Preparation and Characterisation of Dicarboxylatobis(η-cyclopentadienyl)-tungsten(IV) Complexes: a Novel and Convenient Synthesis from $[W(\eta\text{-}C_5H_5)_2H_2]$ using Molecular Oxygen as a Hydrogen Acceptor

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The reactions of $[W(\eta\text{-}C_5H_5)_2H_2]$ (**1**) with carboxylic acids under various conditions were investigated. At room temperature in the dark, the reaction afforded reversibly $[W(\eta\text{-}C_5H_5)_2H_3]^+$ (**3**), whereas the same reaction under irradiation by light yielded $[W(\eta\text{-}C_5H_5)_2(OCOR)_2]$ (**2**) [R = Me, Et, $CH_2{=}C(Me)$, or H] in small amounts. Addition of 1 equivalent of O_2 to the reaction system significantly improved the yields of (**2**) producing water as a by-product. Complexes (**2**) containing unidentate carboxylate were characterised by i.r. and ^1H n.m.r. spectra and by elemental analyses. The formation of the species $[W(\eta\text{-}C_5H_5)_2(OCOMe)(H_2O)]^+$ was proposed on the basis of the ^1H n.m.r. measurements of (**2**; R = Me) in CD_3CO_2D containing D_2O.

Apart from the carboxylato-bridged binuclear tungsten complexes having metal–metal multiple bonds, the chemistry of which has been extensively studied,[1] only a limited number of mononuclear carboxylato derivatives of organotungsten complexes have been reported.[2–5] The tungsten(IV) dihydride $[W(cp)_2H_2]$ (cp = $\eta\text{-}C_5H_5$) (**1**) is protonated reversibly with strong acids such as aqueous HCl and CF_3CO_2H to give the cationic trihydride $[W(cp)_2H_3]^+$.[6] However, the cation reverted to the starting dihydride on attempted isolation and the preparation of the carboxylato derivative by this route has been found to be unsuccessful.

In an attempt to search for a method of preparation of dicarboxylato complexes $[W(cp)_2(OCOR)_2]$ (**2**) starting from (**1**), the protonation behaviour of the dihydride in carboxylic acid under various conditions was investigated. The results showed that (**2**) was obtainable by irradiating (**1**) in carboxylic acid with a mercury lamp and that molecular oxygen plays a novel role by acting as an efficient hydrogen acceptor in the reaction of (**1**) with carboxylic acid. This paper describes the features of these reactions together with some properties of the resulting carboxylates (**2**). The dicarboxylato complexes $[W(cp)_2(OCOR)_2]$ have been prepared for R = Ph or CF_3 by an indirect method: the reaction between corresponding $Na(O_2CR)$ and $[W(cp)_2Cl_2]$ derived from (**1**) by reaction with $CHCl_3$.[4] A preliminary account of a part of the present study has been published.[7]

Results and Discussion

Addition of yellow crystalline $[W(cp)_2H_2]$ (**1**) to acetic acid at room temperature under N_2 immediately afforded a colourless clear solution indicating the formation of $[W(cp)_2H_3]^+ MeCO_2^-$ (**3**) just as reported in the reaction between (**1**) and HCl and CF_3CO_2H.[6] The ^1H n.m.r. spectrum of (**1**) in acetic acid showed a hydride signal at δ −6.23 as a broad singlet whereas the cp ring protons resonated at δ 5.72 as a sharp singlet. Since in C_6D_6 the hydride signal was observed at δ −12.28 as a sharp singlet (cp protons at δ 4.27 as a singlet), the hydrido ligands in complex (**1**) are considered to undergo proton exchange with solvent acetic acid *via* a cationic intermediate (**3**) according to the equilibrium (1). The fact that the hydride signal appeared as a broad singlet in acetic acid but an A_2B pattern in concentrated HCl[6] suggests that the rate of proton exchange is faster in acetic acid than in HCl.

$$[W(cp)_2H_2] + MeCO_2H \rightleftharpoons [W(cp)_2H_3]^+MeCO_2^- \quad (1)$$

On evaporation of the acetic acid from the colourless solution, the yellow complex (**1**) was recovered quantitatively from the system. Use of $MeCO_2D$ in place of $MeCO_2H$ converted (**1**) into $[W(cp)_2D_2]$ as judged by a comparison of the i.r. spectra: ν(W–H) and δ(W–H) bands at 1 910 and 774 cm^{-1}, respectively, for (**1**) shifted to 1 370 and 600 cm^{-1} for the deuteriated analogue. This observation supports the existence of the reversible protonation of (**1**) in solution shown in equation (1).

Heating the clear solution of complex (**1**) in carboxylic acids such as acetic, propionic, and methacrylic acids at 120—140 °C for 4—8 h yielded only trace amounts of the dicarboxylates $[W(cp)_2(OCOR)_2]$ (**2**), with the principal formation of dark coloured precipitates which may be assigned to bimetallic species, produced *via* an intermolecular participation of the ring carbons in the bonding to the metal.[8] Lack of solubility in the usual solvents prohibited their further characterisation.

When the reactions of (**1**) with carboxylic acids were carried out with irradiation using a high-pressure mercury lamp at room temperature under N_2, the solution slowly became dark purple. Amounts of the dicarboxylates were obtained with propionic, methacrylic, and formic acids, but only a trace amount with acetic acid (Table 1). The accompanying evolution of 1.40 mol H_2 per mol of (**1**) was observed in the reaction with methacrylic acid, which was carried out *in vacuo*.

Since the dihydride (**1**) has been known photochemically to generate the very reactive tungstenocene,[9,10] the formation of the dicarboxylato complexes may well be accounted for by assuming intermediary photochemical formation of the tungstenocene and subsequent oxidative addition of the carboxylic acid [equation (2)]. The hydridocarboxylato intermediate in equation (2) has been isolated for R = Me, Et, or Ph,[9b] and the hydridobenzoato derivative has been reportedly converted into dicarboxylate (**2**) by irradiating the former in a solution containing benzoic acid.[9b] As the trihydride cation (**3**) was found to be inert to irradiation, the dihydride (**1**) which exists

$$[W(cp)_2H_2] \xrightarrow[\downarrow H_2]{h\nu} [W(cp)_2] \xrightarrow{RCO_2H}$$
$$[W(cp)_2H(OCOR)] \xrightarrow[\downarrow H_2]{RCO_2H} [W(cp)_2(OCOR)_2] \quad (2)$$

Table 1. Reactions of $[W(cp)_2H_2]$ (**1**) with carboxylic acids RCO_2H (r.t. = room temperature)

RCO_2H		Amount/mmol				Amount of product/mmol			
R	Amount/mmol	$[W(cp)_2H_2]$	O_2	θ_c/°C	*t*/h	$[W(cp)_2(OCOR)_2]$	H_2	CO_2	H_2O
Me	71	0.54	0	140	8.5	Trace[a]	0	0	0
Me	107	0.73	0	r.t.	42[b]	Trace	*c*	0	0
Me	57	0.45	0.45	r.t.	24	0.39	Trace[d]	0.14	1.02
$MeCH_2$	81	0.51	0	140	3.5	Trace[a]	*e*	0	0
$MeCH_2$	81	0.45	0	r.t.	50[b]	0.09	*c*	0	0
$MeCH_2$	54	0.46	0.46	r.t.	24	0.40	Trace	0.03	0.94
$CH_2{=}C(Me)$	35	0.30	0	120	4.5	Trace[a]	*e*	0	0
$CH_2{=}C(Me)$[f]	1.8	0.60	0	r.t.	50[b]	0.21	0.42	0	0
$CH_2{=}C(Me)$	47	0.44	0.44	r.t.	50	0.29	0.01	0.01	0.92
H	108	0.54	0	100	3.0	0	*e*	0	0
H	108	0.49	0	r.t.	50[b]	0.05	*c*	0	0
H	108	0.45	0.45	r.t.	70	0.20	0.02	0.57	*e*

[a] Mainly decomposition products (see text). [b] Irradiated with a 100-W high-pressure mercury lamp. [c] Quantitatively detected. [d] Gas contained CH_4 [4.5 mol per mol of (**1**)]. [e] Not measured. [f] In Et_2O (18 cm^3).

Table 2. I.r. and ^1H n.m.r. data for $[W(cp)_2(OCOR)_2]$ (**2**)

	I.r.[a]/cm^{-1}		^1H N.m.r.[b]/p.p.m.	
R	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	δ(R)	δ(cp)
Me	1 640vs	1 275vs	2.06 (s 6 H, Me)	5.06 (s, 10 H)
$MeCH_2$	1 625vs	1 238vs	1.18 (t, 6 H, Me) 2.34 (q, 4 H, CH_2)	5.06 (s, 10 H)
$CH_2{=}C(Me)$	1 600vs	1 200s	2.15 (s, 6 H, Me) 5.37 (m, 2 H, =CH *trans* to Me) 6.30 (d, 2 H, =CH *cis* to Me)[c]	5.07 (s, 10 H)
H	1 640vs	1 260vs	7.57 (s, 2 H, H)[d]	5.80 (s, 7 H)[d] 5.88 (s, 3 H)[d]

[a] KBr disc. [b] At 60 MHz, room temperature, in C_6D_6 unless stated otherwise. s = Singlet, t = triplet, q = quartet, and m = multiplet. [c] $^2J(H\text{-}H)_{gem}$ = 2.5 Hz. [d] In D_2O. Two cp resonances (7:3) and one OCOH resonance.

according to the equilibrium (**1**) might have selectively reacted in the present system.

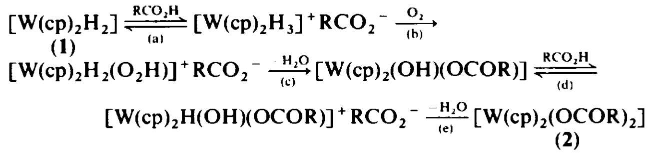
A higher yield of complexes (**2**) was achieved when molecular oxygen (1 equiv.) was introduced to the carboxylic acid solution of (**1**). Addition of O_2 by a syringe to a stirred solution of (**1**) in RCO_2H under vacuum at room temperature immediately resulted in a dark purple colouration and the dicarboxylato complex $[W(cp)_2(OCOR)_2]$ (**2**) was isolated in fairly high yields [equation (3), Table 1]. The reaction was accompanied by the

$$[W(cp)_2H_2] + 2RCO_2H + O_2 \longrightarrow [W(cp)_2(OCOR)_2] + 2H_2O \quad (3)$$

formation of *ca.* 2 equiv. of water and was found not to be affected by the light irradiation. In order to achieve a high yield of (**2**), it is important strictly to regulate the amount of O_2 so that it does not exceed that of the complex, since the product dicarboxylato complex is also somewhat sensitive to oxygen; $[W(cp)_2(OCOMe)_2]$ decomposed slowly in acetic acid in the presence of O_2, evolving CO_2. Furthermore, reaction (3) was accompanied by the formation of a small amount of by-products such as CO_2 and CH_4 (in the case of acetate) as shown in Table 1. A similar oxidative decomposition to give carbon dioxide and the alkyl radical $R^{\bullet}$ has been reported for the iridium(IV) carboxylates, $[IrCl_5(O_2CR)]^{2-}$.[11] Formic acid reacted similarly with (**1**) in the presence of O_2 but rather slowly compared with the other carboxylic acids and 1.27 mol of CO_2 were evolved together with a small amount of H_2 and 44% of $[W(cp)_2(OCOH)_2]$ after 70 h.

Since the starting dihydride is sensitive to dioxygen leading to decomposition, it may be natural to assume that an oxygen molecule interacts initially with the protonated tungsten(VI) species $[W(cp)_2H_3]^+$. This assumption was supported by a blank experiment in which (**1**) with O_2 was allowed to decompose in acetone in the absence of carboxylic acid. The rate of decomposition was much lower than that of the similar reaction in carboxylic acid solution and no water was formed in the former system. The one-electron oxidation of ferrocene by dioxygen in the presence of CF_3CO_2H to give ferrocenium ion has been reported briefly, where the protonated ferrocene was regarded as a key intermediate.[12]

One of the possible mechanisms for the subsequent reaction may be that shown in the Scheme, although an alternative route



$$\underset{(1)}{[W(cp)_2H_2]} \underset{(a)}{\overset{RCO_2H}{\rightleftharpoons}} [W(cp)_2H_3]^+RCO_2^- \xrightarrow[(b)]{O_2} [W(cp)_2H_2(O_2H)]^+RCO_2^- \xrightarrow[(c)]{H_2O} [W(cp)_2(OH)(OCOR)] \underset{(d)}{\overset{RCO_2H}{\rightleftharpoons}} [W(cp)_2H(OH)(OCOR)]^+RCO_2^- \xrightarrow[(e)]{-H_2O} \underset{(2)}{[W(cp)_2(OCOR)_2]}$$

Scheme.

which involves the dihydroxo intermediate $[W(cp)_2H(OH)_2]^+$ cannot be ruled out at the present stage. Insertion of O_2 into a M–H bond to give a hydroperoxo intermediate and its conversion into a hydroxo intermediate has been reported for iridium and rhodium complexes.[13,14] The other possibility that hydrogen peroxide, which might be formed in the system from O_2 and the hydride, may directly attack the complex was excluded by separate experiments in which $[W(cp)_2H_2]$ and $[W(cp)_2H(OCOMe)]$ were allowed to react with H_2O_2 in acetic acid, giving a white uncharacterised decomposition product but

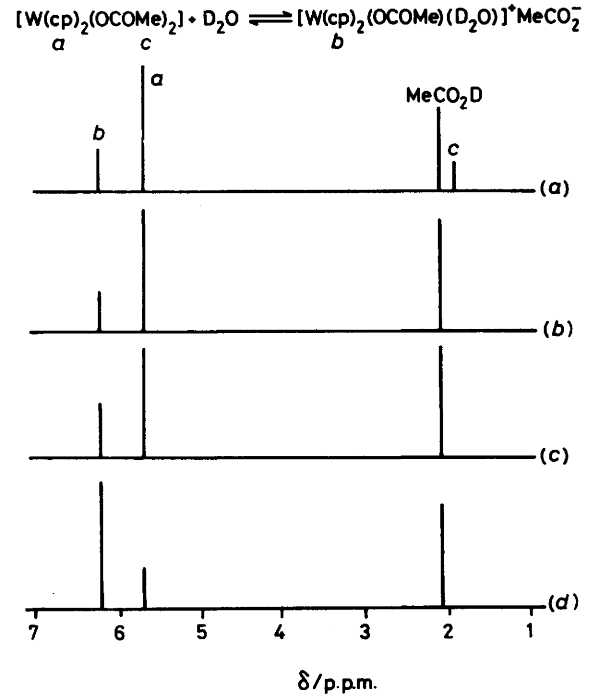


Figure. Proton n.m.r. spectrum of $[W(cp)_2(OCOMe)_2]$ (**2a**) in CD_3CO_2D containing D_2O. Amounts of D_2O added per mol (**2a**): 1.0 (*a*) and (*b*); 2.7 (*c*); and 27.0 mol (*d*). Spectrum (*b*) was recorded 1 h after the measurement of (*a*)

neither $[W(cp)_2(OCOMe)_2]$ nor water. Aleksandrov *et al.*[15] have reported the one-electron oxidation of $[W(cp)_2X_2]$ (X = Cl, Br, or I) with hydrogen peroxide to give $[W(cp)_2X_2]^+ O_2H^- \cdot H_2O_2$.

The purple crystalline dicarboxylato complexes (**2**) are soluble in water, ethanol, acetone, and toluene, except for the diformato complex (**2d**) which is soluble only in water. Their characteristic i.r. and ^1H n.m.r. data are listed in Table 2. Large differences in the bands ascribed to the symmetric and anti-symmetric stretching vibrations of the co-ordinated carboxylate (360—400 cm^{-1}) suggest that the carboxylato ligands are bound in a unidentate manner *via* a single oxygen.[16]

Diacetato complex (**2a**) is very hygroscopic and good crystals were formed only when it was crystallised from water or wet acetone which is not rigorously dried. Judging from the i.r. spectrum of the crystals which differs from that of the water-free powdery sample, especially in that the former has extra bands at 3 400, 1 640, and 1 275 cm^{-1}, we assume that the crystals may contain co-ordinated water and have the formula $[W(cp)_2(OCOMe)(H_2O)]^+MeCO_2^-$ (**4**). Elemental analysis (C, H) of the crystals agreed with this formulation (see Experimental section). On prolonged drying *in vacuo* at 100 °C the crystals turned to a powdery solid, the i.r. spectrum of which was completely the same as that of the water-free sample. The fact that the carboxylato ligand in (**2**) could easily be displaced by other carboxylates (see below) may be accounted for by assuming the reversible formation of (**4**). Formation of the cationic aqua species (**4**) in the solution was further supported by ^1H n.m.r. measurement of (**2a**) in CD_3CO_2D containing an aliquot of D_2O. The spectrum immediately after dissolution [molar ratio D_2O:(**2a**) = 1.0] [Figure (*a*)] consisted of two cp ring-proton resonances at δ 6.21 and 5.70, the former being weaker than the latter, which can be assigned to (**4**) and (**2a**), respectively. The remaining signals observed are one at δ 2.06, assignable to free $MeCO_2D$ which might be formed as a result of the carboxylate exchange between (**2a**) and CD_3CO_2D (see above), and at 1.96 assigned to the methyl protons of the carboxylato ligand in (**2a**) which could be observed only before the equilibrium shown in the Figure was attained. An increase in the ratio D_2O:(**2a**) caused an increase in the relative intensity of the signal at δ 6.21 at the expense of that at δ 5.70 [Figure (*c*) and (*d*)] suggesting a greater contribution of complex (**4**) in the equilibrium at higher concentrations of D_2O. The other dicarboxylato complexes, (**2b**) and (**2c**), were obtained analytically pure through the usual purification procedure, although the formato complex (**2d**) was not pure because of the difficulty in getting rid of traces of water.

The acetato ligand(s) of complex (**2a**) were easily displaced by other carboxylates. Thus, stirring (**2a**) in formic acid at room temperature for 10 min afforded diformato complex (**2d**) quantitatively. More interestingly, the reaction of (**2a**) with a large excess of propionic acid proceeded more slowly to give, after 1 h of the stirring at room temperature, exclusively the mixed carboxylato complex $[W(cp)_2(OCOMe)(OCOEt)]$ (**5**) as judged from its i.r. spectrum [1 640 (sh), 1 630s, 1 425m, 1 360s, 1 290s, and 1 235s cm^{-1}]. Prolonged reaction for 2 d yielded only a small amount of the dipropionate (**2b**). A complex with the same spectrum as (**5**) was obtained by the reaction between (**2b**) and acetic acid under similar conditions. In contrast, the reaction of the diformato complex (**2d**) with an excess of acetic acid only afforded (**2a**) after 50 h. These results suggest not only the possible existence of the cationic aqua species (**4**) but also the significant thermodynamic stability of the mixed carboxylato complex (**5**).

Experimental

Most manipulations were carried out either under dry, oxygen-free nitrogen or argon or *in vacuo* with Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. Infrared spectra were recorded on a JASCO A-202 spectrometer using KBr discs prepared under an inert atmosphere. Nuclear magnetic resonance spectra were measured on a JEOL JNM-PMX-60 spectrometer. G.l.c. was performed on a Shimadzu GC-7APTF or GC-3BT gas chromatograph. Gas evolved during the reaction was measured by a Toepler pump and analysed by g.l.c. using molecular sieve 5A and Unibeads-1S columns. Water in the reaction system was analysed by g.l.c. using a Gaskuropack-54 column (2 m) at 150 °C.

Commercial acetic acid (analytical grade), propionic acid (GR), methacrylic acid (EP), and formic acid (90% aqueous solution, GR) were degassed prior to use and introduced into the reaction flask by a trap-to-trap method. The complex $[W(cp)_2H_2]$ (**1**) was prepared according to the literature method.[17] Irradiation was performed by using a Riko 100-W high-pressure mercury lamp and a Pyrex filter.

Diacetatobis(η-*cyclopentadienyl*)*tungsten*(IV) (**2a**).—The complex $[W(cp)_2H_2]$ (**1**) (0.14 g, 0.45 mmol) was placed in a Schlenk flask fitted with a side arm sealed by a rubber septum. Acetic acid (57 mmol) was added by means of the trap-to-trap method. The mixture was thawed by allowing the temperature to rise from liquid nitrogen temperature, and oxygen (0.45 mmol) was introduced through the rubber septum using a syringe. This caused an immediate change in colour of the solution to dark purple. The system was stirred at room temperature for 24 h. After the reaction, the vapour phase of the system was measured by the Toepler pump and g.l.c. and it was found that 97% of the O_2 originally admitted had been consumed. The remaining acetic acid was removed from the solution by the trap-to-trap method to leave a sticky solid. Triturating the solid in acetone–hexane (1:4 v/v) at room temperature gave a powdery precipitate. After the system had been kept at −40 °C for a while, the precipitate was filtered off, washed three times with hexane at −70°C, and dried *in vacuo*. The brown powder thus obtained was further washed with hot hexane until the washings became colourless in order to remove the unreacted dihydride (**1**). The resulting powder was dissolved in toluene. The solution was filtered and the solvent was evaporated to leave a purple powder of (**2a**) which was found to be spectroscopically pure. Yield 70%. It was not possible to obtain an analytically pure sample of (**2a**) because of the difficulty in removing traces of water. Recrystallisation of the powder from wet acetone or water gave dark brown crystals whose i.r. spectrum differs from that of (**2a**) and which was analysed as $[W(cp)_2(OCOMe)(H_2O)]^+MeCO_2^-$ (**4**) (see text) (Found: C, 36.7; H, 4.30. Calc. for $C_{14}H_{18}O_5W$: C, 37.35; H, 4.05%).

Bis(η-*cyclopentadienyl*)*dipropionatotungsten*(IV) (**2b**).—Essentially the same procedure as for (**2a**) was applied to obtain complex (**2b**). Work-up as above and recrystallisation from acetone yielded deep purple crystals of (**2b**) (Found: C, 41.6; H, 4.70. Calc. for $C_{16}H_{20}O_4W$: C, 41.75; H, 4.40%). Detailed reaction conditions and the yields of the products are listed in Table 1.

Bis(η-*cyclopentadienyl*)*dimethacrylatotungsten*(IV) (**2c**).—Two methods, photochemical reaction and reaction in the presence of O_2, were used to obtain complex (**2c**). Since the latter route is essentially the same as described above, only the former is described below. Detailed reaction conditions and the product yields for both routes are included in Table 1.

Into a Pyrex Schlenk flask containing $[W(cp)_2H_2]$ (**1**) (0.19 g, 0.60 mmol) were placed diethyl ether (18 cm^3) and methacrylic acid (0.15 cm^3, 1.8 mmol) by means of a trap-to-trap method. After being allowed to reach the room temperature, the system was irradiated with the 100-W high-pressure mercury lamp for 50 h with stirring. The evolution of 0.42 mmol of H_2 was observed and the resulting dark purple solution was worked up and recrystallised as described above to give deep purple crystals of (**2c**). Yield 21% (Found: C, 44.1; H, 4.55. Calc. for $C_{18}H_{20}O_4W$: C, 44.65; H, 4.15%).

Bis(η-*cyclopentadienyl*)*diformatotungsten*(IV) (**2d**).—A similar reaction to that described for (**2a**) was applied to prepare complex (**2d**) using aqueous formic acid in place of acetic acid. The reaction conditions and yields are listed in Table 1. It was difficult to obtain analytically pure (**2d**) due to its great tendency to become, possibly, an aqua complex analogous to that, (**4**), postulated for the acetate, which was reflected in its ^1H n.m.r. data (Table 2).

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