A Novel Hydrogen Abstraction from $W(\eta\text{-}C_5H_5)_2H_2$ using Molecular Oxygen: a New Route for the Synthesis of $W(\eta\text{-}C_5H_5)_2(OCOR)_2$

Takashi Ito* and Toshiyuki Nakano

Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

$W(\eta\text{-}C_5H_5)_2(OCOR)_2$ was prepared directly from $W(\eta\text{-}C_5H_5)_2H_2$ by reaction with the carboxylic acid, RCO_2H, in the presence of O_2 and was characterized spectroscopically and chemically.

Although the reversible protonation of Mcp_2H_2 [M = W (**1**), Mo (**2**); cp = $\eta\text{-}C_5H_5$] with CF_3CO_2H or aqueous HCl has been reported to give $[Mcp_2H_3]^+$,[1] little chemistry of the latter has been studied. In the course of an investigation into the protonation behaviour of dihydrides in acetic acid, we found that when molecular oxygen was added to the system it acted as an efficient hydrogen acceptor producing diacetato complexes and water. Apart from the carboxylato-bridged dinuclear tungsten complexes which have a metal–metal quadruple bond,[2] only a limited number of mononuclear carboxylato derivatives of organotungsten have been reported.[3,4] The dicarboxylato complex of type $Wcp_2(OCOR)_2$ (**3**) has so far been prepared for R = Ph and CF_3 by an indirect method from (**1**) *via* Wcp_2Cl_2.[4]

Addition of yellow crystalline Wcp_2H_2 (**1**) to acetic acid at room temperature under N_2 immediately afforded a colourless clear solution indicating the formation of the protonated cation $[Wcp_2H_3]^+MeCO_2^-$ (**4**) as reported for HCl and CF_3CO_2H.[1] In the ^1H n.m.r. spectrum of (**1**) in acetic acid, the hydrido signal, observed at δ −6.23 as a broad singlet, compared with a sharp singlet at δ −12.28 in C_6D_6, indicates proton exchange between solvent acetic acid and the complex *via* a cationic intermediate (**4**). Use of $MeCO_2D$ converted (**1**) into Wcp_2D_2 (ν_{W-D} 1370 cm^{-1}), further confirming the reversible protonation of (**1**) in solution [equation (1)]. On evaporation of the acetic acid from the system, (**1**) was recovered.

$$\underset{(\mathbf{1})}{Wcp_2H_2} + MeCO_2H \rightleftharpoons \underset{(\mathbf{4})}{[Wcp_2H_3]^+MeCO_2^-} \qquad (1)$$

Addition of molecular oxygen (1 equiv.) by syringe to a stirred solution of (**1**) in acetic acid under vacuum at room temperature, immediately resulted in a dark purple colouration and the diacetato complex $Wcp_2(OCOMe)_2$ (**3a**) was isolated in high yield. The reaction was accompanied by the formation of *ca.* 2 equiv. of water. The dipropionato (**3b**) and dimethacrylato (**3c**) complexes were obtained similarly [equation (2), Table 1].

$$\overset{\underset{(\mathbf{2})}{Mocp_2H_2}}{\underset{(\mathbf{1})}{Wcp_2H_2}} + 2RCO_2H \xrightarrow{O_2} \underset{(\mathbf{3})}{Wcp_2(OCOR)_2} + 2H_2O \qquad (2)$$

In order to achieve a high yield of (**3**), it is important 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. This was shown by the evolution of CO_2 [0.31 mol/mol (**1**)] together with CH_4 (0.05) as minor products in reaction (2).† Formic acid (90% aqueous solution) reacted with (**1**) in the presence of O_2 rather slowly compared with the other carboxylic acids and 1.3 mol of CO_2 was evolved together with a small amount of H_2 and 44% of (**3d**) after 70 h.

The purple crystalline dicarboxylato complexes (**3**) are soluble in water, ethanol, acetone, and toluene except the diformato complex (**3d**) which is soluble in water only. They were analysed by i.r. and ^1H n.m.r. spectroscopy and elemental analysis,‡ and were found, on the basis of their i.r. spectra, to possess carboxylato ligands unidentately bonded to the metal *via* a single oxygen.

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† The amounts of gases evolved (H_2, CH_4, and CO_2) were measured by a Toepler pump and analysed by g.l.c.

‡ All compounds have spectral data (i.r. and ^1H n.m.r.) and elemental analyses consistent with the proposed structures.

Table 1. Reaction of Wcp_2H_2 (**1**) with RCO_2H in the presence of O_2.

$[Wcp_2H_2]$/ mmol	$[RCO_2H]$/mmol R		$[O_2]$/ mmol	Time/ h	Products/mmol $Wcp_2(OCOR)_2$		H_2O[a]
0.45	Me	57	0.45	24	(**3a**)	0.39	1.02
0.46	$MeCH_2$	54	0.46	24	(**3b**)	0.40	0.94
0.44	$CH_2{=}C(Me)$	47	0.44	50	(**3c**)	0.29	0.92
0.45	H	108	0.45	70	(**3d**)	0.20	—[b]

[a] Measured by g.l.c. (Gaskuropack 54, 2 m, 150 °C). [b] Not measured.

The molybdenum analogue of (**1**), $Mocp_2H_2$ (**2**) behaved similarly although its reactivity towards carboxylic acids seemed much higher than (**1**). The results for the molybdenum hydride will be reported elsewhere.

Abstraction of the hydridic hydrogen with molecular oxygen has not to our knowledge been found previously, although the O_2-assisted activation of a C–H or an N–H bond in an aromatic ligand co-ordinated to iron has recently been reported.[5,6] Since the starting dihydrides (**1**) and, especially (**2**), are sensitive to dioxygen leading to decomposition, it may be natural to assume that an oxygen molecule interacts initially with the protonated cationic species $[Mcp_2H_3]^+$ to give a hydroperoxo and/or a hydroxo intermediate. Insertion of O_2 into an M–H bond to give a hydroperoxo intermediate followed by deoxygenation with an olefin to give a hydroxo species has been postulated for the ketone synthesis with $IrHCl_2$(cyclo-octa-1,5-diene) and O_2.[7] Furthermore, the conversion of the hydroperoxo complex into the hydroxo intermediate has recently been reported for a rhodium–triphenylphosphine complex.[8]

Dicarboxylato complexes (**3**) were also obtained photochemically,§ although the yields (trace—35%) were considerably lower than those described above. The reaction was accompanied by the evolution of 2 mol of H_2 per mol of dicarboxylato complex, suggesting the intermediate formation of a reactive tungstenocene.[9,10]

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§ Irradiation of (**1**) in RCO_2H with a 100 W high-pressure mercury lamp under N_2.

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