[(DIMETHYLAMINO)METHYL]FERROCENE AS AN AMINE LIGAND: STUDY OF THE BONDING AND X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF THE PENTACARBONYL{[(DIMETHYLAMINO)-METHYL]FERROCENE}TUNGSTEN COMPLEX

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The heterodinuclear complex $[W(CO)_5(Me_2NCH_2Fc)]$ (Fc = ferrocenyl) (**1**) resulting from the reaction of [(dimethylamino)methyl]ferrocene (**2**) and $[W(CO)_6]$ was studied by single-crystal X-ray diffraction. Its molecular structure confirms the coordination of the amine nitrogen in **2** to tungsten (d(W–N) = 2.359(5) Å) and reveals its *trans*-influence in the $W(CO)_5$ moiety. The structure is discussed in relation to several previously referred spectroscopic (IR, UV-VIS, ^{13}C NMR) data.

Keywords: [(Dimethylamino)methyl]ferrocene; Ferrocenes; Carbonyl complexes; Tungsten; Heterodinuclear complex; X-Ray diffraction; Bonding properties; Multinuclear NMR spectroscopy.

Recently, we have reported on the syntheses of two novel heterodinuclear complexes[1] $[M(CO)_5(Me_2NCH_2Fc)]$ (M = Mo, W; Fc = ferrocenyl) and their characterization by mass spectrometry and Mössbauer, IR, UV-VIS and ^{1}H, ^{13}C, ^{15}N NMR spectroscopies. In the meantime, we have succeeded to grow crystals of $[W(CO)_5(Me_2NCH_2Fc)]$ (**1**) suitable for single-crystal X-ray crystallographic study. In order to confirm the proposed bonding properties, the molecular structure of **1** was solved. In this note, the results of this study are reported, including the discussion of the resulting structural parameters in relation to IR, UV-VIS, and ^{13}C NMR spectroscopic data of **1**.

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EXPERIMENTAL

Synthesis and Characteristic Spectral Data of Complex **1**

Complex **1** (see Chart 1) was prepared by reaction of [(dimethylamino)methyl]ferrocene (**2**) (Sigma–Aldrich) with [$W(CO)_6$] (supplied by Sigma–Aldrich), as described previously[1]. IR (ν, cm^{-1}; only CO-stretching region; Nujol/$CHCl_3$): 2 070 m/2 068 m, 1 983 s/1 980 m, 1 932 vs/1 928 vs, 1 919 vs/1 920 vs, 1 885 vs/1 890 s). UV-VIS ($CHCl_3$); ν_{max}, cm^{-1} (ε, l mol^{-1} cm^{-1}): 22 000 (240), 24 860 (1 050), 26 800 sh. ^{13}C NMR (only CO region; $CDCl_3$, 90.57 MHz): 201.72 t, $^1J(^{183}W,^{13}C)$ = 152.60 (*trans*-CO); 199.54 t, $^1J(^{183}W,^{13}C)$ = 132.94 (*cis*-CO). For complete characterization and spectroscopic data, see ref.[1].

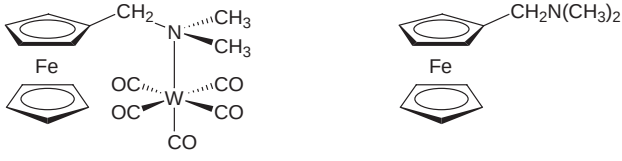
X-Ray Crystallographic Study

X-Ray-quality single crystals were grown from toluene. A suitable crystal was covered with inert oil, mounted on a fine glass fiber and transferred to a diffractometer (Bruker AXS Smart CCD system) in a stream of cold nitrogen. A graphite-monochromated MoKα radiation (λ = 0.71073 Å) was used. Data were corrected in the usual fashion for Lorentz and polarization effects. Absorption correction (multi-scan method SADABS) was employed. The structure was solved by direct method using the SHELXS software package. The refinement on F^2 was carried out by full-matrix least-squares analysis with SHELXL97(ref.[2]). All non-hydrogen atoms were refined with anisotropic thermal parameters, H-atoms riding or as rigid methyl groups.

Crystal data for complex **1**: [$C_{18}H_{17}FeNO_5W$], M_r = 567.03, amber plate, monoclinic, space group $P2_1/c$ (C_{2h}^5 No. 14), a = 14.006(1), b = 10.4223(1), c = 12.823(1) Å, β = 99.383(3)°, V = 1 846.9(2) $Å^3$, Z = 4, D_{calc} = 2.039 g cm^{-3}; T = 173(2) K; μ(MoKα) = 7.04 mm^{-1}, θ range 2.45–28.32°, limiting indices $-15 \le h \le 18$, $-11 \le k \le 13$, $-17 \le l \le 17$, reflections collected 12 257, independent reflections 4 566 (R_{int} = 0.052), data/restraints/parameters 4 566/0/283, goodness-of-fit on F^2 1.032; $R(I > 2\sigma(I))$: R_1 = 0.0451, wR_2 = 0.1046; R (all data): R_1 = 0.0761, wR_2 = 0.1205; extinction coefficient 0.0011(2); largest difference peak/hole: 4.44/–2.07 e $Å^{-3}$.

RESULTS AND DISCUSSION

In order to confirm the bonding features proposed for the heterodinuclear complex **1** on the basis of its spectroscopic investigation[1], its molecular structure has been solved by single-crystal X-ray diffraction analysis. The single crystal suitable for this purpose was obtained by careful recrystallization of **1** from toluene. The molecular structure of complex **1** is presented in Fig. 1. Selected bond lengths and angles are collected in Table I.



1 **2**

CHART 1

The ferrocene moiety in complex **1** (see Fig. 1) adopts the familiar sandwich geometry with almost coplanar cyclopentadienyl (Cp) rings and with the following characteristic structural parameters: Fe–Cp(centroid; C1–C5) 1.636 Å, Fe–Cp(centroid; C6–C10) 1.652 Å, Cp(centroid)–Fe–Cp(centroid) 178.9°, dihedral angle of best planes defined by C1–C5 and C6–C10, respectively, amounting to 0.94(41)°. Both Cp rings are perfectly eclipsed. The η^5-Cp ligation shows unexceptional intra-ring metrical parameters. The average C–C distances of 1.424 and 1.418 Å for substituted and unsubstituted Cp ring, respectively, as well as the average Fe–C distances of 2.036 and 2.046 Å for substituted and unsubstituted Cp ring, respectively, compare favorably with the corresponding metrical parameters of the ferrocenyl group in the closely related uncomplexed molecule of 1,1′-bis{[(dimethylamino)methyl]ferrocene}[3]. It can be concluded that the metrical parameters of the ferrocene moiety in the coordinated Me_2NCH_2Fc amine ligand remains unaffected by the N–W coordination. In this regard, it should be mentioned that this coordination becomes reflected in the UV-VIS spectrum of complex **1**, in particular in the ferrocenyl absorption. It is well known that the ferrocene $^1A_{1g} \rightarrow {}^1E_{1g}$ d-d transition[4] (22 800 cm^{-1}) responds to the electronic nature of the substituent attached to the Cp ring: an electron-releasing substituent such as $-CH_2N(CH_3)_2$ induces a characteristic d-d band shift to larger wavenumbers (non-coordinate Me_2NCH_2Fc:

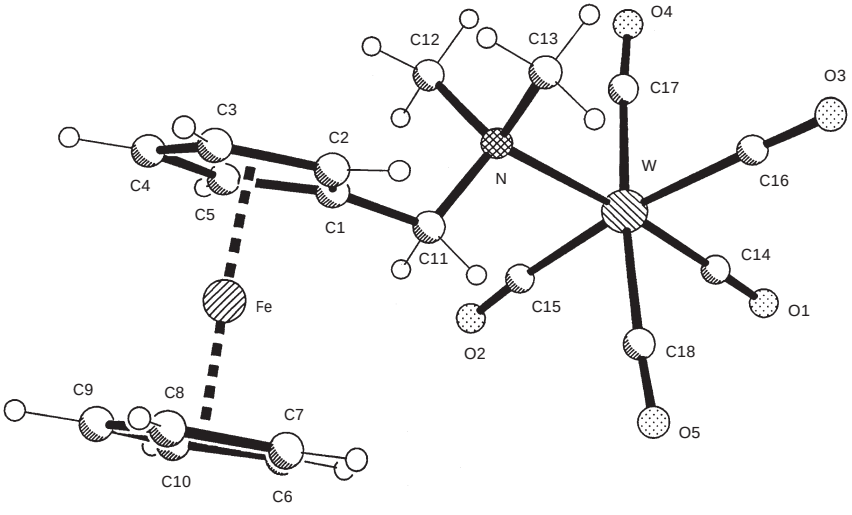


FIG. 1
Molecular structure of complex **1** with the atom-numbering scheme

TABLE I
Selected bond lengths and bond angles for complex **1**

Atoms	Bond lengths, Å	Atoms	Bond lengths, Å
W–C(14)	1.964(8)	C(14)–O(1)	1.159(9)
W–C(15)	2.029(8)	C(15)–O(2)	1.150(9)
W–C(16)	2.052(9)	C(16)–O(3)	1.129(10)
W–C(17)	2.057(8)	C(17)–O(4)	1.135(9)
W–C(18)	2.060(8)	C(18)–O(5)	1.131(9)
N–C(11)	1.508(8)	N–W	2.359(5)
N–C(12)	1.477(9)	C(1)–C(11)	1.506(9)
N–C(13)	1.492(9)		
Atoms	**Angles, °**	**Atoms**	**Angles, °**
C(14)–W–C(15)	84.2(3)	W–C(14)–O(1)	178.4(7)
C(15)–W–C(16)	172.3(3)	W–C(15)–O(2)	174.5(6)
C(16)–W–C(17)	87.2(3)	W–C(16)–O(3)	175.0(7)
C(17)–W–C(18)	175.7(3)	W–C(17)–O(4)	176.0(7)
C(14)–W–C(16)	88.1(3)	W–C(18)–O(5)	175.2(7)
C(14)–W–C(17)	89.1(3)	W–N–C(11)	110.5(4)
C(14)–W–C(18)	87.6(3)	W–N–C(12)	110.9(4)
C(15)–W–C(17)	93.8(3)	W–N–C(13)	110.7(4)
C(15)–W–C(18)	88.6(3)	N–W–C(14)	176.1(3)
C(16)–W–C(18)	89.9(3)	N–W–C(15)	91.9(2)
N–C(11)–C(1)	115.8(5)	N–W–C(16)	95.7(3)
C(11)–N–C(12)	108.5(6)	N–W–C(17)	91.5(3)
C(11)–N–C(13)	108.6(5)	N–W–C(18)	91.9(2)
C(12)–N–C(13)	107.5(6)		

22 840 cm^{-1}), while an electron-withdrawing substituent acts in the opposite direction. As to complex **1**, the remarkable shift of this "ferrocene" d-d band to smaller wavenumbers (**1**: 22 000 cm^{-1}) is observed[1]. The reason for this spectral behavior may be seen in the "Umpolung" or in the change of the electronic nature of the $-CH_2N(CH_3)_2$ substituent from electron-releasing in the non-coordinate Me_2NCH_2Fc molecule to the electron-withdrawing in **1** due to the N-W donor–acceptor interaction.

The formation of the new N–W bond does not significantly affect the original pseudotetrahedral arrangement around the nitrogen atom in $-CH_2N(CH_3)_2$, as documented by comparing the average N–C bond lengths in **1** (1.492 Å) with those in 1,1′-bis{[(dimethylamino)methyl]ferrocene}[3] (1.461 Å), and the C–N–C bond angles in **1** (107.5–108.5°) with the corresponding angles in 1,1′-bis{[(dimethylamino)methyl]ferrocene}[3] (109.0–111.8°). The C–N–W bond angles in **1** are also very close to undistorted tetrahedron.

The coordination geometry adopted by the hexacoordinated tungsten(0) centre can be described as a distorted octahedron characterized by: (i) non-equal *trans*-positioned W–N (2.359 Å) and W–C(14) (1.964 Å) bonds; (ii) four nearly uniform *cis* W–C bonds (probably with the *cis* W–C(15) bond shorter by about 0.03 Å than the other three *cis* W–C bonds); (iii) angles N–W–C(14) 176.1°, C(15)–W–C(16) 172.3°, C(17)–W–C(18) 175.7° as well as five W–C–O bond angles ranging from 175.0 to 178.4°, all deviating from linearity.

With regard to the bonding situation in the $W(CO)_5$ moiety of complex **1**, the following structural parameters are of importance: (i) the *trans* W–C(14) bond is significantly shorter than all the *cis* W–C bonds; (ii) the *trans* W–C(14) bond (1.964 Å) is apparently shorter than the average W–C bond (2.025 Å) in the parent complex $[W(CO)_6]$ (ref.[5]); (iii) the *trans* C–O bond (1.159 Å) is distinctly longer than the average C–O bond (1.130 Å) in $[W(CO)_6]$ (ref.[5]), while the average *cis* C–O bond (1.136 Å) is only slightly longer than the C–O bond in $[W(CO)_6]$. These structural findings can be related to the following spectroscopic data for **1** (ref.[1]): (i) the four *cis*-CO stretching frequencies corresponding to the symmetry-related CO-stretching modes of $[W(CO)_6]$ are shifted by 46, 27, 45, and 58 cm^{-1} to lower wavenumbers, while the analogous frequency shift of the *trans*-CO stretching to lower wavenumbers amounts to 125 cm^{-1} (ref.[1]); (ii) the carbonyl ^{13}C nuclear resonances in **1** occur at lower field compared to carbonyl shielding of parent $[W(CO)_6]$ (191.10 ppm) and the *trans* CO ligand is more deshielded than the *cis* CO ligands.

Both the structural and related spectroscopic data for complex **1** can be interpreted on the following common basis. The donor–acceptor N-W interaction increases a negative charge on W, which causes expansion of the d-orbitals of W with concurrent increase of the W(dπ)–CO(π*) overlap. This effect is more pronounced for W–*trans* CO than W–*cis* CO bonds. Ligands in mutual *trans* positions compete for electrons in particular d-orbital of the central atom. By replacing one strong π-acceptor CO group with the Me_2NCH_2Fc ligand, which is a σ-donor only, the W–CO bond in the *trans* position becomes strengthened, while the *trans* C–O bond becomes weakened. The consequences of this *trans* influence in **1** manifest in the observed shorter W–*trans* CO bond and longer *trans* C≡O bond, in the lower *trans*-CO stretching frequency and in the downfield shift of the *trans* ^{13}CO resonance as well as in the larger value of the coupling constant *trans* $^1J(^{183}W,^{13}C)$ = 152.60 Hz in comparison with *cis* $^1J(^{183}W,^{13}C)$ = 132.94 Hz and with $^1J(^{183}W,^{13}C)$ = 126.2 Hz for $[W(CO)_6]$.

It is interesting to note that both the structural and spectroscopic data gained for complex **1** correspond to those found for other $[W(CO)_5L]$ complexes, where L is an axially symmetric amine ligand. Thus, the W–C and C≡O bond lengths in **1** are very similar to those found for $[W(CO)_5L]$ complexes (*e.g.* L = dimethylamine[6a], pyridine[6b], piperidine[6c]) and the ^{13}C NMR data observed for carbonyls in **1** are also very similar to those found for $[W(CO)_5(C_6H_{11}NH_2)]$ complex (δ 201.9 ppm for CO *trans*; δ 199.1 ppm for CO *cis*; *trans* $^1J(^{183}W,^{13}C)$ = 127 Hz)[7]. While the infrared CO-stretching region of **1** comprises five bands due to the low symmetry of **1**, other $[W(CO)_5L]$ complexes (*e.g.* L = piperidine, pyrrolidine, diethylamine, cyclohexylamine, pyridine)[8], retaining the ideal C_{4v} symmetry, possess only three infrared-allowed CO-stretching vibrations, as described previously[1].

CCDC 154270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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