

**2D HetCOR NMR Spectrum and Structure of
tricarbonyl(η^5 -formylcyclopentadienyl)methyltungsten
(CO)₃(CH₃)W(η^5 -C₅H₄CHO)**

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Abstract

Reaction of sodium formylcyclopentadienide with hexacarbonyltungsten led to (CO)₃(η^5 -C₅H₄CHO)WNa. Treatment of the metal carbonyl anion with methyl iodide led to (CO)₃(CH₃)W(η^5 -C₅H₄CHO) **2**. The structure of **2** has been determined by X-ray diffraction studies: space group, P₁; monoclinic; a = 7.791(2), b = 11.455(3), c = 12.819(3) Å, α = 98.16(2), β = 98.74(2), γ = 104.85(2)[°]; Z = 2. Both cisoid and transoid conformations of the methyl ligand toward the formyl carbon were observed. The twist angles are 80.7[°] and 154.0[°] for methyl ligands in cisoid and transoid **2**, respectively. The exocyclic carbon is bent toward the tungsten atom with an angle θ of 1.95[°] in cisoid conformation, whereas in transoid conformation the exocyclic carbon is turned away from the tungsten atom with an angle θ of -0.82[°]. The chemical shifts of C(2,5) and C(3,4) on the Cp ring has been assigned using two-dimensional HetCOR NMR spectroscopy. The electron density distribution in the cyclopentadienyl ring of the Cp(W) was discussed on the basis of ¹³C NMR data and compared with calculations via the density functional B3LYP exchange-correlation method.

Keywords: Tungsten, Tricarbonylcyclopentadienylmethyltungsten, Formyl, HetCOR

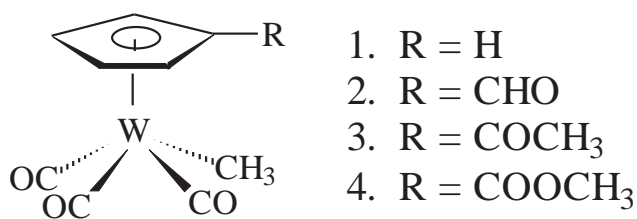
NMR, B3LYP

1. Introduction

In the last few years, a steadily increasing number of systems with exciting new biological activities have been prepared by the conjugation of organometallic compounds to bio(macro)molecules [1,2]. The potential applications of these systems, including use as antitumor agents [3], antibacterial agents [4], and radiopharmaceuticals [5], have prompted us to study compound tricarbonyl(η^5 -formylcyclopentadienyl)methyltungsten

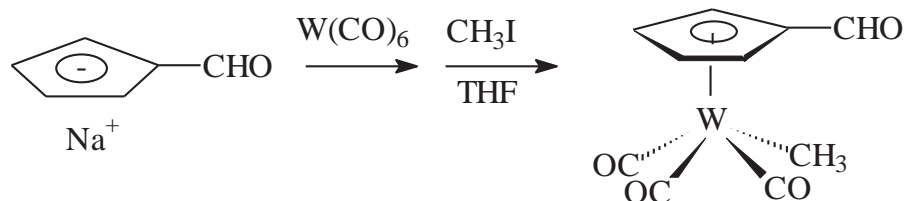
2.

The preparation and NMR data of **2** have been previously reported [6]. However its ^{13}C NMR data has not been examined thoroughly. Herein, we report the 2D NMR spectra and the crystal structure of **2**. Based on the 2D HetCOR correlation spectrum, unequivocal assignments for the C(2,5) and C(3,4) of the Cp(W) ring of **2** were made.

**2. Results**

Tricarbonyl(η^5 -formylcyclopentadienyl)methyltungsten **2** was obtained in a yield of 82% [6] from a reaction between formylcyclopentadienylsodium and hexacarbonyltungsten in refluxing DMF, followed by removal of the solvent, addition of THF, treatment with methyl iodide, and subsequent purification by chromatography and

vacuum sublimation.



The ^1H NMR spectrum of **2** exhibited a singlet owing to the $\text{W}(\text{CH}_3)$ protons at δ 0.46 ppm and a 1H singlet at δ 9.61 ppm owing to formyl proton. An A_2B_2 pattern, as is typical of similarly substituted cyclopentadienyl ring protons in many other metallo-aromatic systems [7, 8], was also observed. The spectrum consists a pair of apparent triplets, in which the downfield triplet can be assigned to the H (2,5) protons of the Cp ring. This assignment was made on the basis that the carbonyl group would exert a strong diamagnetic anisotropic effect and exhibit an electron-withdrawing property. As expected, H (2,5) would be deshielded to a greater extent than the protons on the more remote 3- and 4-positions. Analogous assignments have been made unequivocally for monosubstituted ferrocenes from the NMR spectra of 2,5-dideuterioferrocene derivatives. Accordingly, the following assignments were made: H(2,5) and H(3,4) of Cp(W) resonate at δ 5.72 and δ 5.59 ppm, respectively, for complex **2** (Table 1).

The assignments of ^{13}C NMR spectra for **2** were based on standard ^{13}C NMR [9], 2D HetCOR, and DEPT correlation techniques. They were also compared with other metallo-aromatic systems [10]. Four relatively less intense signals were observed at δ 224.99, δ 212.69, δ 184.90, and δ 102.01 ppm corresponding to the terminal carbonyl carbons, the formyl carbon, and the C(1) of Cp(W), respectively. Chemical shifts at δ -32.31 was assigned to methyl ligand carbon on W. The line assignments for the C(2–5) of Cp(W) were more difficult to make. Based on the 2D HetCOR results (Fig. 1), in which the magnetic fields of ^1H and ^{13}C NMR spectra increase toward the right and upper

side, respectively, the upfield chemical shifts of C(2,5) correlate with the downfield chemical shifts of H(2,5) (δ 5.72) and the downfield chemical shifts of C(3,4) correlate with the upfield chemical shifts of H(3,4) (δ 5.59). Accordingly, chemical shifts at δ 91.16 and 95.17 ppm were assigned to C(2,5) and C(3,4), respectively, of Cp(W) (Table 2). These assignments reveal that positions 3 and 4 on the substituted Cp ring in **2** are more sensitive to electron-withdrawing substituents, as previously found for ferrocene derivatives [10].

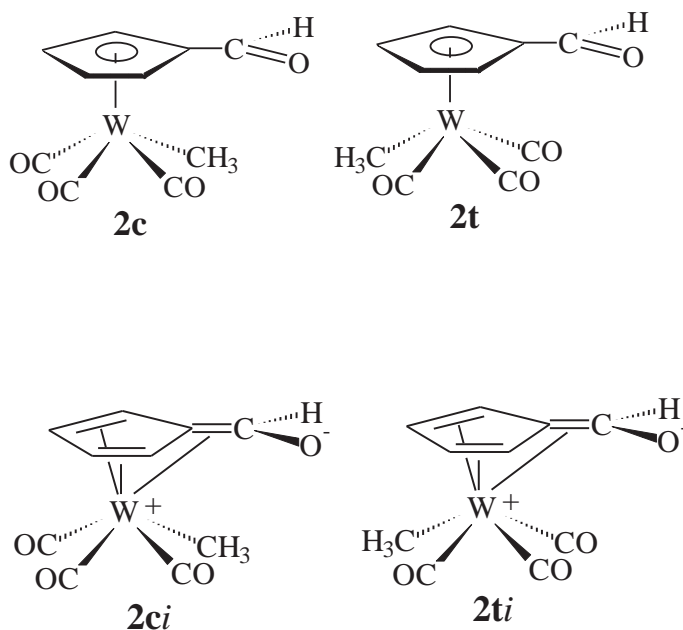
The molecular structures of cisoid **2** and transoid **2** are shown in Fig. 2a and Fig. 2b, respectively. Selected bond distances and angles are given in Table 3. The atomic coordinates of the atoms are listed in Table 4. For the purpose of comparison, the selected structural data of **3** (Fig. 3) [11] are also listed in Table 5.

3. Discussion

From Table 5, several interesting features are revealed. The lengths of W–C(ring), C(ring)–C(exocyclic), and W–C(exocyclic) are comparable with each other. The bond length of C(ring)(C1)–carbonyl carbon(exocyclic carbon) is comparatively short in all cases, (1.478(17) Å in cisoid **2**, 1.467(13) Å in transoid **2**, and 1.471(9) Å in **3** (cisoid)). The expected C(Cp)–C(sp³) single bond distance is 1.48 Å [12].

3.1 cisoid **2** versus transoid **2**

Both cisoid and transoid conformations were observed in **2**. Curiosity was aroused about whether conformer **2c** or **2t** would be the favored structure thermodynamically. We calculated the rotational barrier (4.36 kcal mol⁻¹) of Cp ring with respect to W–Cp(cen.) axis using B3LYP/LANL2DZ. The cisoid conformer **2c** is more favored by 0.23 kcal mol⁻¹ than transoid conformer **2t**.



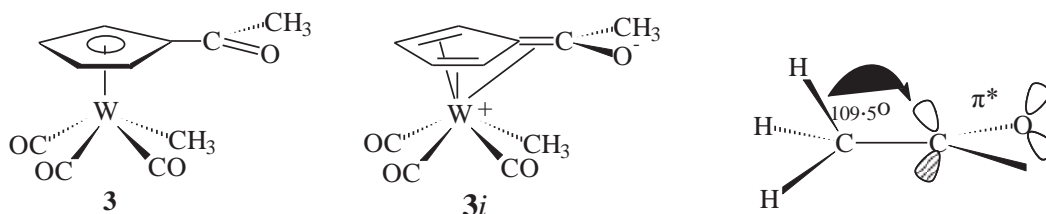
Cisoid **2** bears a large value of positive θ (1.95°), whereas transoid **2** bears a negative value of negative θ (-0.42°). The ability of the exocyclic double bond to donate electron density to the tungsten atom, reestablishing the favored 18-electron count, leads to the exocyclic carbon bending towards the tungsten atom (**2ci**). A positive value of θ would be anticipated. The θ angle is defined as the angle between the exocyclic C–C bond (C(1)–C(6) in cisoid **2**) and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal. The large positive θ value of cisoid **2** reveals that there is a, to some extent, contribution of canonical form **2ci** to **2c**.

In cisoid **2**, the methyl ligand is located at the site toward the exocyclic organic carbonyl carbon with a twist angle of 80.7° (Fig. 2). The twist angle is defined as the torsional angle between the methyl carbon atom, the W atom, the Cp ring center, and the ring C atom bearing the exocyclic carbon. The twist angles of C(7), C(8), and C(9) are 149.8° , 101.6° , and 25.7° , respectively. The preference ($0.23 \text{ kcal mol}^{-1}$) for the cisoid conformer **2c** over the transoid conformer **2t** may be related to the ability of the exocyclic

double bond of **2c** to donate electron density to the tungsten atom, such that it is trans to the two better π -accepting ligands, i.e. CO [13].

3.2 cisoid **2** versus cisoid **3**

The smaller contribution of canonical form **3i** than that of **2ci** to each of the corresponding structure **3** and **2c** may explain a smaller value of θ (-0.44°) in **3** and a large value of positive θ (1.95°) in cisoid **2**.



This phenomenon is plausible, since formyl exerts a greater capability of electron-withdrawing than acetyl substituent on the Cp(W) ring. In the case of acetyl derivative **3**, the electron-donating property of the $-\text{CH}_3$ group weakens the electron-withdrawing capability of $\text{C}=\text{O}$, and the hyperconjugation [14] between $-\text{CH}_3$ and the carbonyl group diminishes the extent of the contribution of **3i** to **3**. The smaller contribution of **3i** to **3** leads to a smaller θ . The contribution of the canonical form **2ci** to **2c** was also revealed by the carbon-carbon bond lengths in the Cp(W). The short bond lengths, in Å, of C(2)–C(3) (1.390(19)) and C(4)–C(5) (1.401(19)) in cisoid **2**; and the longer bond lengths of C(1)–C(2) (1.420(12)) and C(1)–C(5) (1.439(17)) in cisoid **2** were determined.

After obtaining the X-ray structures of **2**, the average charges of C(2,5) and C(3,4) for complex **2** (-0.4182 and -0.3419 in cisoid **2**; -0.6066 and -0.3329 in transoid **2**) were

determined by ab-initio calculations (Table 6). These values correlated well with the unequivocal assignments of the ^{13}C chemical shifts (Table 2).

4. Conclusion

Several important findings may be drawn as follows and electronic effects appear to account for all the observations.

- (a) The chemical shifts for C(2,5) and C(3,4) of **2** (CHO) and **3** (COCH₃) follow the assignment of the ferrocene analog.
- (b) The relative deshielding on C(2,5) and C(3,4) of **2** was correlated with the atomic charges of C(2,5) and C(3,4) determined from ab-initio calculation.
- (c) The greater potential of the exocyclic double bond of **2c** (**2ci**) to donate electron density to the tungsten atom may account the preference (0.23 kcal mol⁻¹) for the cisoid conformer **2c** over the transoid conformer **2t**.

5. Experimental

5.1 Preparation of tricarbonyl(η^5 -formylcyclopentadienyl)methyltungsten

To the slurry of sodium sand (0.39 g, 17.0 mmol) in 80 ml of THF at 0°C, was added freshly cracked cyclopentadiene (1.38 ml, 16.7 mmol). The mixture was stirred until the sodium was reacted. Additional cyclopentadiene was used as necessary to completely consume the sodium. To this pink solution of sodium cyclopentadienide, ethyl formate (3.01 ml, 16.7 mmol) was added. The mixture was stirred at room temperature for 15 min. After refluxing for 1h, the THF was removed under vacuum. The resulting dark residue was washed with ethyl ether until the extracts were colorless and then dried to give

sodium formylcyclopentadienide. Hexacarbonyltungsten (4.01 g, 11.38 mmol) and 100 ml of DMF were added and the mixture refluxed for 4 h. The DMF was removed under vacuum to give **black** oil. The oil was dissolved in 100 ml of THF, and excess CH₃I was slowly added. The mixture was allowed to stir at room **temperature** for 4.5 h. The THF was removed under vacuum to give an oily solid. The residue was extracted with ethyl ether and then washed with distilled water three times, dried with anhydrous magnesium sulfate. The solution was filtered, concentrated to give tricarbonyl(η^5 -formylcyclopentadienyl)methyltungsten **2** (3.56 g, 83%) as a yellow solid. An analytical sample, m.p. 135°C(dec.), was obtained as a yellow crystals by **vacuum sublimation** at 80°C/ 0.1 mmHg.

Proton NMR(CDCl₃): δ (relative intensity, multiplicity, assignment): 0.46 (W(CH₃)); 5.59 (2H, t, $J = 2.4$ Hz, Cp(W) H(3,4)); 5.72 (2H, t, $J = 2.4$ Hz, Cp(W) H(2,5)); 9.61 (CHO). Carbon-13 NMR (CDCl₃): δ (assignment): -32.31 (W(CH₃)); 91.16 (Cp(W), C(2,5)); 95.17 (Cp(W), C(3,4)); 102.01 (Cp(W), C(1)); 184.90 (-C(O)-); 212.69, 224.99 (W-C \equiv O)).

5.2. X-ray Diffraction analysis of **2**

The intensity data were collected on a Siemens R3m/V diffractometer with a graphite monochromator (Mo-K α radiation). $\theta - 2\theta$ scan data were collected at room temperature (23°C). The data were corrected for absorption, Lorentz and polarization effects. The absorption correction is according to the empirical psi rotation. The details of crystal data and intensity collection are summarized in Table 7.

The structures were solved by direct methods and were refined by full matrix least squares refinement based on F values. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were positioned at calculated coordinate with a fixed isotropic thermal parameter ($U = U(\text{attached atom}) + 0.01 \text{ \AA}^2$).

Atomic scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography* [15]. All calculations were performed on a PC computer using Shelex software package [16].

5.3 Computational Method

Calculations based on DFT are carried out using B3LYP hybrid method involving three-parameter Becke exchange functional [17] and a Lee-Yang-Parr correlation functional [18]. All calculations are performed using the Gaussian 09 program [19]. The geometries for **2** are taken from the crystallographic data. The atomic charges have been analyzed using the Mulliken population analysis.

Acknowledgements

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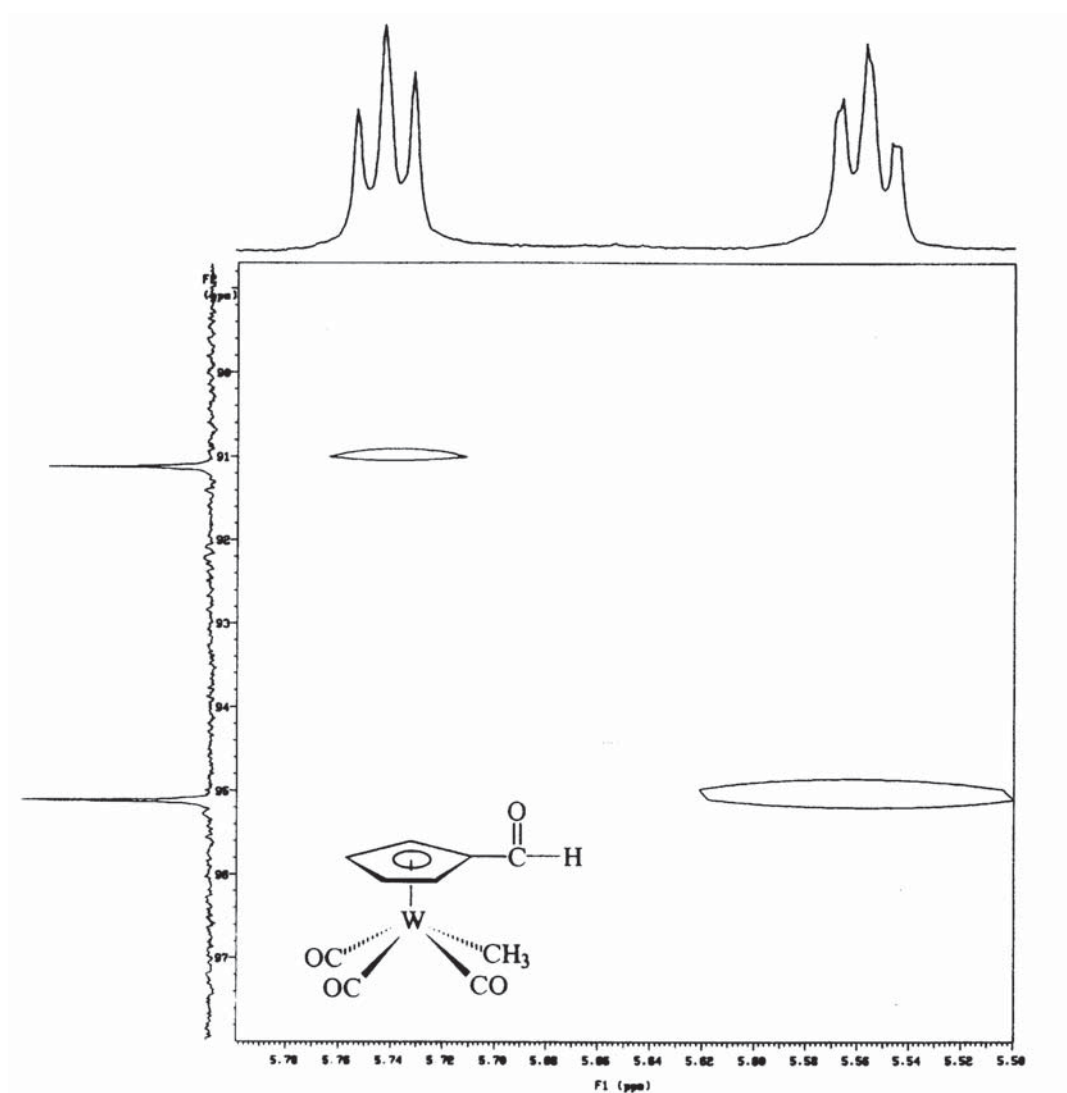


Fig. 1. Two-dimensional ^1H - ^{13}C HetCOR NMR spectrum of **2** in CDCl_3 .

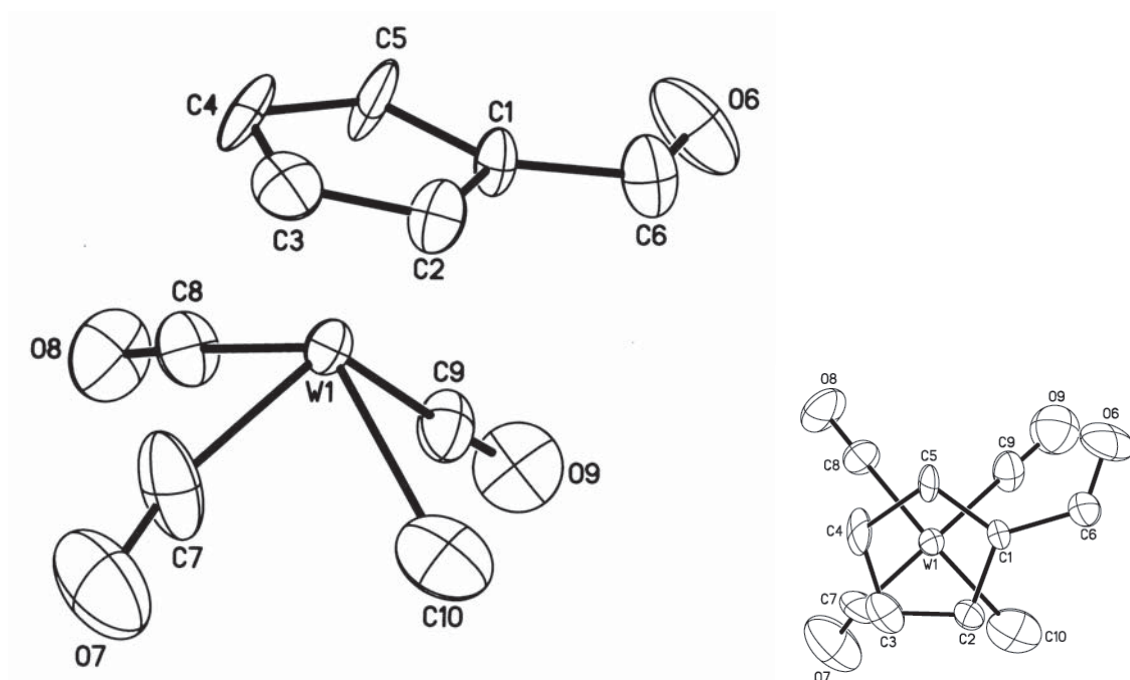


Fig. 2a Molecular configuration of cisoid 2

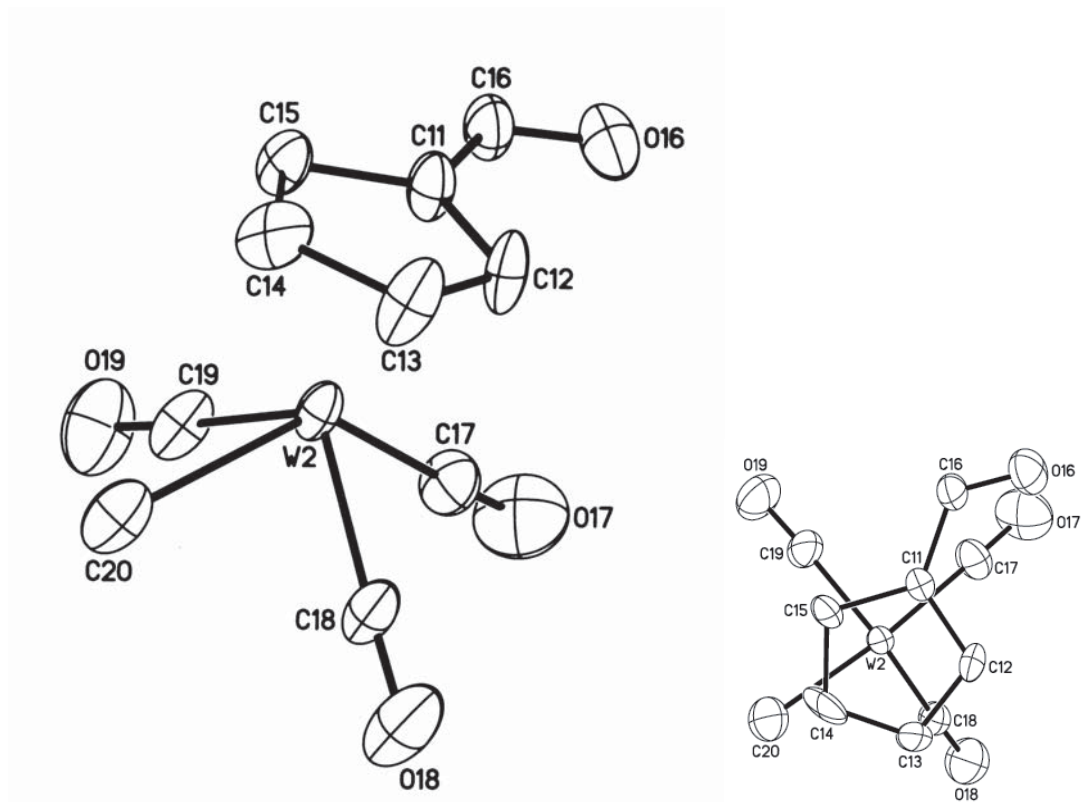


Fig. 2b Molecular configuration of transoid 2

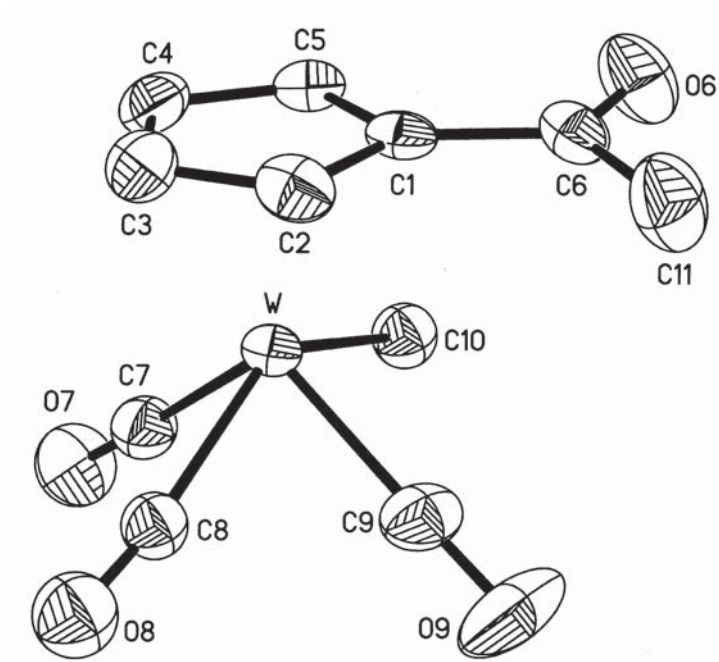


Fig. 3 Molecular configuration of **3**

Table 1
¹H NMR data and Δ^a

Compound	Cp ¹ (W) δ (ppm)			W(CH ₃)	Others
	H(2,5)	H(3,4)	Δ ^a (ppm)		
(CO) ₃ (CH ₃)WCp 1	5.40 (H(1–5))		0	0.42	
(CO) ₃ (CH ₃)W(C ₅ H ₄ CHO) 2	<u>5.72</u>	5.59	0.13	0.46	9.61 (CHO)
(CO) ₃ (CH ₃)W(C ₅ H ₄ COCH ₃) 3	<u>5.71</u>	5.53	0.18	0.44	2.33 (COCH ₃)
(CO) ₃ (CH ₃)W(C ₅ H ₄ COOCH ₃) 4	<u>5.79</u>	5.46	0.33	0.48	3.83 (–OCH ₃)

^a Δ = δ[H(2,5)] – δ[H(3,4)]

(+: H(2,5)downfield, H(3,4) upfield; – : H(2,5) upfield, H(3,4) downfield). The lower-field chemical shift of each pair is underlined.

Table 2
 $^{13}\text{C}\{^1\text{H}\}$ NMR data and Δ^a

Compound	Cp ¹ (W) δ (ppm)				-C(O)-	W(CO)	W(CH ₃)	Others
	C(1)	C(2,5)	C(3,4)	Δ^a (ppm)				
(CO) ₃ (CH ₃)WCp 1	91.18 (C(1-5))					216.21, 229.29	-34.98	
(CO) ₃ (CH ₃)W(C ₅ H ₄ CHO) 2	102.01	91.16	<u>95.17</u>	-4.01	184.90	212.69, 224.99	-32.31	
(CO) ₃ (CH ₃)W(C ₅ H ₄ COCH ₃) 3	102.60	91.60	<u>94.19</u>	-2.59	192.94	213.75, 225.97	-32.27	26.22(COCH ₃)
(CO) ₃ (CH ₃)W(C ₅ H ₄ COOCH ₃) 4	95.64	92.89	<u>93.17</u>	-0.28	164.54	214.09, 226.62	-32.52	52.20 (OCH ₃)

$$^a \Delta = \delta[\text{C}(2,5)] - \delta[\text{C}(3,4)]$$

(+: C(2,5)downfield, C(3,4) upfield; -: C(2,5) upfield, C(3,4) downfield). The lower-field chemical shift of each pair is underlined.

Table 3a
 Selected bond length (Å) and selected bond angles (°) for cisoid **2**

W(1)–C(1)	2.328(11)	C(7)–W(1)–C(9)	113.6(6)
W(1)–C(2)	2.356(12)	C(7)–W(1)–C(8)	77.6(6)
W(1)–C(3)	2.367(15)	C(9)–W(1)–C(8)	75.7(6)
W(1)–C(4)	2.336(14)	C(9)–W(1)–C(10)	75.0(5)
W(1)–C(5)	2.280(13)	C(7)–W(1)–C(10)	72.2(7)
C(1)–C(2)	1.420(12)	C(8)–W(1)–C(10)	124.1(6)
C(1)–C(5)	1.439(17)	W(1)–C(7)–O(7)	166.1(18)
C(1)–C(6)	1.478(17)	W(1)–C(8)–O(8)	177.5(12)
C(2)–C(3)	1.390(19)	W(1)–C(9)–O(9)	177.3(13)
C(3)–C(4)	1.411(18)	Cp(cen.)–W(1)–C(7)	121.42
C(4)–C(5)	1.401(19)	Cp(cen.)–W(1)–C(8)	118.61
W(1)–C(7)	2.002(13)	Cp(cen.)–W(1)–C(9)	124.87
W(1)–C(8)	2.003(13)	Cp(cen.)–W(1)–C(10)	117.27
W(1)–C(9)	1.990(13)	C(1)–C(6)–O(6)	124.5(13)
W(1)–C(10)	2.344(17)	C(6)–C(1)–C(2)	126.5(10)
C(7)–O(7)	1.127(20)	C(6)–C(1)–C(5)	127.3(9)
C(8)–O(8)	1.127(18)		
C(9)–O(9)	1.153(18)		
C(6)–O(6)	1.185(14)		
W(1)..Cp(cen.)	2.001		
Dihedral angles between planes			
Cp(cen.), W(1), C(7) and Cp(cen.), W(1), C(1)			149.77
Cp(cen.), W(1), C(8) and Cp(cen.), W(1), C(1)			101.58
Cp(cen.), W(1), C(9) and Cp(cen.), W(1), C(1)			25.73
Cp(cen.), W(1), C(10) and Cp(cen.), W(1), C(1)			80.69
Cp(W1) and carbonyl plane (C1, C6, O6)			4.80

Table 3b
Selected bond length (Å) and selected bond angles (°) for transoid **2**

W(2)–C(11)	2.300(10)	C(17)–W(2)–C(19)	77.0(5)
W(2)–C(12)	2.315(14)	C(17)–W(2)–C(18)	76.2(4)
W(2)–C(13)	2.355(14)	C(19)–W(2)–C(18)	107.7(5)
W(2)–C(14)	2.362(14)	C(19)–W(2)–C(20)	75.0(5)
W(2)–C(15)	2.338(11)	C(17)–W(2)–C(20)	128.4(5)
C(11)–C(12)	1.418(15)	C(18)–W(2)–C(20)	72.4(5)
C(11)–C(15)	1.448(15)	W(2)–C(17)–O(17)	177.6(10)
C(11)–C(16)	1.467(13)	W(2)–C(18)–O(18)	178.2(9)
C(12)–C(13)	1.406(16)	W(2)–C(19)–O(19)	176.4(11)
C(13)–C(14)	1.415(20)	Cp(cen.)–W(2)–C(17)	117.71
C(14)–C(15)	1.413(13)	Cp(cen.)–W(2)–C(18)	124.30
W(2)–C(17)	2.052(12)	Cp(cen.)–W(2)–C(19)	127.73
W(2)–C(18)	1.979(10)	Cp(cen.)–W(2)–C(20)	113.73
W(2)–C(19)	1.993(13)	C(11)–C(16)–O(16)	123.7(11)
W(2)–C(20)	2.253(14)	C(16)–C(11)–C(12)	127.6(10)
C(17)–O(17)	1.100(17)	C(16)–C(11)–C(12)	124.6(10)
C(18)–O(18)	1.114(13)		
C(19)–O(19)	1.148(18)		
C(16)–O(16)	1.169(15)		
W(2)..Cp(cen.)	1.997		

Dihedral angles between planes

Cp(cen.), W(2), C(17) and Cp(cen.), W(2), C(11)	29.95
Cp(cen.), W(2), C(18) and Cp(cen.), W(2), C(11)	137.55
Cp(cen.), W(2), C(19) and Cp(cen.), W(2), C(11)	48.53
Cp(cen.), W(2), C(20) and Cp(cen.), W(2), C(11)	153.99
Cp(W2) and carbonyl plane (C11, C16, O16)	3.29

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
W1	1337(1)	2985(1)	8726(1)	36(1)
W2	4107(1)	7977(1)	6501(1)	38(1)
O8	-1717(14)	3896(12)	7509(9)	97(5)
O9	-2135(15)	1777(13)	9586(12)	116(6)
O7	2666(20)	5800(13)	9619(15)	148(9)
O6	-146(15)	-663(9)	8408(11)	110(5)
O18	4962(14)	9124(10)	8923(7)	94(5)
O19	1086(13)	8961(11)	5323(9)	93(5)
O17	672(15)	6620(12)	7334(10)	107(6)
O16	1716(12)	4391(8)	5455(8)	72(4)
C8	-607(15)	3560(11)	7925(10)	63(5)
C9	-866(17)	2249(11)	9279(10)	61(5)
C7	2275(20)	4816(13)	9184(15)	95(7)
C10	2259(20)	3429(16)	10601(14)	105(8)
C6	1243(16)	101(11)	8781(11)	65(5)
C1	2033(13)	1142(9)	8277(8)	43(3)
C2	3709(13)	2062(10)	8681(9)	52(4)
C3	3926(17)	2903(12)	7994(11)	66(5)
C4	2400(20)	2549(14)	7148(10)	74(6)
C5	1217(19)	1480(12)	7324(9)	66(5)
C18	4674(15)	8728(10)	8047(8)	53(4)
C19	2160(15)	8598(12)	5782(9)	59(5)
C17	1878(16)	7115(11)	7062(10)	57(4)
C20	5387(19)	10009(13)	6651(11)	74(6)
C16	2315(15)	5195(9)	5030(9)	54(4)
C11	4040(14)	6143(9)	5474(8)	48(4)
C12	5211(16)	6281(11)	6473(10)	61(5)
C13	6723(15)	7298(13)	6561(10)	69(5)
C14	6508(15)	7804(12)	5621(10)	67(5)
C15	4859(13)	7107(9)	4933(9)	48(4)

Table 5
Selected structural data of **2** and **3**

Compound	Bond length (Å)		$\theta_M(^{\circ})^a$	M--C(exocyclic)
	W–C(ring) (average)	C(Cp(W))–C(exocyclic)		
2 (CO) ₃ (CH ₃)W(C ₅ H ₄ CHO) cisoid	2.334(13)	1.478(17) (C1–C6)	1.95	3.297
(CO) ₃ (CH ₃)W(C ₅ H ₄ CHO) transoid	2.334(13)	1.467(13) (C11–C16)	–0.82	3.298
3 (CO) ₃ (CH ₃)W(C ₅ H ₄ COCH ₃)	2.331(6)	1.471(9) (C1–C6)	–0.44	3.298

^a $\theta_M(^{\circ})$: the θ angle is defined as the angle between the exocyclic C–C(or N) bond and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal.

Table 6
Selected net atomic charges for **2** (cisoid and transoid) using the LANL2DZ basis set

	C(1)	C(2)	C(3)	C(4)	C(5)
2 cisoid	0.29063	–0.41806	–0.26647	–0.41735	–0.41831
2 transoid	0.29875	–0.69473	–0.32803	–0.33776	–0.51850

Table 7
Selected crystal data and refinement parameters for **2**

Identification code	920035	
Empirical formula	$C_{20}H_{16}WO_8$	
Color; Habit	Yellow; Chunk	
Formula weight	752.0	
Temperature	296 K	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 7.791(2) \text{ \AA}$	$\alpha = 98.16(2)^\circ$
	$b = 11.455(3) \text{ \AA}$	$\beta = 98.74(2)^\circ$
	$c = 12.819(3) \text{ \AA}$	$\gamma = 104.85(2)^\circ$
Volume	$1498.3(7) \text{ \AA}^3$	
Z	2	
Density (calculated)	2.327 Mg/m^3	
Absorption coefficient	10.753 mm^{-1}	
F(000)	696	
Diffractometer used	Siemens R3m/V	
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)	
Crystal size	$0.40 \times 0.34 \times 0.20 \text{ mm}^3$	
2θ Range	2.5 to 50.00°	
Scan Type	$\theta/2\theta$	
Scan Speed	Variable; 2.93 to $14.65^\circ/\text{min}$. in ω	
Scan Range (ω)	1.04° plus K α -separation	
Background Measurement	Stationary crystal and stationary Counter at beginning and end of scan, each for 25.0% of total scan time	
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $0 \leq l \leq 15$	
Reflections collected	4120 (3171 $\geq 3.0 \sigma(I)$)	
Independent reflections	3816 (2910 $\geq 3.0 \sigma(I)$)	
Max. and min. transmission	0.9890 and 0.2551	
Solution	Direct Methods	
Extinction Correction	$\chi = 0.00037(7)$, where $F^* = F[1 + 0.002 \chi F^2/\sin(2\theta)]^{-1/4}$	
Hydrogen Atoms	Riding model, fixed isotropic U	
Weighting Scheme	$w^{-1} = \sigma^2(F) + .00027F^2$	
Number of Parameters refined	272	
Largest and Mean Δ/σ	0.001, 0.000	
Data-to-Parameter Ratio	10.7:1	
Goodness-of-fit	0.85	

Final R indices (obs. Data)]

R = 0.0346, Rw = 0.0387

Largest diff. peak and hole

1.87 and -0.97 e.Å⁻³

化合物 $(\text{CO})_3(\text{CH}_3)\text{W}(\eta^5\text{-C}_5\text{H}_4\text{CHO})$ 二維異核 NMR 光譜及結構分析

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摘 要

$(\text{C}_5\text{H}_4\text{CHO})\text{Na}^+$ 與 $\text{W}(\text{CO})_6$ 反應得 $(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{W}:\text{Na}^+$. 後者與 CH_3I 作用得化合物 $(\text{CO})_3(\text{CH}_3)\text{W}(\eta^5\text{-C}_5\text{H}_4\text{CHO})$ (**2**). **2** 的結構已由 X-ray 繞射法解析出. 晶體參數如下: Space group, P_{-1} ; triclinic; $a = 7.791(2)$, $b = 11.455(3)$, $c = 12.819(3)$ Å, $\alpha = 98.16(2)$, $\beta = 98.74(2)$, $\gamma = 104.85(2)^\circ$; $Z = 2$. X-ray 結晶體中可觀察到兩種 conformation—配位在金屬鎢上的甲基與五環上甲醛的位向相同的 cisoid 及位向相反的 transoid conformation. Cisoid **2** 其五環上甲醛基的碳的 θ 角為 1.95° , 然 transoid **2** 其 θ 角為 -0.82° . 經由二維異核相對應 NMR 光譜儀, 化合物 **2** 五環 C(2-5)的 ^{13}C 化學位移得以確認. 文中以 B3LYP correlation–exchange 的理論計算法得出的電子密度分佈情形, 其結果呼應由 ^{13}C NMR 化學位移所得之 Cp(W) 的電子密度分佈.

關鍵字: 鎢, $[\eta^5\text{-環戊二烯}]$ 三羰甲基鎢, 甲醛基, HetCOR NMR, B3LYP