# Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) with Lewis Acids resulting in Adduct Formation, Dimer Scission or Both. Structure of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$

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*$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) react with Lewis Acids E = $SnX_2$, $SnX_4$, $ZnX_2$, $CdX_2$, $AsCl_3$, $NiCl_2 \cdot 6H_2O$ and $AgNO_3$ (X = F, Cl, Br or I) to form adducts of the type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ where there are N → E bonds between the μ-CNR ligand and the Lewis acid. The adducts have been identified by IR and, where possible, $^1H$ NMR spectroscopy, but only a few could be isolated and analysed. Often they decomposed to mononuclear species* e.g. *the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]/AgNO_3$ adduct ultimately deposits silver metal and gives $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ as the sole product in high yields. Other Lewis acids* e.g. *$CoI_2$, $CuCl_2 \cdot 4H_2O$ or $BF_3 \cdot OEt_2$ cleave the dimers, apparently without adduct formation, but only the principal cleavage product from the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]/BF_3 \cdot OEt_2$ reaction could be identified. It was $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$ and its structure has been determined using X-ray diffraction techniques.*

*[Structure solved by the heavy-atom method from photographic data and refined by full-matrix least-squares to* R = *0.071 for 370 non-zero unique reflexions. Crystals of this compound are orthorhombic with space group* $Pca2_1$, Z = *4,* a = *12.998 ± 0.012,* b = *6.305 ± 0.006, and* c = *16.603 ± 0.015* Å.*] The cation has the usual 'piano-stool', half-sandwich ligand arrangement about the Fe atom.*

## Introduction

The Lewis base character of the N atom of the μ-CNR ligand in various $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = $C_5H_5$, $C_5H_4Me$, or $C_9H_7$; R = alkyl, benzyl, or aryl; n = 1 or 2) has been well established. Lewis acids, E, such as $H^+$ [1, 2, 3], $Me^+$, [3, 4] or $MeCO^+$ [5] form $[Fe_2(\eta\text{-dienyl})_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ adducts with N → E bonds (L = CO or CNR).

We describe here the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$, (I), to a limited extent only, and of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$, (II), with metal and metalloid halides and other salts which can act as Lewis acids. Adducts may be formed and many have been isolated. Some undergo slow cleavage to mononuclear species. In other instances adducts are not detected and only cleavage products have been observed. The structure of one such compound, $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$, has been determined by X-ray diffraction methods. Similar adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with more powerful Lewis acids such as the trihalides or trialkyls of boron or aluminium have already been reported together with the structure of one, $[Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2\{\mu\text{-}CO(AlEt_3)\}_2]$ [6]. Weaker Lewis acids such as $ZnCl_2$ do not form such adducts [7].

## Experimental

Literature methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (n = 0 [8], 1 [9], and 2 [10]), $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ [11], and CNMe [12]. Other chemicals were purchased and used as received.

The reactions were carried out at room temperature under an atmosphere of nitrogen in solvents which had been dried and deoxygenated by refluxing over calcium hydride and distilled prior to use.

Equimolar quantities of $[Fe_2(\eta\text{-}C_5H_5)_2)CO)_2(L)(CNMe)]$ (L = CO or CNMe) (0.5 g) and the metal halide were stirred in benzene, chloroform, or tetra-

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TABLE I. Melting Point and Analytical Data for some Compounds Described in the Text.

| E | M.p. (°C) | Analysis[a] | | |
|---|---|---|---|---|
| | | %C | %H | %N |
| *[$Fe_2(\eta$-$C_5H_5)_2(CO)_3(CNMe)$]/E Adducts* | | | | |
| $CdI_2 \cdot CH_2Cl_2$ | 120–122 | 20.9(20.9) | 1.4(1.6) | 1.5(1.5) |
| *[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$]/E Adducts* | | | | |
| $ZnCl_2$ | 102–105 | 37.7(37.3) | 3.3(3.1) | 5.4(5.4) |
| $ZnI_2 \cdot$½THF | dec. 95 | 34.1(34.4) | 4.2(3.2) | 4.0(4.0) |
| $CdCl_2 \cdot$½THF | 128–130 | 35.9(36.1) | 3.6(3.0) | 5.3(4.7) |
| $CdBr_2$ | dec. 130 | 30.3(29.4) | 3.3(2.5) | 3.5(4.3) |
| $CdI_2$ | dec. 120 | 27.6(27.6) | 3.1(2.6) | 3.4(3.5) |
| $SnCl_2$ | 30–32 | 34.3(33.7) | 3.6(2.8) | 4.8(4.9) |
| *[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$]/E Cleavage Products* | | | | |
| $AgNO_3$[b] | dec. 85 | 37.8(38.0) | 3.2(3.2) | 10.5(11.1) |
| $BF_3$[c] | dec. 220 | 37.0(37.5) | 3.7(3.4) | 8.1(8.8) |

[a]Found with calculated values in parentheses. [b][$Fe(\eta$-$C_5H_5)(CO)(CNMe)NO_3$]. [c][$Fe(\eta$-$C_5H_5)(CO)(CNMe)_2$][$BF_4$].

hydrofuran (50 ml). For $ZnX_2$, $CdX_2$, $SnX_4$ or $AsCl_3$ (X = F, Cl, Br or I) the reaction mixtures changed colour from purple to brown with almost instantaneous adduct formation. The adducts could be isolated by partial removal of the solvent at reduced pressures, but not all of them gave consistent analyses and attempts to purify them further failed except for [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2 \cdot ZnCl_2$] which was recrystallized from dichloromethane–hexane mixtures. The adducts from [$Fe_2(\eta$-$C_5H_5)_2$-$(CO)_2(CNMe)_2$] and $AgNO_3$ or $NiCl_2 \cdot 6H_2O$ precipitated immediately from tetrahydrofuran solution. $CoI_2$, $CuCl_2 \cdot 4H_2O$ and $BF_3 \cdot OEt$ did not form adducts with [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$] and the decomposition products could not be identified except in the last case where, if the reaction mixture was allowed to stand at –25 °C, it deposited a 30% yield of yellow crystals of [$Fe(\eta$-$C_5H_5)(CO)$-$(CNMe)_2$][$BF_4$].

Dissolution of the [$Fe_2(\eta$-$C_5H_5)(CO)_2(CNMe)_2$]/$AgNO_3$ adduct in tetrahydrofuran (100 ml) resulted in its slow decomposition with the formation of [$Fe(\eta$-$C_5H_5)(CO)(CNMe)NO_3$]. If an extra equivalent of $AgNO_3$ was added, the rate of this reaction increased markedly. Silver metal was deposited as a grey powder. It was filtered off, the solvent removed from the filtrate at reduced pressure, and the residue recrystallized from toluene/hexane mixtures. The yield of [$Fe(\eta$-$C_5H_5)(CO)(CNMe)NO_3$] was 78% based on the weight of [$Fe_2(\eta$-$C_5H_5)_2(CO)_2$-$(CNMe)_2$] used.

[$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2 \cdot ZnCl_2$- (0.1 g) was dissolved in liquid ammonia (20 ml) and the solvent allowed to evaporate at room temperature. The residue was dissolved in toluene, filtered, and pentane added to the filtrate. On cooling it, crystals of [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(CNMe)_2$] were precipitated. They were filtered off, washed with cold pentane, and dried (yield = 73%).

Analytical data and melting points of the various pure products are summarised in Table I. The analyses were carried out in the Analytical Laboratory of University College, Dublin.

Infrared spectra were measured on a Perkin Elmer 337 IR spectrometer equipped with a Hitachi-Perkin Elmer readout recorder. The spectra were calibrated [13] with CO, DCl, and $H_2O$ vapour so that peak positions in the 1600–2200 $cm^{-1}$ region are accurate to ±2 $cm^{-1}$. The IR spectra in this region are summarised in Table II.

Proton NMR spectra were measured on a Perkin Elmer R12B spectrometer in $CDCl_3$ solution using $Me_4Si$ as an internal standard. Spectra obtained by redissolving previously isolated adducts in $CDCl_3$ were not reproducible or satisfactory. In most instances there was sample decomposition with broad, ill-defined resonance peaks. Consequently the adducts were prepared *in situ* by dissolving the [$Fe_2(\eta$-$C_5H_5)_2(CO)_2(L)(CNMe)$] complex (0.1 g) in the minimum volume of $CDCl_3$ and adding an equimolar amount of the Lewis acid. The NMR spectra thus obtained which were of good quality

TABLE II. The IR and $^1$H NMR Spectra of some Adducts and Cleavage Products Derived from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) and Lewis Acids E.

| E | IR Absorption Bands[a] | | | | $\eta^5$-$C_5H_5$ | $^1$H NMR Resonances[b] | | |
|---|---|---|---|---|---|---|---|---|
| | A[$\nu(CN_\mu)$] | B[$\nu(CO_\mu)$] | C[$\nu(CO_t)$] | D[$\nu(CO_t)$] | | $\mu$-CN(E)Me | t-CNMe | Others |
| *Adducts*; L = CO | | | | | | | | |
| $ZnCl_2$ | 1597(2.5) | 183(2.8) | 1990(2.8) | 2023(10) | | | | |
| $CdCl_2$ | 1597(2.1) | 1831(2.9) | 1992(2.7) | 2022(10) | 4.76(s) | 3.18(s) | | $H_2O$ = 3.45(br) |
| $CdI_2$ | 1596(3.1) | 1820(3.0) | 1987(3.0) | 2022(10) | | | | |
| $SnCl_2$ | 1598(2.5) | 1832(3.2) | 1994(3.3) | 2025(10) | 4.81(s) | 3.25(s) | | |
| $SnI_2$ | 1597(2.5) | 1831(3.6) | 1994(5.1) | 2026(10) | | | | |
| *Adducts*; L = CNMe | E[$\nu(CN_\mu)$] | F[$\nu(CO_\mu)$] | G[$\nu(CO_t)$] | H[$\nu(CN_t)$] | | | | |
| $ZnCl_2$ | 1585(4.7) | 1811(7.0) | 1998(10) | 2180(6.6) | 4.90(s,br) | 4.05(s) | 3.06(s) | $H_2O$ = 3.45(br) |
| $ZnBr_2$ | 1585(4.6) | 1807(6.4) | 1987(10) | 2181(6.7) | | | | |
| $ZnI_2 \cdot ½THF$ | 1586(4.6) | 1811(5.7) | 1988(10) | 2183(6.6) | | | | |
| $CdCl_2 \cdot ½THF$ | 1593(5.5) | 1805(8.1) | 1984(10) | 2178(7.8) | 5.10, 5.06 | 4.17(s) | 3.17(s) | $H_2O$ = 3.45(br) |
| $CdBr_2$ | 1593(7.2) | 1812(8.2) | 1987(10) | 2180(7.2) | | | | |
| $CdI_2$ | 1585(7.1) | 1814(7.2) | 1991(10) | 2181(7.8) | 4.90, 4.81 | 4.03(s) | 3.06(s) | |
| $SnF_2$ | 1591(4.0) | 1805(5.7) | 1985(10) | 2177(6.8) | | | | |
| $SnCl_2$ | 1591(4.4) | 1806(5.6) | 1986(10) | 2181(6.7) | 4.99(s,br) | 4.00(s) | 3.05(s) | |
| $SnBr_2$ | 1591(4.3) | 1806(6.3) | 1985(10) | 2178(7.0) | | | | |
| $SnI_2$ | 1587(4.2) | 1807(6.5) | 1984(10) | 2180(7.0) | | | | |
| $SnI_4$ | 1589(5.0) | 1817(5.7) | 1988(10) | 2180(6.8) | | | | |
| $AsCl_3$ | 1599(5.0) | 1813(5.5) | 1990(10) | 2185(7.0) | | | | |
| $NiCl_2 \cdot 6H_2O$ | 1593(4.2) | 1802(6.1) | 1982(10) | 2177(7.8) | | | | |
| $AgNO_3$[c,d] | 1570(m) | 1795(m) | 1962(s) | 2164(m) | | | | |
| *Cleavage products*; L = CNMe | | | | | | | | |
| $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$[d] | | | 1982(s) | 2191(s) | | | | |
| $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$[e] | | | 2023(10) | 2203(9.0) 2228(7.8) | | | | |

[a]Peak positions ($cm^{-1}$) with relative peak heights in parentheses. Measured in $CHCl_3$ solution unless stated otherwise. [b]P.p.m. downfield from $Me_4Si$. Measured in $CDCl_3$ solution. S = singlet, br = broad. [c]IR spectrum measured for nujol mull. (w) = weak, (m) = medium and (st) = strong absorption band intensity. [d]From reaction of (II) with $AgNO_3$. [e]From reaction of (II) with $BF_3 \cdot OEt_2$ $\nu(BF_4)$ = 1050 $cm^{-1}$ (very broad).

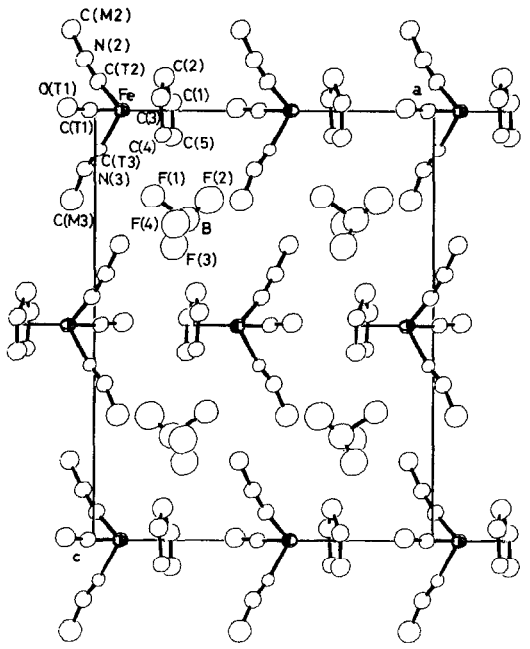


Fig. 1. Geometry of the $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$ and $[BF_4]^-$ ions, their crystal packing, and the atom labelling.

are summarized in Table II. As a check, the IR spectra of these solutions were run as soon as the NMR spectra had been obtained. All showed that only the adducts were present. In other cases the NMR spectra could not be obtained due to excessive sample decompositon or low adduct solubility.

Attempts were made to obtain the mass spectra of the adducts on a VG 70-70M mass spectrometer. They were not successful and only ions due to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) were detected.

*Crystal Data*

$C_{10}H_{11}BF_4N_2OFe$, $M$ = 317.9, Orthorhombic, $a$ = 12.998 ± 0.012, $b$ = 6.305 ± 0.006, $c$ = 16.603 ± 0.015 Å, $U$ = 1360.7 Å$^3$, $D_m$ = 1.55 (by flotation), $Z$ = 4, $D_c$ = 1.551 g cm$^{-3}$, $F(000)$ = 640, $\mu$(Mo-K$_\alpha$) = 8.9 cm$^{-1}$. Systematic absences $h0l$ if $h \neq 2n$ and $Okl$ if $l \neq 2n$, space group $Pca2_1$ (No. 29) or $Pcam$ (non-standard No. 57).

Cell parameters were determined from precession photographs using Mo-K$_\alpha$ radiation. Intensities were estimated visually from layers 0–2 about [010], 0–4 about [001] and 0–3 about [011]. They were corrected for Lorentz and polarisation effects but not for extinction. The structure factors were placed on a common scale by internal correlation, and 370 non-zero unique reflexions obtained. Scattering factors were taken from ref. 14 and all calculations

TABLE III. Final Atomic Parameters with Estimated Standard Deviations in Parentheses (Coordinates: Fractional × $10^3$ – Anisotropic Thermal Parameter × $10^4$ in the Form $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

| | $x/a$ | $y/b$ | $z/c$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Fe | 77.3(3) | 134.6(7) | 0 | – |
| C(T1) | −18(2) | 314(4) | −1(4) | 4.3(6) |
| C(T2) | 9(3) | −36(7) | −66(2) | 4.6(9) |
| C(T3) | 15(2) | −3(7) | 94(2) | 3.0(7) |
| O(T1) | −84(2) | 436(3) | −6(3) | 7.0(6) |
| N(2) | −32(2) | −146(6) | −118(2) | 5.3(9) |
| N(3) | −29(3) | −91(5) | 138(2) | 4.9(9) |
| C(M2) | −72(3) | −279(7) | −186(3) | 6.4(11) |
| C(M3) | −69(4) | −191(9) | 210(3) | 9.3(16) |
| C(1) | 227(2) | 86(5) | −18(2) | 5.4(8) |
| C(2) | 203(3) | 180(8) | −75(3) | 7.4(14) |
| C(3) | 192(3) | 343(7) | −30(2) | 6.2(11) |
| C(4) | 199(3) | 300(7) | 57(2) | 5.0(10) |
| C(5) | 228(4) | 96(7) | 62(3) | 6.7(11) |
| B | 270(8) | −235(12) | 256(7) | 11.4(22) |
| F(1) | 170(2) | −290(4) | 202(2) | 10.0(7) |
| F(2) | 337(3) | −326(7) | 210(3) | 14.6(11) |
| F(3) | 234(3) | −354(5) | 316(2) | 13.0(10) |
| F(4) | 238(4) | −45(5) | 266(3) | 14.1(10) |
| H(1) | 240 | −142 | −33 | 6.0 |
| H(2) | 196 | 172 | −135 | 6.0 |
| H(3) | 178 | 489 | −59 | 6.0 |
| H(4) | 187 | 401 | 102 | 6.0 |
| H(5) | 246 | 18 | 113 | 6.0 |

| | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 60(2) | 244(11) | 32(1) | 1(7) | 0(5) | −10(13) |

were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

With $Z$ = 4 the centrosymmetric space group ($Pcam$) imposes the symmetry constraints on the ions of 2, $m$ or $\bar{1}$. For the cation only $m$ is chemically feasible whereas 2 or $m$ is possible for the $BF_4$ anion. The three-dimensional Patterson synthesis indicated the non-centric space group to be correct and the structure was successfully solved by the heavy-atom method and refined on this basis. Refinement was by full-matrix least squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity but in the final stages given by $w = (12.0 + 0.5|F_o|)^{-1}$. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. The final $R$ was 0.071 and $R'$ $[=(\Sigma w\Delta^2/\Delta w|F_o|^2)^{1/2}]$ was 0.086. A final difference map shows no peak $>|0.5|$ eÅ$^{-3}$. The final atomic parameters are given in Table III. A list of structure factors is available from the authors on request. Figure 1 shows the geometry of the ions [15], their crystal packing and the atom labelling. The bond lengths and angles within the ions are given in Table IV.

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviation in Parentheses.

| | | | |
|---|---|---|---|
| (a) Bond lengths (Å)[a] | | | |
| Fe–C(T1) | 1.68(3) | Fe–Cp | 1.75 |
| Fe–C(T2) | 1.77(4) | Fe–C(T3) | 1.96(4) |
| C(T2)–N(2) | 1.23(4) | CT(3)–N(3) | 1.08(4) |
| N(2)–C(M2) | 1.50(5) | N(3)–C(M3) | 1.44(5) |
| C(T1)–O(T1) | 1.15(3) | C(3)–C(4) | 1.46(5) |
| C(1)–C(2) | 1.47(6) | C(4)–C(5) | 1.34(6) |
| C(2)–C(3) | 1.28(5) | C(5)–C(1) | 1.45(5) |
| B–F(1) | 1.63(9) | B–F(3) | 1.33(10) |
| B–F(2) | 1.29(10) | B–F(4) | 1.28(7) |
| (b) Angles (°)[a] | | | |
| C(T1)–Fe–C(T2) | 92(2) | Cp–Fe–C(T1) | 127 |
| C(T1)–Fe–C(T3) | 90(2) | Cp–Fe–C(T2) | 127 |
| C(T2)–Fe–C(T3) | 91(1) | Cp–Fe–C(T3) | 120 |
| Fe–C(T2)–N(2) | 173(1) | Fe–C(T3)–N(3) | 170(3) |
| C(T2)–N(2)–C(M2) | 175(4) | C(T3)–N(3)–C(M3) | 166(4) |
| Fe–C(T1)–O(T1) | 176(1) | F(1)–B–F(2) | 96(6) |
| C(5)–C(1)–C(2) | 108(3) | F(1)–B–F(3) | 91(6) |
| C(1)–C(2)–C(3) | 104(4) | F(1)–B–F(4) | 90(5) |
| C(2)–C(3)–C(4) | 115(4) | F(2)–B–F(3) | 115(7) |
| C(3)–C(4)–C(5) | 105(4) | F(2)–B–F(4) | 135(9) |
| C(4)–C(5)–C(1) | 107(4) | F(3)–B–F(4) | 109(9) |

[a]Cp is the centroid of the cyclopentadienyl ring.

## Results and Discussion

The initial products from the reactions of electrophilic metal or metalloid halides E = $ZnX_2$, $CdX_2$, $SnX_2$, $SnI_4$ or $AsCl_3$ (X = F, Cl, Br or I) with (II) in tetrahydrofuran, benzene or chloroform were the red-brown 1:1 adducts $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2 \cdot E]$. The reactions may be reversed by a strong base, *e.g.* liquid ammonia removes $ZnCl_2$ from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2 \cdot ZnCl_2]$. IR and NMR spectroscopy suggest that the yields of the adducts are virtually quantitative, and the former enables them to be identified unequivocally (see below). All of the adducts may be isolated by partial or complete removal of the reaction solvent at reduced pressures. However, consistent analytical data could only be obtained for those compounds thus isolated where E = $ZnCl_2$, $ZnI_2 \cdot \frac{1}{2}$THF. (THF = tetrahydrofuran), $CdCl_2 \cdot \frac{1}{2}$THF, $CdBr_2$, $CdI_2$, and $SnCl_2$. Only the $ZnCl_2$ derivative could be successfully purified further by recrystallization (from dichloromethane–hexane mixtures) and even this decomposed immediately in acetone solution. Generally the adducts were stable towards oxygen in the solid state. In solution they tended to decompose to species which did not contain $\mu$-CO or $\mu$-CNR ligands, especially in solvents such as acetone.

IR spectroscopy showed that under conditions similar to the above, brown 1:1 $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe) \cdot E]$ adducts are formed by (I) and E = $SnCl_2$, $SnI_2$ and $CdI_2$. Only the last could be isolated as an analytically pure solid.

The adduct obtained from $AgNO_3$ in tetrahydrofuran solution was identified spectroscopically. It could be isolated, but was unstable and always contaminated with silver metal. It decomposed on attempted purification or if left in contact with its reaction mixture, especially if more $AgNO_3$ was added. Then IR absorption bands due to its $\mu$-ligand disappeared, silver was deposited as a grey powder and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ isolated in high yield from the reaction mixture. No adduct could be detected when (I) and $AgNO_3$ reacted in tetrahydrofuran solution. Silver powder was precipitated immediately and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ isolated from the reaction mixture. The overall course of both of these reactions is related to that of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with $AgNO_3$ which gives $[Fe(\eta\text{-}C_5H_5)(CO)_2NO_3]$ as the sole product [16].

A red solid was rapidly precipitated during the reaction of (II) and $NiCl_2 \cdot 6H_2O$ in tetrahydrofuran. Its IR spectrum was comparable to those of other adducts (Table II). It contained nickel (dimethylglyoxime test), but it could not be characterised further due to its instability in solution.

Adduct formation could not be detected during the reaction of (II) with $CoI_2$, $CuCl_2 \cdot 4H_2O$, or $BF_3 \cdot OEt_2$. The dimer was cleaved very rapidly. The IR spectra of the reaction mixtures showed that a

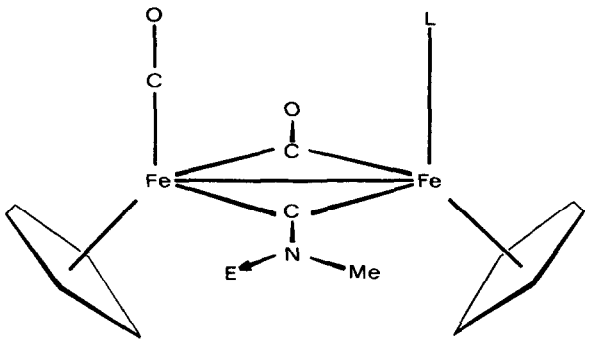


Fig. 2. Proposed structure for the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ adducts (L = CO or CNMe).

number of products were formed and that none contained bridging CO or CNR ligands. Only one could be identified, $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$ from the $BF_3 \cdot OEt_2$ reaction (see below). It is worth pointing out that even when pure adducts were isolated, the IR spectra of the reaction mixtures often showed weak absorption bands due to the presence of cleavage products.

*IR and NMR Spectra and Structure of the Adducts*

The IR spectra of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)\cdot E]$ adducts (L = CO or CNMe) show four absorption bands in the 1500–2200 $cm^{-1}$ region (Table II). They are assigned as follows, A and E to $\nu(CN_\mu)$, B and F to $\nu(CO_\mu)$, C, D and G to $\nu(CO_t)$ and H to $\nu(CN_t)$ vibrational modes. Their frequencies and relative intensities are comparable with those of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)R\}]^+$ cations [3, 4]. Therefore it is reasonable to propose that the adducts have the related $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ structure (Fig. 2) in which the dimers act as monodentate ligands through the N atoms of their $\mu$-CNMe groups towards the metal or metalloid atoms of $ZnX_2$, $CdX_2$, $SnX_2$, $SnI_4$, $AsCl_3$, $AgNO_3$ or $NiCl_2 \cdot 6H_2O$. The relative intensities of the absorption bands C:D [17] indicates a *cis* structure for the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CNMe)]$ moiety when L = CO, But the presence of small amounts of the *trans* isomer is not ruled out. On the other hand when L = CNMe we are not able to tell, on the basis of infrared spectroscopy, if the moiety has a *cis* or a *trans* structure, although it is the *cis* which is illustrated in Fig. 2.

The $^1H$ NMR spectra are in accord with the proposed structures. They show resonances due to the $C_5H_5$ protons at *ca.* 5 ppm, those due to the methyl protons of the $\mu$-CN(Me)E ligand, and those due to the methyl protons of the L = CNMe ligand when appropriate. Their relative integrations are always 10:3:3 and all are singlets except when L = CNMe and E = $CdCl_2$ or $CdI_2$. These have doublet cyclopentadienyl proton resonances due to the two $C_5H_5$ environments. The doublets are not resolved when L = CNMe and E = $SnCl_2$ or $ZnCl_2$, but the band envelopes are very broad.

Although the $\mu$-CO ligands of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ are able to interact with powerful Lewis acids such as the trialkyls or trihalides of boron or aluminium to give rather unstable 1:1 and 1:2 adducts [6], they are inert with respect to weaker Lewis acids such as $ZnCl_2$. The greater basicity of N as compared with O allows (I) and (II) to form stable 1:1 adducts with weak Lewis acids. The electrophilic attack takes place at the $\mu$-CNR and not $\mu$-CO ligands so that of all of the possible isomers of both isocyanide complexes (refs. 9 and 10 and references therein). only *cis* and/or *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ form adducts. We have not observed the formation of adducts based on $[Fe_2(\mu\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$, possibly because of steric effects (*cf.* the use of $H^+$ and $R^+$ as Lewis acids in refs. 2 and 4).

*IR Spectra and Structure of the Cleavage Products Including $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$*

Some Lewis acids cleave (I) and (II) into products which do not contain $\mu$-CO or $\mu$-CNR ligands with or without the detectable formation of adducts as intermediates. However the exact nature of these ultimate products is not clear except in two instances. The oxidative cleavage of both dimers by $AgNO_3$ to give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ along with silver metal is to be expected. Silver (I) salts have been employed extensively as oxidising agents in organometallic chemistry [16]. However, we were very surprised that $BF_3 \cdot OEt_2$ should oxidatively cleave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ to $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$. To confirm the nature of this product beyond all reasonable doubt we undertook an X-ray diffraction study on a single crystal grown from the reaction mixture. Unfortunately even the best crystal thus obtained was of very poor quality, but the data obtained from it was sufficient to confirm that obtained by IR spectroscopy and analysis (Tables I and II). It showed that the compound is ionic with well-defined anions and cations having shortest anion–cation distances of 3.06 Å [F(4) to C(3)] and cation–cation distances of 3.26 Å [O(T1) to C(3)]. The dimensions of $[BF_4]^-$ indicate that there is disorder associated with its positioning. Attempts to clarify the situation using difference maps were unsuccessful. This, together with the somewhat high thermal parameters found for the atoms, almost certainly results from the lack of medium to high angle intensity data as 75% of the recorded data is for $2\theta < 35°$, a consequence of poor crystal quality.

The environment of the iron atom in the cation is pseudo-octahedral as defined for compounds of the type $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$ [18] and is very similar

to that found in $[Fe(\eta\text{-}C_5H_5)(CO)_3][PF_6]$ [19]. The bond lengths and angles within the $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$ cation are also in accord with those found in related dimeric compounds with terminal isocyanide ligands [20].

## Conclusions

Adducts of the general type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$ (L = CO or CNMe) are formed when (I) or (II) interact with many Lewis acids, E. However these adducts are often unstable and decompose to products which do not contain $\mu$-CO or $\mu$-CNMe ligands, a process which is solvent dependent. For other Lewis acids, adduct formation was not observed, but dimer cleavage was very fast at room temperature. It seems reasonable to suggest that under such circumstances adduct formation is a necessary prerequisite for dimer cleavage. Furthermore dimer cleavage may be symmetrical *e.g.* (II) and $AgNO_3$ give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$, or unsymmetrical *e.g.* (II) and $BF_3{\cdot}OEt_2$ give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$.

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