The structures of two $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(L)]$ complexes (C_7H_8 = Norbornadiene; L = CNMe or PPh_3)

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Abstract

Two $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(L)]$ complexes (C_7H_8 = norbornadiene) have been prepared and their structures determined by X-ray diffraction. When L = CNMe, the coordination about Fe is best described as trigonal bipyramidal with the apical positions occupied by CNMe and one C=C. It is distorted towards square pyramidal, in part due to the short 'bite' of the C_7H_8 ligand. When L = PPh_3, a similar distortion is found, but it is so great that the coordination about Fe is close to square pyramidal, with an apical CO ligand. The relevance of these structures to the rotation of the diene ligand in $[Fe(\eta^4\text{-diene})(CO)_3]$ complexes is discussed.

Key words: Iron; Diene; Isocyanide; Phosphine; Carbonyl; Crystal structure

1. Introduction

The complex $[Fe(CO)_5]$ [1] and its $[Fe(\eta^2\text{-alkene})_n(CO)_{5-n}]$ (n = 1 or 2) derivatives [2] adopt trigonal bipyramidal (tbp) structures in which the C=C lie in the equatorial plane. In contrast, derivatives of $[Fe(\eta^4\text{-cyclobutadiene})(CO)_3]$ have the piano-stool structure [3], while those of $[Fe(\eta^4\text{-diene})(CO)_3]$, when the diene is a 1,3-diene or 1,5-cyclooctadiene, have square-pyramidal (sp) coordination about Fe with the diene in basal coordination positions [4]. Exceptions to these generalizations are to be found for the complexes of the substituted norbornadienes, dimethyl-7-X-8,9,10-trinorborna-2,5-diene-2,3-dicarboxylate (X = H or Me_3Si) [5] and of bicyclo[2.2.2]octa-2,3-dienes [6] in which one C=C bears two CN or two CO_2Et substituents. In all four compounds there is approximately tbp coordination about Fe, with the C=C occupying one axial and one equatorial site. This could be a consequence of the presence of two electron-withdrawing substituents on one C=C, which would make it a significantly better π-acceptor than the other C=C and perhaps favour axial/equatorial substituted tbp over basal/basal substituted sp coordination (see below). However, we have prepared and determined the structures of two $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(L)]$ complexes, and have shown that the coordination about iron when L = CNMe is tbp distorted towards sp, and when L = PPh_3 it is sp distorted towards tbp.

2. Experimental section

Chemicals were purchased from the usual commercial sources.

Infrared spectra were obtained on a Perkin-Elmer 1710 or 1720 FTIR spectrometer. Analyses were carried out by the Analytical Laboratory of University College, Dublin.

2.1. Preparation of $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(L)]$ (L = CNMe and PPh_3; C_7H_8 = norbornadiene)

A solution of $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$ [7] (1 g) and L (L = CNMe or PPh_3; mol ratio 1:1) in dried and deoxygenated hexane (200 ml) at room temperature

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and under nitrogen was photolyzed in an Applied Photophysics Photochemical Reactor with a 400 W mercury lamp. The reaction was monitored by IR spectroscopy, and when it was complete the mixture was chromatographed (benzene-hexane mixtures on alumina). Removal of the solvent and recrystallization of the residue from toluene-hexane mixtures gave yellow crystals of [Fe(η^4-C_7H_8)(CO)$_2$(CNMe)] (Analyses, found(calculated for $C_{11}H_{11}FeNO_2$) C 53.9(53.9); H 4.5(4.5); N 5.5(5.7)%, IR data, ν(CN) 2145(3), ν(CO) 1981(8), 1928(10) cm^{-1} in hexane solution with relative peak heights in parentheses), and [Fe(η^4-C_7H_8)(CO)$_2$(PPh$_3$)] (Analyses, found (calculated for $C_{27}H_{23}Feo_2P$ C 70.0(69.6), H 5.1(5.0); P 6.8(6.9)%; IR data, ν(CO) 1965(10), 1905(9) cm^{-1} in hexane solution with relative peak heights in parentheses), both in *ca.* 30% yield. Crystals for the X-ray diffraction study were grown from toluene-pentane mixtures at −20°C.

2.2. Crystal structure determination

Crystal data are given in Table 1. The structures were solved by direct methods, SHELX86 [8] and refined by full matrix least squares using SHELX-93 [9]. Data were collected on an Enraf-Nonius CAD4 diffractome-

TABLE 1. Crystal data for [Fe(η^4-C_7H_8)(CO)$_2$(CNMe)], **2**, and [Fe(η^4-C_7H_8)(CO)$_2$(PPh$_3$)], **3**

	2	**3**
Crystal size (mm)	0.34 × 0.30 × 0.25	0.5 × 0.55 × 0.28
Formula	$C_{11}H_{11}NFeO_2$	$C_{27}H_{23}FeO_2P$
M (a.m.u.)	245.060	466.298
	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a(Å)	12.446(2)	9.755(1)
b(Å)	5.9737(6)	9.8196(7)
c(Å)	14.611(2)	13.611(1)
α(°)	90	88.68(1)
β(°)	102.33(1)	80.17(1)
γ(°)	90	60.69(1)
U(Å^3)	1061.3(3)	1117.4(6)
Z	4	2
D_c (g cm^{-3})	1.534	1.386
μ(cm^{-1})	13.24	18.75
F(000)	504	484
Radiation	Mo Kα	Mo Kα
Graphite monochromator	λ = 0.71069 Å	λ = 0.71069 Å
Diffractometer	Enraf-Nonius CAD4F	Enraf-Nonius CAD4F
Orienting reflections, range	25, 13 < θ < 20°	25, 13 < θ < 20°
Temperature (°C)	22	22
Absorption coefficient (mm^{-1})	1.398	0.768
Scan method	ω-2θ	ω-2θ
θ Range	2.85–31.96	2.38–31.96
Index ranges	$-8 <= h < 13$ $0 <= k < 6$ $-15 <= 1 < 15$	$0 <= h < 11$ $-11 <= k < 11$ $-15 <= 1 < 15$
Reflections collected	2691	6775
Independent reflections [R(int)]	2531 [0.0090]	6209 [0.0265]
Total $I > 3cI$	2110	4779
No. of parameters fitted	180	306
Goodness-of-fit on F^2 [a]	0.845	0.935
Final R indices [$I > 3c(I)$] [a]	$R_1 = 0.0295$ $wR_2 = 0.0929$	$R_1 = 0.0391$ $wR_2 = 0.1131$
Final R indices (all data) [a]	$R_1 = 0.0367$ $wR_2 = 0.0999$	$R_1 = 0.0517$ $wR_2 = 0.1209$
Extinction coefficient	0.028(3)	
Largest difference peaks (e/Å^3)	0.309/− 0.391	0.794/− 0.413

[a] $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on Fs).
$wR_2 = [[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]^{1/2}$ (based on Is).
$w = q/[(\sigma F_o)^2 - (a^* P)^2 + (b^* P) + d + e^* \sin(\theta)]$.
Goodness-of-fit $= [\Sigma w(|F_o^2| - |F_c^2|)^2/N_{obs} - N_{parameters})]^{1/2}$.

ter using Mo Kα radiation (λ = 0.71069 Å) and corrected for Lorentz and polarization effects but not for absorption except in the latter stages of the refinement when L = CNMe when an absorption correction was applied. For L = CNMe, all hydrogen atoms were located and refined isotropically whilst the non-hydrogen atoms were refined anisotropically. For L = PPh_3 the hydrogen atoms of the norbornadiene ligand were located and refined with a common isotropic parameter (0.061) and those of the PPh_3 ligand were included in calculated positions and refined with a common isotropic thermal parameter (0.062) whilst the non-hydrogen atoms were refined anisotropically. Calculations were carried out on a VAX 6610 computer. The ORTEP program was used to obtain the drawings [10]. Fractional atomic coordinates are given in Tables 2 and 3, and Selected bond angles and bond lengths in Tables 4 and 5. The following tables have been deposited at the Cambridge Crystallographic Data Centre: complete bond lengths and bond angles, anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters.

3. Results and discussion

The reaction of [Fe(CO)$_5$] with norbornadiene gives mixtures of organic products as well as [Fe(η^4-C_7H_8)(CO)$_3$] (**1**) [7]. It proved difficult to obtain satisfactory crystals of the latter. However, it undergoes CO substitution on photolysis with CNMe or PPh_3. Excellent crystals of [Fe(η^4-C_7H_8)(CO)$_2$(L)] {L = CNMe, **2**; L = PPh_3, **3**) were obtained and subjected to X-ray diffraction studies. Molecular structures and atom labelling schemes are shown in Figs. 1 and 2, and selected bond lengths and angles are given in Tables 4 and 5. The structure of **2** is of particularly high quality, even hydrogen atom positions being located very precisely.

TABLE 2. Fractional Atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameter (Å$^2 \times 10^3$) for [Fe(η^4-C_7H_8)(CO)$_2$-(CNMe)], (**2**), *U*eq is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
Fe(1)	4999(1)	3696(1)	7291(1)	34(1)
O(1)	6116(2)	5974(3)	5991(1)	77(1)
O(2)	3060(2)	6474(3)	7243(2)	79(1)
N(1)	3929(1)	551(3)	5767(1)	50(1)
C(1)	5194(2)	2843(3)	9169(1)	50(1)
C(2)	4850(2)	1342(3)	8309(1)	44(1)
C(3)	5811(2)	898(3)	7987(1)	50(1)
C(4)	6734(2)	2118(4)	8664(2)	57(1)
C(5)	6417(2)	4507(4)	8372(1)	54(1)
C(6)	5477(2)	4977(3)	8686(1)	49(1)
C(7)	6353(2)	1954(4)	9592(2)	63(1)
C(8)	4323(1)	1804(3)	6340(1)	41(1)
C(9)	3472(2)	−1029(4)	5064(2)	58(1)
C(10)	5700(2)	5072(3)	6516(1)	48(1)
C(11)	3812(2)	5371(3)	7260(1)	48(1)

TABLE 3. Fractional Atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameter (Å$^2 \times 10^3$) for [Fe(η^4-C_7H_8)(CO)$_2$-(PPh_3)] (**3**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U(eq)
Fe(1)	1779(1)	3084(1)	7776(1)	32(1)
P(1)	4159(1)	2814(1)	7777(1)	31(1)
O(1)	345(2)	6044(2)	8956(1)	59(1)
O(2)	1398(2)	4115(2)	5764(1)	66(1)
C(26)	927(2)	4859(2)	8497(1)	41(1)
C(27)	1583(2)	3686(2)	6546(1)	41(1)
C(1)	1051(3)	1112(2)	8989(2)	50(1)
C(2)	−21(2)	2788(2)	8742(2)	50(1)
C(3)	−178(2)	2707(2)	7755(2)	49(1)
C(4)	813(2)	967(2)	7398(2)	50(1)
C(5)	2493(2)	742(2)	7362(2)	44(1)
C(6)	2624(2)	852(2)	8360(2)	44(1)
C(7)	593(3)	187(3)	8348(2)	56(1)
C(8)	4629(2)	2918(2)	9017(1)	34(1)
C(9)	6000(2)	2952(2)	9141(1)	43(1)
C(10)	6328(2)	3001(2)	10085(2)	48(1)
C(11)	5281(3)	3046(2)	10921(1)	49(1)
C(12)	3915(2)	3033(2)	10817(1)	49(1)
C(13)	3584(2)	2960(2)	9869(1)	41(1)
C(14)	4630(2)	4205(2)	7082(1)	36(1)
C(15)	3407(2)	5676(2)	6923(1)	44(1)
C(16)	3766(3)	6729(2)	6398(2)	57(1)
C(17)	5310(3)	6337(3)	6030(2)	65(1)
C(18)	6540(3)	4890(3)	6169(2)	63(1)
C(19)	6198(2)	3826(2)	6685(2)	49(1)
C(20)	5833(2)	961(2)	7172(1)	36(1)
C(21)	6937(2)	−181(2)	7675(2)	46(1)
C(22)	8186(3)	−1552(2)	7148(22)	64(1)
C(23)	8322(3)	−1798(3)	6149(2)	68(1)
C(24)	7199(3)	−678(3)	5643(2)	64(1)
C(25)	5975(2)	687(2)	6155(2)	52(1)

In **2**, the coordination about the metal atom is close to trigonal bipyramidal, tbp, with the axial sites occupied by MeNC and one C=C of the NBD ligand. The other C=C lies in the equatorial plane of the complex so that the angle between the FeC$_2$ and Fe(CO)$_2$ planes is 4.4°. The major deviations from tbp are threefold. First, the angle at OC–Fe–CO is small (104.0° *versus* 120°). Second, there is no plane of symmetry which would bisect the OC–Fe–CO angle and include the Fe atom, the CNMe ligand, Mx and Mq (these are the mid-points of the axial and equatorial C=C bond respectively). Third, the MeNC–Fe–Mx angle is 160.1°, probably owing to the restricted bite of the C_7H_8 ligand, but only in part since the corresponding angle in **5** below is 167.5°. The different Mq–Fe–(CO) angles (134.8° *versus* 120.9°) suggests that there is limited distortion towards square-pyramidal, sp, with

TABLE 4. Bond lengths (Å) and bond angles (°) for $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(CNMe)]$ (**2**)

Bond Lengths	Fe(1)–C(10)	1.773(2)
	Fe(1)–C(11)	1.777(2)
	Fe(1)–C(8)	1.849(2)
	Fe(1)–C(2)	2.083(2)
	Fe(1)–C(3)	2.100(2)
	Fe(1)–C(6)	2.140(2)
	Fe(1)–C(5)	2.158(2)
	O(1)–C(10)	1.148(2)
	O(2)–C(11)	1.141(2)
	N(1)–C(8)	1.151(2)
	N(1)–C(9)	1.421(2)
	C(1)–C(2)	1.529(3)
	C(1)–C(6)	1.533(3)
	C(1)–C(7)	1.537(3)
	C(1)–H(1)	1.02(3)
	C(2)–C(3)	1.401(3)
	C(2)–H(2)	0.85(2)
	C(3)–C(4)	1.530(3)
	C(3)–H(3)	1.04(3)
	C(4)–C(5)	1.517(3)
	C(4)–C(7)	1.532(3)
	C(4)–H(4)	0.93(3)
	C(5)–C(6)	1.374(3)
	C(5)–H(5)	0.85(3)
	C(6)–H(6)	0.97(2)
	C(7)–H(7)	1.02(3)
	C(7)–H(8)	0.93(3)
	C(9)–H(9)	0.90(4)
	C(9)–H(10)	0.90(3)
	C(9)–H(11)	0.85(4)
Bond Angles	C(10)–Fe(1)–C(11)	104.01(9)
	C(10)–Fe(1)–C(8)	90.57(8)
	C(11)–Fe(1)–C(8)	94.74(8)
	C(10)–Fe(1)–C(2)	154.18(8)
	C(11)–Fe(1)–C(2)	101.44(8)
	C(8)–Fe(1)–C(2)	91.62(8)
	C(10)–Fe(1)–C(3)	115.29(9)
	C(11)–Fe(1)–C(3)	140.56(8)
	C(8)–Fe(1)–C(3)	88.40(8)
	C(2)–Fe(1)–C(3)	39.12(8)
	C(10)–Fe(1)–C(6)	111.61(8)
	C(11)–Fe(1)–C(6)	83.32(8)
	C(8)–Fe(1)–C(6)	157.58(8)
	C(2)–Fe(1)–C(6)	67.08(7)
	C(3)–Fe(1)–C(6)	79.41(8)
	C(10)–Fe(1)–C(5)	85.79(8)
	C(11)–Fe(1)–C(5)	115.99(8)
	C(8)–Fe(1)–C(5)	149.04(8)
	C(2)–Fe(1)–C(5)	79.20(8)
	C(3)–Fe(1)–C(5)	65.82(8)
	C(6)–Fe(1)–C(5)	37.29(8)
	C(8)–N(1)–C(9)	178.3(2)
	C(2)–C(1)–C(6)	99.30(13)
	C(2)–C(1)–C(7)	101.6(2)
	C(6)–C(1)–C(7)	100.6(2)
	C(2)–C(1)–H(1)	116 (2)
	C(6)–C(1)–H(1)	114 (2)
	C(7)–C(1)–H(1)	122.1(14)
	C(3)–C(2)–C(1)	106.1(2)
	C(3)–C(2)–Fe(1)	71.07(11)
	C(1)–C(2)–Fe(1)	97.96(10)
	C(3)–C(2)–H(2)	124 (2)
	C(1)–C(2)–H(2)	125 (2)
	Fe(1)–C(2)–H(2)	116 (2)
	C(2)–C(3)–C(4)	105.6(2)
	C(2)–C(3)–Fe(1)	69.81(10)
	C(4)–C(3)–Fe(1)	98.67(13)
	C(2)–C(3)–H(3)	124.0(14)
	C(4)–C(3)–H(3)	126.3(13)
	Fe(1)–C(3)–H(3)	115.5(14)
	C(5)–C(4)–C(3)	98.8(2)
	C(5)–C(4)–C(7)	101.4(2)
	C(3)–C(4)–C(7)	102.1(2)
	C(5)–C(4)–H(4)	119 (2)
	C(3)–C(4)–H(4)	120 (2)
	C(7)–C(4)–H(4)	113 (2)
	C(6)–C(5)–C(4)	106.7(2)
	C(6)–C(5)–Fe(1)	70.64(10)
	C(4)–C(5)–Fe(1)	96.71(12)
	C(6)–C(5)–H(5)	124 (2)
	C(4)–C(5)–H(5)	123 (2)
	Fe(1)–C(5)–H(5)	111 (2)
	C(5)–C(6)–C(1)	106.2(2)
	C(5)–C(6)–Fe(1)	72.06(11)
	C(1)–C(6)–Fe(1)	95.51(10)
	C(5)–C(6)–H(6)	126.8(14)
	C(1)–C(6)–H(6)	124 (2)
	Fe(1)–C(6)–H(6)	114 (2)
	C(4)–C(7)–C(1)	93.61(14)
	C(4)–C(7)–H(7)	111 (2)
	C(1)–C(7)–H(7)	115 (2)
	C(4)–C(7)–H(8)	109 (2)
	C(1)–C(7)–H(8)	117 (2)
	H(7)–C(7)–H(8)	111 (3)
	N(1)–C(8)–Fe(1)	177.0(2)
	N(1)–C(9)–H(9)	108 (3)
	N(1)–C(9)–H(10)	109 (3)
	H(9)–C(9)–H(10)	123 (3)
	N(1)–C(9)–H(11)	111 (2)
	H(9)–C(9)–H(11)	109 (3)
	H(10)–C(9)–H(11)	96 (3)
	O(1)–C(10)–Fe(1)	177.4(2)
	O(2)–C(11)–Fe(1)	179.0(2)

C(10)O as the axial ligand. The Fe–C bond lengths to the equatorial C=C are very similar and shorter than those to the axial C=C, whereas the equatorial C=C bond length is longer than the axial. These dimensions are consistent with stronger back-bonding to the equatorial as opposed to the axial olefin, as predicted by Hoffmann *et al.* [11].

The structure of **2** may be compared with those of $[Fe(\eta^2\text{-}C_{12}H_8)(CO)_4]$ (**4**) ($C_{12}H_8$ = acenaphthylene) [12], and $[Fe(\eta^4\text{-}NBD^*)(CO)_3]$, (**5**) ($NBD^*$ = dimethyl 7-X-8,9,10-trinorborna-2,5-diene-2,3-dicarboxlate where X = H) [5]. In the former the coordination is very close to tbp, with the olefinic carbon atoms lying in the equatorial plane and a equatorial OC–Fe–CO

TABLE 5. Selected bond lengths (Å) and bond angles (°) for [Fe(η^4-C_7H_8)(CO)$_2$(PPh$_3$)] (3)

Bond lengths (Å)			
Fe(1)–P(1)	2.2054(8)	Fe(1)–C(26)	1.753(2)
Fe(1)–C(27)	1.773(2)	Fe(1)–C(2)	2.142(2)
Fe(1)–C(3)	2.119(2)	Fe(1)–C(5)	2.109(2)
Fe(1)–C(6)	2.119(2)	P(1)–C(8)	1.840(2)
P(1)–C(14)	1.837(2)	P(1)–C(20)	1.832(2)
O(1)–C(26)	1.154(2)	O(2)–C(27)	1.146(2)
C(1)–C(2)	1.524(3)	C(1)–C(6)	1.526(3)
C(1)–C(7)	1.533(3)	C(1)–H(1)	0.91(2)
C(2)–C(3)	1.386(3)	C(2)–H(2)	0.99(2)
C(3)–C(4)	1.533(3)	C(3)–H(3)	0.88(3)
C(4)–C(5)	1.534(3)	C(4)–H(4)	0.93(2)
C(4)–C(7)	1.525(3)	C(5)–H(5)	0.88(2)
C(5)–C(6)	1.398(3)	C(6)–H(6)	1.00(3)
C(7)–H(7)	1.04(3)	C(7)–H(8)	0.94(2)
Bond Angles (°)			
C(26)–Fe(1)–P(1)	88.76(6)	C(27)–Fe(1)–P(1)	98.22(6)
C(27)–Fe(1)–C(26)	103.10(8)	C(2)–Fe(1)–P(1)	139.42(6)
C(2)–Fe(1)–C(26)	83.45(8)	C(2)–Fe(1)–C(27)	122.35(9)
C(3)–Fe(1)–P(1)	165.28(6)	C(3)–Fe(1)–C(26)	103.87(8)
C(3)–Fe(1)–C(27)	86.41(8)	C(3)–Fe(1)–C(2)	37.97(8)
C(5)–Fe(1)–P(1)	98.65(6)	C(5)–Fe(1)–C(26)	160.64(8)
C(5)–Fe(1)–C(27)	93.56(8)	C(5)–Fe(1)–C(2)	79.29(8)
C(5)–Fe(1)–C(3)	67.00(8)	C(6)–Fe(1)–P(1)	87.45(6)
C(6)–Fe(1)–C(26)	124.85(8)	C(6)–Fe(1)–C(27)	131.89(8)
C(6)–Fe(1)–C(2)	65.59(8)	C(6)–Fe(1)–C(3)	79.16(8)
C(6)–Fe(1)–C(5)	38.62(8)	C(8)–P(1)–Fe(1)	115.61(5)
C(14)–P(1)–Fe(1)	116.81(6)	C(14)–P(1)–C(8)	103.87(7)
C(20)–P(1)–Fe(1)	114.44(6)	C(20)–P(1)–C(8)	104.05(8)
C(20)–P(1)–C(14)	100.08(8)	O(1)–C(26)–Fe(1)	178.5(2)
O(2)–C(27)–Fe(1)	177.5(2)	C(2)–C(1)–C(6)	98.3(2)
C(7)–C(1)–C(2)	101.8(2)	C(7)–C(1)–C(6)	101.7(2)
H(1)–C(1)–C(2)	118 (2)	H(1)–C(1)–C(6)	115 (2)
H(1)–C(1)–C(7)	119 (2)	C(3)–C(2)–C(1)	106.3(2)
H(2)–C(2)–C(3)	124.6(14)	H(2)–C(2)–C(1)	126.2(14)
H(3)–C(3)–C(2)	119 (2)	C(4)–C(3)–C(2)	105.7(2)
H(3)–C(3)–C(4)	131 (2)	C(5)–C(4)–C(3)	99.1(2)
C(7)–C(4)–C(3)	101.8(2)	C(7)–C(4)–C(5)	101.9(2)
H(4)–C(4)–C(3)	116 (2)	H(4)–C(4)–C(5)	117 (2)
H(4)–C(4)–C(7)	118 (2)	C(6)–C(5)–C(4)	105.2(2)
H(5)–C(5)–C(6)	128 (2)	H(5)–C(5)–C(4)	123 (2)
H(6)–C(6)–C(5)	124.9(14)	C(5)–C(6)–C(1)	106.4(2)
H(7)–C(7)–C(1)	116.4(14)	H(6)–C(6)–C(1)	125.4(14)
H(8)–C(7)–C(1)	112 (2)	C(4)–C(7)–C(1)	93.7(2)
H(8)–C(7)–H(7)	113 (2)	H(7)–C(7)–C(4)	105.8(14)
		H(8)–C(7)–C(4)	115 (2)

angle of 115.1°. In the latter, the coordination is distorted tbp with the restricted bite of the C_7H_8 ligand reducing the OC(14)–Fe–Mx angle to 167.5° and a equatorial OC–Fe–CO angle of 105.4°. The distortion towards sp is limited. In the light of the predictions by Hoffmann *et al.* [11] it is not surprising that the C=C bearing the electron-withdrawing CO_2Me groups lies in the equatorial plane whereas the unsubstituted C=C is an axial ligand. However, comparison of the Fe–C and C=C distances suggest that in **5** the equatorial C=C is more strongly bound to Fe than in **2** but the axial C=C is less strongly bound. It is not clear if this is due to the difference between axial CO *versus* CNMe or the equatorial $C_2(CO_2Me)_2$ *versus* C_2H_2.

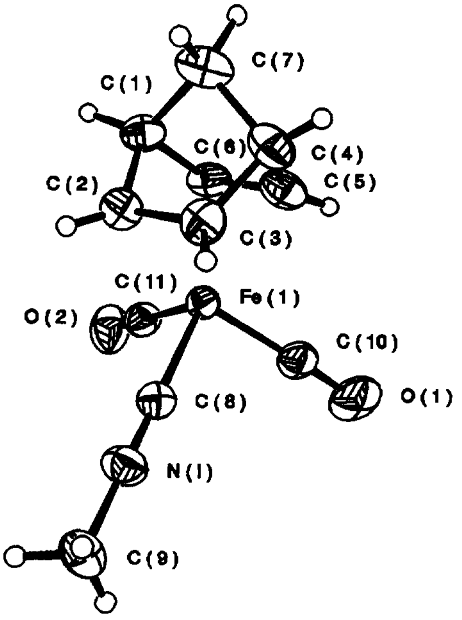

Fig. 1. Molecular structure and atom labelling for [Fe(η^4-C_7H_8)(CO)$_2$(CNMe)] (2).

At first glance the structure of **3** is similar to that of **2** with CNMe replaced by PPh$_3$, but the coordination is so distorted from tbp that it is closer to sp with C(27)

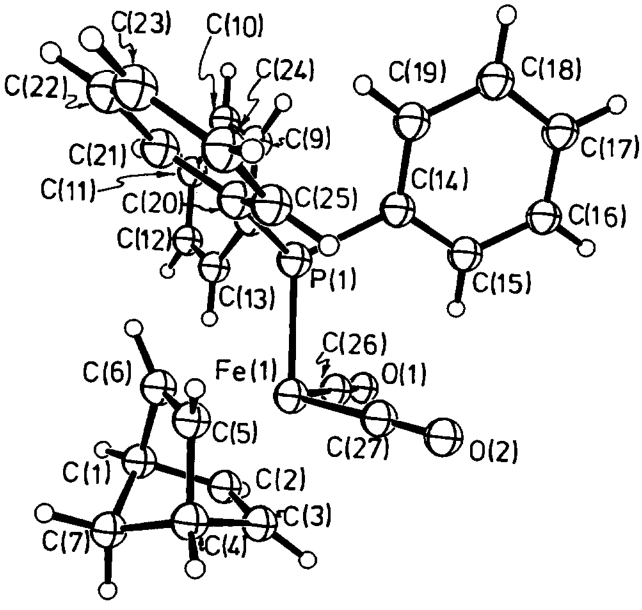

Fig. 2. Molecular structure and atom labelling for [Fe(η^4-C_7H_8)(CO)$_2$(PPh$_3$)] (3).

in the apical position, and the PPh_3, C(26)O and the NBD ligand occupying the four equatorial sites such that the two C=C of the latter are almost perpendicular to the Fe,Mq,Mx plane with Fe–Mx–C(2) = 90.9° and Fe–Mq–C(6) = 90.7°. The small bite of the C_7H_8 ligand distorts the basal square, but its two *trans* angles are not as different as they are in **2** for example; Mq–Fe–C(26) = 143.2° and Mx–Fe–P(1) = 155.9°. Furthermore, the dimensions of the two FeC_2 moieties suggest that although the bonding between Fe and the two C=C double bonds are not identical, the differences are not as marked as in **2** and may be due in part at least to the different *trans* ligands, CO and PPh_3.

When the structure of **3** is compared with that of [Fe(η^2-DEM)(CO)$_3$(PPh$_3$)] (**6**) (DEM = diethylmaleate) [13], it can be seen that the latter has a tbp structure in which the C=C lies in the equatorial plane. However, the two equatorial Mq–Fe–CO angles differ (134.7 *vs.* 115.7°) and the coordination is distorted towards sp with C(2)O acting as the apical ligand and the two *trans* angles of 134.7 (Mq–Fe–C(1)O) and 172.2° (P–Fe–C(3)O). A similar distortion is not observed in the related [Fe(η^2-DEM)(CO)$_3$(PPh$_3$)] complex (DEF = diethylfumarate) complex where the PPh_3 ligand occupies an equatorial rather than an axial site of a tbp [13].

The coordination about Fe in **3** is a distorted variant on the usual sp form found in [Fe(η^4-1,3-diene)(CO)$_3$] complexes. However, in the latter PPh_3 occupies the apical site [4,14], whereas in **3** it is equatorial.

It has been suggested that in [Fe(η^4-C_7H_8)(CO)$_3$] there is facile rotation of the C_7H_8 ligand about its centroid–Fe axis so that its CO ligands appear equivalent at higher temperatures as evidenced by spectroscopic data [15]. Similar processes may take place in [Fe(η^4-C_7H_8)(CO)$_2$(L)] such as **2** and **3**. If so, the coordination polyhedra observed for these compounds in the solid state may be regarded as 'snapshots' of the diene rotation. If the C_7H_8 ligand in 2 is rotated by 90° about its centroid–Fe axis and the Fe–CNMe bond is moved through 9°, the result is a sp molecule with an axial CNMe ligand. Similar rotations through different angles lead to other tbp or sp isomers whose interligand angles differ by only small amounts from those observed for **2**.

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