

^{57}Fe Mössbauer spectroscopic studies on $\text{M}(\text{CO})_5$ (azaferrocene) complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). The crystal structures of $\text{W}(\text{CO})_5$ (azaferrocene) and $\text{W}(\text{CO})_5$ (2,5-dimethylazaferrocene)

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Received 18 December 1996; revised 1 February 1997

Abstract

^{57}Fe Mössbauer spectroscopic studies on $\text{M}(\text{CO})_5$ (azaferrocene) complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) as well as the crystal structures of $\text{W}(\text{CO})_5$ (azaferrocene) and $\text{W}(\text{CO})_5$ (2,5-dimethylazaferrocene) are reported. The complexation of azaferrocene to the $\text{M}(\text{CO})_5$ moiety brings about only a small change in the quadrupole splitting. The structures of both tungsten complexes reveal a significant shortening of the W–C bonds *trans* to the nitrogen. These data indicate that azaferrocene behaves as a relatively strong σ -donor and there is no evidence for any π -acceptor properties. © 1997 Published by Elsevier Science S.A.

Keywords: Crystal structure; Azaferrocene

1. Introduction

The bonding and electronic structure of compounds of the type $\text{M}(\text{CO})_5\text{L}$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ and $\text{L} = \text{amine}$) have been widely studied primarily to gain an insight into their photoreactivity [1–4]. This work has facilitated the $\text{M}(\text{CO})_5$ entity being used to examine bonding properties of the L (ligand) utilizing X-ray crystallography, IR, multinuclear NMR and other techniques [5–8]. We have carried out extensive studies on azaferrocene and a number of its metal complexes [9–11]. During the course of this work we have found that in [bis(azaferrocene)iron(III)porphyrin] complexes there was strong evidence that azaferrocene behaved as a good σ -donor but was a very poor π -acceptor [11]. As the bonding in complexes of the type $\text{M}(\text{CO})_5\text{L}$ is now well understood, we have used the $\text{M}(\text{CO})_5$ (azaferrocene) complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{azaferrocene}$ or 2,5-dimethylazaferrocene) to study the nature of the bonding between M and the nitrogen atom in azaferrocene. We report here ^{57}Fe Mössbauer spectroscopic

studies on $\text{Cr}(\text{CO})_5$ (azaferrocene) (1), $\text{Mo}(\text{CO})_5$ (azaferrocene) (2), $\text{W}(\text{CO})_5$ (azaferrocene) (3) and $\text{W}(\text{CO})_5$ (2,5-dimethylazaferrocene) (4), along with the crystal structures of 3 and 4. The latter are discussed in relation to similar structures. The findings from this work provide direct evidence for the good σ -donor and poor π -acceptor properties of azaferrocene.

2. Experimental

2.1. Compound preparation

Azaferrocene and 2,5-dimethylazaferrocene were prepared by standard procedures [12,13]. Complex 3 was prepared from $\text{W}(\text{CO})_5(\text{THF})$ and azaferrocene as described earlier [9]. This procedure was now employed to synthesize complexes 1, 2 and 4. The isolated yields were 55, 67 and 83% respectively. Anal. 1 Found: C, 44.7; H, 2.3; N, 3.6. Calc.: C, 44.4; H, 2.4; N, 3.7%. 2 Found: C, 40.0; H, 1.9; N, 3.0. Calc.: C, 39.8; H, 2.1; N, 3.3%. 4 Found: C, 35.8; H, 2.6; N, 2.6. Calc.: C, 35.7; H, 2.4; N, 2.6%. ^1H NMR (Varian Gemini 2000 spectrometer, 200 MHz, CDCl_3 , δ): 1 5.63, s, 2H, 2,5-pyrrolyl; 4.70, s, 2H, 3,4-pyrrolyl; 4.47, s, 5H, C_p .

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2 5.32, s, 2H, 2,5-pyrrolyl; 4.68, s, 2H, 3,4-pyrrolyl; 4.43, s, 5H, C_p. 4 4.61, s, 2H, 3,4-pyrrolyl; 4.29, s, 5H, C_p; 2.61, s, 6H, CH₃.

The ⁵⁷Fe Mössbauer spectra were recorded at 78 K for solid samples using an instrument and techniques previously described [14].

2.2. Crystal structure determination

Crystals of **3** and **4** suitable for X-ray analysis were grown from layered chloroform–heptane during 2–3 days.

Crystal data and experimental details are listed in Table 1. Accurate unit-cell constants were determined from a least-squares fit to the θ values of 25 reflections measured on a Siemens P3 diffractometer. The intensity data were collected using graphite-monochromated Mo K α radiation and ω - 2θ scan technique. Ψ -Scan absorption corrections were made [15] (minimum transmission for **3** and **4**: 0.553 and 0.553, maximum 0.729 and 0.619). The structures were solved by Patterson and

Fourier methods using SHELXTL programs [16] and refined using the SHELXL-93 program package [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions (C–H 0.93 Å) and refined isotropically by riding mode. Non-hydrogen atomic coordinates are given in Tables 2 and 3 and selected bond lengths and angles in Table 4.

3. Results and discussion

Previously we reported that azaferrocene reacts with the photochemically generated W(CO)₅(THF) to afford W(CO)₅(azaferrocene) (**3**). In this work we have used the same procedure to prepare Cr(CO)₅(azaferrocene) (**1**) and Mo(CO)₅(azaferrocene) (**2**), from azaferrocene and Cr(CO)₅(THF) and Mo(CO)₅(THF) respectively. We prepared W(CO)₅(2,5-dimethylazaferrocene) (**4**) from W(CO)₅(THF) and 2,5-dimethylazaferrocene. The structures of these compounds were confirmed by elemental analysis and ¹H NMR (see Section 2). The

Table 1
Crystallographic data for compounds **3** and **4**

	3	4
Empirical formula	C ₁₄ H ₉ FeNO ₅ W	C ₁₆ H ₁₃ FeNO ₅ W
Formula weight	510.92	538.97
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	8.854(2)	18.506(4)
<i>b</i> (Å)	12.815(3)	14.408(3)
<i>c</i> (Å)	13.818(3)	13.351(3)
α (°)	82.41(3)	
β (°)	83.68(3)	100.82(3)
γ (°)	88.06(3)	
Volume (Å ³)	1544.4(6)	3496(3)
Z	4	8
Density (calc.) (g cm ⁻³)	2.197	2.048
Absorption coefficient (mm ⁻¹)	8.402	7.428
<i>F</i> (000)	960	2048
Crystal size (mm ³)	0.2 × 0.2 × 0.25	0.2 × 0.2 × 0.15
Index ranges	-13 ≤ <i>h</i> ≤ 13, -19 ≤ <i>k</i> ≤ 19, 0 ≤ <i>l</i> ≤ 20	-23 ≤ <i>h</i> ≤ 24, -18 ≤ <i>k</i> ≤ 18, -14 ≤ <i>l</i> ≤ 0
Reflections collected	11230	15654
Independent reflections <i>I</i> > 2σ(<i>I</i>)	10662	7695
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	10661/0/398	7695/0/434
Goodness-of-fit on <i>F</i> ²	1.097	1.184
<i>R</i> (<i>F</i>) ^a	0.0510	0.0295
<i>wR</i> (<i>F</i> ²) ^b	0.1424	0.0783
Extinction coefficient	0.0121(4)	0.00055(5)
$\Delta\rho_{\min}$ (e Å ⁻³)	-3.96	-0.78
$\Delta\rho_{\max}$ (e Å ⁻³)	2.65	1.17
Av. dist. of $\Delta\rho_{\max}$ from W atom (Å)	1.28	0.82

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR(F^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$; $w(1) = 1 / [\sigma^2(F_o^2) + (0.049P)^2 + 11.80P]$; $w(2) = 1 / [\sigma^2(F_o^2) + (0.031P)^2 + 4.70P]$, $P = (\max(F_o^2, 0) + 2F_c^2) / 3$.

crystal structures of **3** and **4** are broadly as expected for compounds of this type and are discussed in detail later.

3.1. ^{57}Fe Mössbauer spectroscopy

The Mössbauer data for complexes **1–4** are presented in Table 5. Compound **3**, azaferrocene and 2,5-dimethylazaferrocene have been discussed previously [9]. The Q.S. values for azaferrocenes are larger than that of ferrocene, showing that initially the pyrrolyl rings are more electron-rich than the C_p rings. In terms of the bonding orbitals to the iron, the e_1 molecular orbital from the pyrrolyl ring is more electron-donating, so the pyrrolyl ring requires less backbonding from the

Table 2
Atomic coordinates for compound **3**

Atom	x	y	z
W(1)	0.22206(4)	0.14110(2)	0.27357(2)
Fe(1)	0.55037(14)	0.26311(8)	0.38617(8)
N(1)	0.4338(8)	0.1425(5)	0.3509(5)
O(1)	0.0908(10)	-0.0537(6)	0.4190(6)
O(2)	0.3742(10)	-0.0165(6)	0.1316(6)
O(3)	0.0543(11)	0.2877(7)	0.4210(6)
O(4)	0.3335(12)	0.3363(6)	0.1196(6)
O(5)	-0.0678(9)	0.1408(8)	0.1651(7)
C(2)	0.5834(9)	0.1376(7)	0.3112(7)
C(3)	0.6801(10)	0.1275(7)	0.3868(8)
C(4)	0.5851(11)	0.1267(6)	0.4754(7)
C(5)	0.4371(10)	0.1352(6)	0.4517(5)
C(6)	0.4493(13)	0.4050(7)	0.3457(9)
C(7)	0.5912(16)	0.4002(8)	0.2971(11)
C(8)	0.6936(18)	0.3840(10)	0.370(2)
C(9)	0.612(4)	0.3763(11)	0.4590(17)
C(10)	0.460(2)	0.3907(8)	0.4451(11)
C(11)	0.1408(10)	0.0157(7)	0.3670(7)
C(12)	0.3230(10)	0.0412(7)	0.1822(6)
C(14)	0.2971(11)	0.2683(7)	0.1759(6)
C(13)	0.1164(11)	0.2371(8)	0.3680(7)
C(15)	0.0394(10)	0.1417(9)	0.2054(7)
W(21)	0.79085(3)	0.32653(2)	0.90123(2)
Fe(21)	1.18493(12)	0.21068(8)	0.80594(8)
N(21)	1.0126(7)	0.2364(5)	0.9091(4)
O(21)	0.6189(8)	0.1504(6)	1.0509(6)
O(22)	0.8590(10)	0.4430(8)	1.0807(7)
O(23)	0.7301(9)	0.2225(8)	0.7146(6)
O(24)	0.9278(11)	0.5188(6)	0.7540(7)
O(25)	0.4730(8)	0.4391(6)	0.9010(6)
C(22)	1.0333(10)	0.1297(6)	0.9044(6)
C(23)	1.1784(12)	0.0977(8)	0.9256(7)
C(24)	1.2519(10)	0.1892(9)	0.9446(6)
C(25)	1.1461(9)	0.2714(7)	0.9344(6)
C(26)	1.1294(13)	0.2387(14)	0.6658(7)
C(27)	1.213(2)	0.3223(12)	0.6884(9)
C(28)	1.3538(16)	0.2803(15)	0.7111(9)
C(29)	1.3525(15)	0.1749(13)	0.7039(9)
C(30)	1.2155(18)	0.1497(13)	0.6770(9)
C(31)	0.6847(9)	0.2111(6)	0.9961(6)
C(32)	0.8361(11)	0.4000(8)	1.0173(7)
C(33)	0.8845(10)	0.4499(7)	0.8085(7)
C(34)	0.7514(10)	0.2570(8)	0.7833(7)
C(35)	0.5906(11)	0.4004(7)	0.9002(7)

Table 3
Atomic coordinates for compound **4**

Atom	x	y	z
W(1)	0.54519(1)	0.22893(1)	0.15376(2)
Fe(1)	0.72719(1)	0.36477(4)	0.14796(5)
N(1)	0.6532(2)	0.3021(2)	0.2198(3)
O(1)	0.5721(3)	0.0489(3)	0.2916(4)
O(2)	0.4623(3)	0.3175(5)	0.3180(5)
O(3)	0.6117(3)	0.1248(4)	-0.0169(4)
O(4)	0.4833(4)	0.3825(4)	-0.0097(5)
O(5)	0.3963(3)	0.1353(5)	0.0655(5)
C(2)	0.6617(2)	0.3961(3)	0.2475(4)
C(3)	0.7349(3)	0.4127(3)	0.2931(5)
C(4)	0.7734(3)	0.3286(3)	0.2942(4)
C(5)	0.7230(2)	0.2616(3)	0.2483(3)
C(6)	0.6926(5)	0.3605(7)	-0.0059(5)
C(7)	0.7018(6)	0.4494(7)	0.0256(7)
C(8)	0.7740(7)	0.4620(6)	0.0733(7)
C(9)	0.8092(4)	0.3755(8)	0.0674(6)
C(10)	0.7578(5)	0.3150(5)	0.0201(5)
C(11)	0.5667(3)	0.1151(4)	0.2450(4)
C(12)	0.4947(3)	0.2885(5)	0.2606(6)
C(13)	0.5897(4)	0.1632(4)	0.0454(5)
C(14)	0.5083(3)	0.3329(5)	0.0494(6)
C(15)	0.4521(4)	0.1689(5)	0.0983(5)
C(16)	0.6004(3)	0.4647(4)	0.2372(5)
C(17)	0.7387(3)	0.1610(3)	0.2384(4)
W(21)	0.94747(1)	0.96053(1)	0.18460(1)
Fe(21)	0.76937(4)	0.81631(4)	0.20317(5)
N(21)	0.8304(2)	0.9345(2)	0.2106(3)
O(21)	0.9930(4)	1.0930(5)	0.3740(5)
O(22)	0.8998(3)	1.1381(3)	0.0474(4)
O(23)	1.0145(3)	0.7838(4)	0.3072(5)
O(24)	0.9320(3)	0.8259(3)	-0.0054(3)
O(25)	1.1053(2)	0.9999(3)	0.1463(4)
C(22)	0.8088(3)	0.9171(3)	0.3042(4)
C(23)	0.7319(3)	0.9157(3)	0.2903(5)
C(24)	0.7041(3)	0.9318(3)	0.1863(5)
C(25)	0.7649(2)	0.9428(3)	0.1376(4)
C(26)	0.8083(6)	0.6898(4)	0.2554(6)
C(27)	0.7318(6)	0.6926(4)	0.2429(8)
C(28)	0.7032(4)	0.7107(4)	0.1433(8)
C(29)	0.7605(5)	0.7200(4)	0.0916(6)
C(30)	0.8259(3)	0.7070(4)	0.1586(6)
C(31)	0.9731(4)	1.0454(5)	0.3078(5)
C(32)	0.9146(3)	1.0741(3)	0.0965(4)
C(33)	0.9881(3)	0.8475(4)	0.2654(5)
C(34)	0.9345(3)	0.8763(3)	0.0621(4)
C(35)	1.0471(3)	0.9857(4)	0.1613(4)
C(36)	0.8620(4)	0.9100(5)	0.4039(4)
C(37)	0.7624(3)	0.9676(4)	0.0297(4)

e_2 iron-based orbitals [9,18]. This causes an enhanced Q.S. relative to ferrocene [9]. On complexing to the $\text{M}(\text{CO})_5$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) the Q.S. values for the azaferrocene are around $0.05(1) \text{ mm s}^{-1}$ smaller than that of the uncomplexed molecule. Such a relatively small decrease would be expected if the N atom was σ -bonded to the $\text{M}(\text{CO})_5$ with no concomitant π -backbonding from the metal atoms. The loss of electron density from the pyrrolyl nitrogen atom on σ -bonding to the metal will cause a slight polarization of the ring

Table 4
Selected bond lengths (Å) and angles (°)

	3a	3b	4a	4b
W(1 or 21)–C(11 or 31)	2.023(9)	2.025(8)	2.037(6)	2.033(5)
W(1 or 21)–C(12 or 32)	2.033(9)	2.046(10)	2.035(7)	2.041(5)
W(1 or 21)–C(13 or 33)	2.042(9)	2.025(9)	2.029(7)	2.019(6)
W(1 or 21)–C(14 or 34)	2.053(9)	2.037(9)	2.072(7)	2.014(6)
W(1 or 21)–C(15 or 35)	1.959(8)	1.982(9)	1.945(6)	1.961(5)
W(1 or 21)–N(1 or 21)	2.259(7)	2.250(6)	2.285(3)	2.289(4)
O(1 or 21)–C(11 or 31)	1.136(11)	1.139(10)	1.134(7)	1.125(7)
O(2 or 22)–C(12 or 32)	1.134(11)	1.134(12)	1.139(8)	1.134(6)
O(3 or 23)–C(13 or 33)	1.127(11)	1.135(11)	1.137(8)	1.137(7)
O(4 or 24)–C(14 or 34)	1.120(11)	1.130(11)	1.101(8)	1.151(8)
O(5 or 25)–C(15 or 35)	1.153(11)	1.138(11)	1.150(7)	1.149(6)
C(15 or 35)–W(1 or 21)–C(11 or 31)	89.0(4)	86.9(3)	85.9(2)	86.2(3)
C(15 or 35)–W(1 or 21)–C(12 or 32)	88.7(4)	90.0(4)	87.9(3)	87.0(2)
C(11 or 31)–W(1 or 21)–C(12 or 32)	89.4(4)	89.6(4)	89.1(3)	89.0(2)
C(15 or 35)–W(1 or 21)–C(13 or 33)	90.9(4)	90.6(4)	88.3(3)	88.1(3)
C(11 or 31)–W(1 or 21)–C(13 or 33)	88.7(4)	92.3(4)	89.4(2)	92.7(3)
C(12 or 32)–W(1 or 21)–C(13 or 33)	178.0(4)	178.0(4)	176.1(2)	174.7(2)
C(15 or 35)–W(1 or 21)–C(14 or 34)	88.7(4)	89.1(4)	84.8(3)	87.4(2)
C(11 or 31)–W(1 or 21)–C(14 or 34)	177.7(4)	175.7(3)	170.6(2)	173.5(3)
C(12 or 32)–W(1 or 21)–C(14 or 34)	90.5(3)	88.9(4)	91.7(3)	92.2(3)
C(13 or 33)–W(1 or 21)–C(14 or 34)	91.4(4)	89.2(4)	89.1(3)	85.6(3)
C(15 or 35)–W(1 or 21)–N(1 or 21)	179.2(4)	176.9(3)	178.8(3)	178.7(2)
C(11 or 31)–W(1 or 21)–N(1 or 21)	91.8(3)	90.1(3)	94.7(2)	93.4(2)
C(12 or 32)–W(1 or 21)–N(1 or 21)	91.4(3)	90.0(3)	91.1(2)	91.7(2)
C(13 or 33)–W(1 or 21)–N(1 or 21)	89.1(3)	93.9(3)	92.7(2)	93.2(2)
C(14 or 34)–W(1 or 21)–N(1 or 21)	90.5(3)	89.5(3)	94.6(2)	93.0(2)
O(1 or 21)–C(11 or 31)–W(1 or 21)	177.9(9)	176.1(7)	173.4(5)	174.2(5)
O(2 or 22)–C(12 or 32)–W(1 or 21)	177.4(8)	178.1(10)	174.9(6)	176.7(5)
O(3 or 23)–C(13 or 33)–W(1 or 21)	177.7(10)	176.7(10)	177.0(6)	175.6(7)
O(4 or 24)–C(14 or 34)–W(1 or 21)	176.7(9)	175.4(9)	173.3(6)	175.3(7)
O(5 or 25)–C(15 or 35)–W(1 or 21)	179.1(11)	177.3(8)	178.4(8)	179.0(6)

electrons so that the ring-based e_1 orbitals will donate slightly less electron density to the iron atom. The iron will therefore need to use a little more of its e_2 electrons in backbonding to the pyrrolyl ring and hence, as the electrons in the e_2 molecular orbitals make twice as much contribution to the Q.S. as those in the e_1 molecular orbitals, the Q.S. will decrease [18].

In the case of 2,5-dimethylazaferrocene on bonding to $W(CO)_5$, there is little change in the Q.S., suggesting very little change in iron to ring bonding. Hence the only way this can occur is if the N atom of the pyrrolyl ring is purely σ -bonded to the tungsten atom. If backbonding from W to N had taken place we would expect

an increase in Q.S. as the e_1 molecular orbital population increases.

3.2. Crystal structures of 3 and 4

The unit cells of 3 and 4 each contain two crystallographically independent molecules (**3a/3b**, **4a/4b**). A view of the molecule **4a** (with its numbering scheme) is given in Fig. 1. The same numbering scheme is used for the atoms in molecules **3a** and **4a** (except for the two methyl groups in the latter). The atoms in molecules **3b** and **4b** are numbered 20 + X, where X is the number of the corresponding atom in molecule **3a** or **4a**. The

Table 5

⁵⁷Fe Mössbauer spectroscopic data for azaferrocenes and their $M(CO)_5$ complexes at 78 K

Compound	I.S. (mm s^{-1})	Q.S. (mm s^{-1})	Γ (mm s^{-1})	
1	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₄)]	0.54(1)	2.51(1)	0.14(1)
2	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₄)Cr(CO) ₅]	0.53(1)	2.45(1)	0.10(1)
3	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₄)Mo(CO) ₅]	0.54(1)	2.46(1)	0.13(1)
4	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₄)W(CO) ₅]	0.58(2)	2.47(3)	0.16(2)
5	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₂ Me ₂)]	0.55(1)	2.48(1)	0.13(1)
6	[Fe(η^5 -C ₅ H ₅)(η^5 -NC ₄ H ₂ Me ₂)W(CO) ₅]	0.52(1)	2.47(1)	0.13(1)

I.S., isomer shift; Q.S., quadrupole shift; Γ , half-width at half-height.

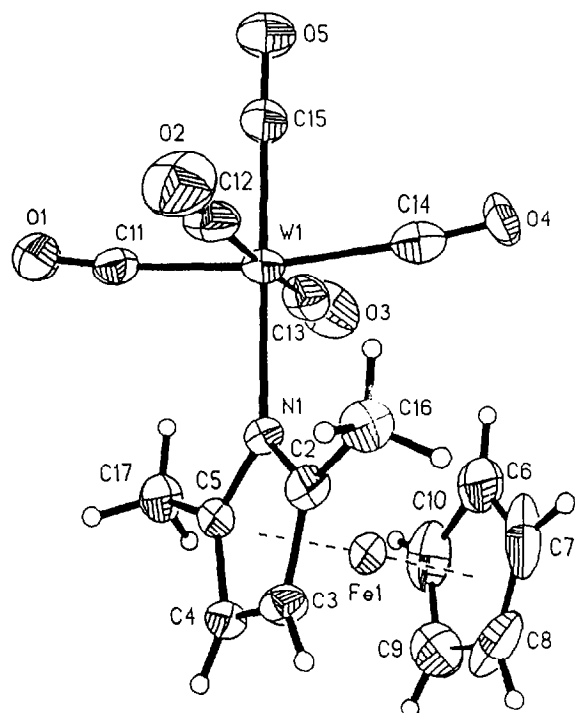


Fig. 1. View of molecule **4a** with numbering scheme.

molecule **3a** has a staggered conformation, whereas **3b**, **4a** and **4b** have an eclipsed one (Fig. 2: $C-C_p-C_{pN}-C' = 30(1)$ vs. $4(1)$, $2(1)$ and $1(1)^\circ$; C_p and C_{pN} being the centroids of the cyclopentadienyl and pyrrolyl ligand respectively). All five-membered rings are planar and nearly parallel in the same complex (the interplanar angles vary from $2(1)$ to $4(1)^\circ$). The methyl groups deviate from the respective plane opposite to the Fe atom from $0.075(9)$ to $0.097(10)$ Å. The W atoms display a distorted octahedral coordination (Table 4) The W–N bond lengths are shorter in molecules **3a** and **3b** than those in molecules **4a** and **4b** (average $2.255(6)$ vs.

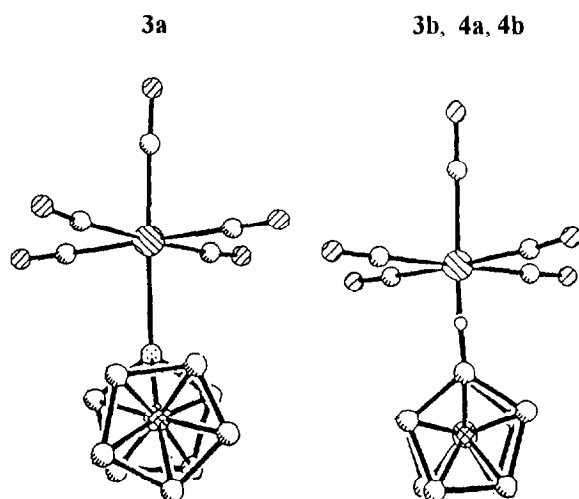


Fig. 2. Conformation of azaferrocene five-membered rings in molecules **3a**, **3b**, **4a** and **4b**.

$2.287(4)$ Å). The W–C bonds in the *trans* positions to the nitrogen atoms are shorter than those in the *cis* positions (average $1.962(7)$ vs. $2.035(8)$ Å). In both compounds **3** and **4** the W–N bonds are not exactly coplanar with the azacyclopentadienyl rings. The deviations of W atoms from the least-square plane of these rings ranges from $0.171(1)$ to $0.271(1)$ Å and the angles between the W–N bond and the normal to this ring (tilt angle) from $83.0(3)$ to $85.8(1)^\circ$. The carbonyls that are *cis* to the nitrogen atom show bending away from the azaferrocene moieties (*cis* W–C–O angle average $177.0(9)^\circ$ in **3a** and **3b**), especially in molecules **4a** and **4b** (*cis* W–C–O average $175.0(6)^\circ$) in which the methyl groups cause more steric interactions. This effect is also reflected in the C–W–C and C–W–N angles (Table 4). Short intramolecular C–C contacts between the CH_3 and *cis* CO groups in **4** range from $3.185(8)$ to $3.399(8)$ Å. Thus the substitution of the pyrrolyl ring causes greater deformation of the octahedral coordination of the W(0) atom as manifested in the structure of **4**.

Information on the mode of binding of azaferrocene to the tungsten is most likely to be found (i) in the W–N and *trans* W–C bond lengths, and (ii) by comparing these with the analogous bond lengths in $[W(CO)_5L]$ (where L = piperidine, pyridine or CO). The relevant data are presented in Table 6.

Two points need to be stressed before considering these data: firstly that the azaferrocene moiety experiences less steric hindrance as observed in the tilt angles (defined as above) on binding to $W(CO)_5$ ($83.0(3)$ to $85.8(1)^\circ$) than it encounters on binding to iron or cobalt porphyrins [11] (66 – 67°) (where the tilt angles are defined as “the dihedral angles between the pyrrolyl ligand planes and the mean plane of the porphyrin core”); secondly a non-sterically hindered five-membered planar ring would be expected to form shorter bonds to $W(CO)_5$ than a six-membered ring such as pyridine if its bonding properties were identical. From Table 6 it is obvious that the W–N bond lengths for the

Table 6
W(0) bond lengths (Å) in compounds **3** and **4** and in some related molecules

Compound	W–C _{trans}	W–C _{cis}	W–N	Ref.
3 molecule a	1.959(8)	2.039(9) ^a	2.259(7)	This work
molecule b	1.982(9)	2.033(9) ^a	2.250(6)	This work
4 molecule a	1.945(6)	2.044(7) ^a	2.285(3)	This work
molecule b	1.961(5)	2.027(6) ^a	2.289(4)	This work
$[W(CO)_5(\text{pip})]$	1.963(6)	2.044(11)	2.330(5)	[3]
$[W(CO)_5(\text{py})]$	2.00(1)	2.04(1)	2.26(1)	[4]
$[W(CO)_5(\text{pa})]$	1.967(15)	2.04(1) ^a	1.967(5)	[19]
$[W(CO)_6]$	2.03(1) ^{a,b}	2.03(1) ^{a,b}		[20]

^a Averaged value.

^b Calculated from the data in Ref. [20]. pip = piperidine; py = pyridine; pa = 2-propenylamine.

azaferrocene complexes are similar, showing firstly the presence of some steric hindrance but much less than in the iron porphyrin complexes [11]. It can be seen from Table 6 that complexes with amines that display only σ -bonding properties (piperidine and pa) have shorter W–CO *trans* bond lengths than that in the pyridine complex. It is generally accepted that this is due to the stronger π -bonding from W to CO. The fact that piperidine is a better σ -donor and poorer π -acceptor than pyridine is demonstrated by a *trans*-influence on the W–CO_{*trans*} bond length (1.963(6) Å), which is shorter than that in the pyridine complex. It is generally accepted that this is due to the stronger π -bonding from W to CO. The averaged value of the W–C_{*trans*} bond lengths in the azaferrocene complexes is 1.962(7) Å, which is smaller than that in the pyridine complex and permits the suggestion that even though the azaferrocene is sterically hindered it is a better σ -donor than pyridine and comparable to piperidine. Table 6 presents a structure of the W(CO)₅ complex with a sterically unhindered aliphatic amine. The W–N bond is short, however the W–C_{*trans*} bond is of similar length to those of 3 and 4. This N atom is a strong σ -donor and contains no orbitals for any kind of π -overlap. The fact that the W–C_{*trans*} bond is of similar length to those of compounds 3 and 4 is therefore strong evidence that the azaferrocene ligand in the latter compounds is solely σ -donor, and the fact that their W–N bonds are longer is due to steric hindrance rather than weaker σ -donor properties. It should be realised that 3 and 4 contain what may still be considered as sp² hybridised N rather than the sp³ nitrogen in aliphatic amines. This also implies that azaferrocene is a very poor π -acceptor, otherwise longer W–C_{*trans*} bonds would be expected as the W atoms would show less tendency for backbonding.

4. Conclusions

The two crystal structures and the Mössbauer data provide convincing evidence that azaferrocene ligands in 3 and 4 are good σ -donors but have little or no π -acceptor properties.

Acknowledgements

This research was supported by the British–Polish joint research collaboration programme (British Council Grant KBN WAR/992/046/) and by a grant from the Technical University of Łódź.

References

- [1] G.L. Geoffroy, M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979, pp. 45–89 and references cited therein.
- [2] H. Daamen, A. Oskam, D.J. Stufkens, *Inorg. Chim. Acta* 32 (1979) 249.
- [3] C. Moralejo, C.H. Langford, P.H. Bird, *Can. J. Chem.* 69 (1991) 2033.
- [4] L. Tutt, J.I. Zink, *J. Am. Chem. Soc.* 108 (1986) 5830.
- [5] W. Buchner, W.A. Schenk, *Inorg. Chem.* 23 (1984) 132.
- [6] M.S. Davies, R.K. Pierens, M.J. Aroney, *J. Organomet. Chem.* 458 (1993) 141.
- [7] M.J. Aroney, M.S. Davies, T.V. Hambley, R.K. Pierens, *J. Chem. Soc., Dalton Trans.* (1994) 91.
- [8] P.S. Wang, M.G. Richmond, M. Schwartz, *J. Am. Chem. Soc.* 114 (1992) 7595.
- [9] A. Houlton, R.M.G. Roberts, J. Silver, J. Zakrzewski, *J. Organomet. Chem.* 456 (1993) 107.
- [10] J. Zakrzewski, C. Giannotti, *Coord. Chem. Rev.* 140 (1995) 169 and references cited therein.
- [11] M. Cesario, C. Giannotti, J. Guilhem, J. Silver, J. Zakrzewski, *J. Chem. Soc., Dalton Trans.* (1997) 47.
- [12] J. Zakrzewski, C. Giannotti, *J. Organomet. Chem.* 388 (1990) 175.
- [13] K.K. Joshi, P.L. Pauson, A.R. Quazi, W.H. Stubbs, *J. Organomet. Chem.* 1 (1964) 471.
- [14] M.Y. Hamed, R.C. Hider, J. Silver, *Inorg. Chim. Acta* 66 (1982) 13.
- [15] A.C.T. North, D.C. Phillips, F.S.A. Mathews, *Acta Crystallogr. A* 24 (1968) 251.
- [16] G.M. Sheldrick, *SHELXTL* vers. 4.1, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.
- [17] G.M. Sheldrick, *SHELXL-93*, Program for Refinement of Crystal Structures from Diffraction Data, University of Göttingen, 1992.
- [18] A. Houlton, J.R. Miller, R.M.G. Roberts, J. Silver, *J. Chem. Soc., Dalton Trans.* (1990) 2181.
- [19] A. Parlier, H. Hudler, J.C. Daran, C. Alvarez, F.D. Reyes, *J. Organomet. Chem.* 327 (1987) 339.
- [20] F. Heinemann, H. Schmidt, K. Peters, D. Thiery, *Z. Kristallogr.* 198 (1992) 123.