analysis[38], it may be safely assumed that a like conformation is valid for the diazepine derivative (Ia). On the basis of this information, it is possible to correlate the changes in coupling constants on complexation for both heterocyclic systems from considerations of changes in dihedral angles[39] and π-electron density. There is a diminution in the dihedral angle H_b–C_3–C_4–H_d upon $Fe(CO)_3$ complex formation (IIa) due to the flattening of the N_1–N_2–C_3 portion of the ring which thus results in a modest increase in the magnitude of the coupling constant ($\Delta J_{bc} = J_{bc}$(IIa)–J_{bc}(Ia) = 1.5 Hz. The dihedral angle H_c–C_4–C_5–H_d changes significantly becoming larger in the complex in agreement with the observed decrease in magnitude of coupling constant (ΔJ_{cd} = 3.9 Hz). The long range coupling J_{ce} remains virtually the same (ΔJ_{ce} = 0.1) upon complexation due to the nature of the change (N_2–C_3–C_4–H_c becoming planar and the C_5–C_6 bridge flipping upward) creating an almost identical situation with respect to the dihedral angle associated with H_c and H_e. The dihedral angle H_d–C_5–C_6–H_e becomes smaller on complex formation but the coupling constant decreases in magnitude (ΔJ_{de} = 1.2 Hz). It appears that the dominant factor responsible for this divergent result is the lack of the expected increased π-character of the C_5–C_6 double bond due to the effect of the $Fe(CO)_3$ group. Finally, the change in coupling constant ΔJ_{ef} = 0.8 Hz upon complexation is that expected as a result of the C_6–C_7 double bond breaking sp^2 character with the atoms N_2–N_1–C_7 reaching coplanarity and the C_5–C_6 bridge flipping upward and out of the plane.

Table 7 records the NMR spectra of compounds (IIb), (IIc), and (VII). Very slight changes in chemical shift and coupling constants are observed upon introduction of methyl groups into the diazepine ring presumably indicating no divergence from the conformation of the parent system (IIa). Comparison of the NMR spectrum of (IIa) with that of the ruthenium tricarbonyl derivative (VII) shows no great differences in position of proton resonance or coupling constants. Contrary to some general trends[40] but in agreement with another study[29], change of metal within the same group of the periodic table has no significant effect on these parameters.

The NMR spectrum of the (1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine)iron tricarbonyl complex (V) shows, besides signals due to aromatic protons at τ 1.93 (m, 2H), 2.25 (m, 2H) and 2.53–3.12 (m, 11H) and the *N*-methyl function at τ 7.02 (s, 3H), two doublets ($J_{ce} = J_{ec}$ = 2 Hz) at τ 5.26 and 5.06 each corresponding to 1 hydrogen. These are assigned to H_e and H_c respectively on the basis of the charge density qualitatively expected at these two protons as a result of interaction with the N_1-lone pair of electrons. Comparison of the NMR spectrum[6] of the ligand (IV)

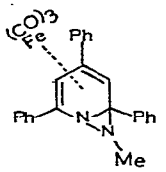
TABLE 7

100 MHz NMR SPECTRA OF 1*H*-1,2-DIAZEPINE COMPLEXES[a]

Compound	Chemical shifts, τ values[b]						Coupling constants (Hz)
	$NCOCH_3$	H_3	H_4	H_5	H_6	H_7	
(IIb)	7.69 (s)	7.89[c] (s)	6.81 (dd)	4.91 (o)	5.41 (o)	3.61 (dd)	$J_{4,5}=J_{5,4}=7.5$, $J_{4,6}=J_{6,4}=2$, $J_{5,6}=J_{6,5}=4.5$, $J_{5,7}=J_{7,5}=2$, $J_{6,7}=J_{7,6}=7$
(IIc)	7.63 (s)	3.16 (s)	8.09[c] (s)	5.03 (br, d)	5.62 (dd)	3.66 (dd)	$J_{5,6}=J_{6,5}=4.5$, $J_{6,7}=J_{7,6}=6.5$, $J_{7,5}=2$
(VII)	7.65 (s)	3.08 (d)	6.57 (o)	4.64 (o)	5.03 (m)	3.60 (dd)	$J_{3,4}=J_{4,3}=6$, $J_{4,5}=J_{5,4}=7$, $J_{4,6}=J_{6,4}=1.5$, $J_{5,3}=0.5$, $J_{5,6}=J_{6,5}=4.5$, $J_{5,7}=J_{7,5}=2$, $J_{6,7}=J_{7,6}=7$

[a] For NMR spectrum of V, see Discussion. [b] Multiplicity between brackets. s=singlet, d=doublet, dd=double doublet, m=multiplet, o=octet, br=broad. [c] Ring C–CH_3 resonance.

with that of the complex (V) points to the latter having a more planar heterocyclic ring structure in agreement with the conclusions drawn above concerning geometrical changes associated with formation of the complex (IIa) from (Ia). Furthermore, the similarity of coupling constants J_{ce} in compounds (IIa) and (V) should be noted. Thus we favor the assignment of structure (V) to the (1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine)iron tricarbonyl complex although it should be pointed out that, due to the highly substituted pattern, in particular, a phenyl group rather than H at C_3, the NMR spectral data does not lead to a clear choice between (V) and the bicyclic structure (XIII). For this reason, an X-ray analysis of this compound is presently under investigation.



(XIII)

The azepine–$Fe(CO)_3$ adduct (IXa) shows fluxional character[41] by virtue of the rapid movement of the metal atom from one diene unit to another[30,31]. In the case of (IIa), no changes in the NMR spectrum were observed in the temperature range of −40° to +50°C. This result also implies that the energy barrier due to hindered rotation of the –N–CO function must be quite low.

EXPERIMENTAL

1-Acetyl-1*H*-1,2-diazepine, 3-methyl-1-acetyl-1*H*-1,2-diazepine and 4-methyl-1-acetyl-1*H*-1,2-diazepine were synthesised by the photolysis of the 1-(acetylimino)-pyridinium ylides as previously described[1b]. 1-*p*-Toluenesulphonyl-1*H*-1,2-diazepine and 1-benzoyl-1*H*-1,2-diazepine were prepared according to published procedures[1a,2] 1-Methyl-3,5,7-triphenyl-1*H*-1,2-diazepine was synthesised by the reaction of 2,4,6-

triphenylthiapyrilium perchlorate with methylhydrazine[6]. Triruthenium dodecacarbonyl was purchased from Strem Chemicals, Andover, Massachusetts. Diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl in glacial acetic acid[7]. Column and thin layer chromatography was carried out on silica gel or alumina. Solvents were reagent grade and degassed before use. All reactions and subsequent manipulations were performed under a nitrogen atmosphere.

Microanalyses were carried out by A. B. Gygli, Toronto and by Alfred Bernhard, Fritz Pregl Strasse, Elbach über Engelskirchen, Germany. Analytical data for new compounds are summarised in Table 8. High resolution infrared spectra in the $\nu(C\equiv O)$ region were recorded on a Beckman IR 9 instrument in hexane solution. Routine infrared spectra were measured in chloroform solution using a Beckman IR 10 spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian T-60 and HA-100 spectrometers in deuteriochloroform solution with tetramethylsilane as internal reference. Mass spectra were determined on a Hitachi–Perkin–Elmer RMU-6E spectrometer at 70 eV. The Mössbauer equipment has been previously described in detail[8]. Samples were examined as mulls with the absorber at 78°K and source at room temperature. The accuracy of the Mössbauer parameters is ± 0.01 mm/sec. Ultraviolet spectra were measured on a Hitachi EPS-3T spectrophotometer.

Preparation of $Fe(CO)_3$ adducts

The following general synthetic procedure was used: The diazepine (0.5 g) and a slight excess of diiron nonacarbonyl were stirred at room temperature in the dark in dry degassed benzene for 8–10 h. The reaction mixture was then filtered and the filtrate evaporated to dryness. The residue was dissolved in 60–80° petroleum ether and chromatographed on silica gel. Elution with 4/1 benzene/ethyl acetate gave clear yellow solutions of the complexes. The yellow solutions were then evaporated to dryness and recrystallised from petroleum ether (60–80°).

The above procedure gave the following compounds: (1-acetyl-1*H*-1,2-diazepine)iron tricarbonyl (IIa) (yellow); (3-methyl-1-acetyl-1*H*-1,2-diazepine)iron tricarbonyl (IIb) (yellow); (4-methyl-1-acetyl-1*H*-1,2-diazepine)iron tricarbonyl (IIc) (yellow); (1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine)iron tricarbonyl (V) (red); (1-*p*-toluenesulphonyl-1*H*-1,2-diazepine)iron tricarbonyl (VIa) (yellow); (1-benzoyl-1*H*-1,2-diazepine)iron tricarbonyl (VIb) (yellow).

Preparation of (1-acetyl-1H-1,2-diazepine)ruthenium tricarbonyl (VII) (pale yellow)

The diazepine (0.4 g) and triruthenium dodecacarbonyl (0.5 g) were stirred together in benzene for 58 h. Unreacted carbonyl and impurities were filtered off and the filtrate evaporated to dryness. Cyclohexane (100 ml) was added and the mixture stirred for 1 h. Reduction of the solution volume to ca. 6 ml followed by filtration and chromatography on alumina gave two yellow bands on elution with cyclohexane. The first band was found to be $Ru_3(CO)_{12}$. The second band was eluted and the solution taken to dryness. Recrystallisation from n-heptane gave a small yield of yellow needles of the tricarbonyl adduct.

TABLE 8

ANALYTICAL DATA FOR DIAZEPINE COMPLEXES

Complex	M.p. (°C)	Analysis, found (calcd.) (%)			MeOH[a] λ_{max}	ε_{max}
		C	H	N		
(IIa)	71.5–72	43.79	3.06	10.12	256	1.70×10^4
		(43.48)	(2.90)	(10.15)	310 (sh)	8.7×10^3
(VII)	77–78	37.75	2.05	9.33	226	2.02×10^4
		(37.38)	(2.51)	(8.72)	260 (sh)	1.57×10^4
(IIb)	112–113	45.40	3.51	9.48	257	1.7×10^4
		(45.55)	(3.48)	(9.66)	310 (sh)	6.1×10^3
(IIc)	138–140	45.48	3.66	9.85	258	1.84×10^4
		(45.55)	(3.48)	(9.66)	310 (sh)	6.05×10^3
(V)	141–142	67.83	4.38	5.87	253	3.81×10^4
		(68.08)	(4.23)	(5.88)	310 (sh)	1.05×10^4

[a] The complexes were stable in methanol solution indefinitely.

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