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Reaction studies on some functionalized alkyl transition metal compounds and the crystal structure of $[Cp(CO)_3W\{(CH_2)_3NO_2\}]$

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Abstract

The reactions of the halogenoalkyl compounds $[Cp(CO)_3W\{(CH_2)_nX\}]$ ($Cp = \eta^5\text{-}C_5H_5$; $n = 3–5$; $X = Br, I$) and $[Cp(CO)_2(PPhMe_2)Mo\{(CH_2)_3Br\}]$ with the nucleophiles $Z = CN^-$ and N_3^- gave compounds of the type $[Cp(CO)_3W\{(CH_2)_nZ\}]$ for the tungsten compounds, whilst cyclic carbene compounds were obtained from the reactions of the molybdenum compound. The reactions of $[Cp(CO)_3W\{(CH_2)_nBr\}]$ ($n = 3, 4$) and $[Cp(CO)_2(PPhMe_2)Mo\{(CH_2)_3Br\}]$ with NO_3^- gave $[Cp(CO)_3W\{(CH_2)_nONO_2\}]$ and $[Cp(CO)_2(PPhMe_2)Mo\{(CH_2)_3ONO_2\}]$, respectively. The reaction of $[Cp(CO)_3W\{(CH_2)_nBr\}]$ with $AgNO_2$ gave $[Cp(CO)_3W\{(CH_2)_nNO_2\}]$. In the solid state the complex $[Cp(CO)_3W\{(CH_2)_3NO_2\}]$ crystallizes in a distorted square pyramidal geometry. In this molecule the nitropropyl chain deviates from the ideal, all-*trans* geometry as a result of short, non-hydrogen intermolecular N–O···O–N contacts. The reactions of the heterobimetallic compounds $[Cp(CO)_3W\{(CH_2)_3\}ML_y]$ $\{ML_y = Mo(CO)_3Cp, Mo(CO)_3Cp^*$ and $Mo(CO)_2(PMe_3)Cp$; $Cp^* = \eta^5\text{-}C_5(CH_3)_5\}$ with PPh_3 and CO were found to be totally metalloselective, with the ligand always attacking the metal site predicted by the reactions of the corresponding monometallic analogues above with nucleophiles. Thus the compounds $[Cp(CO)_3W\{(CH_2)_3\}C(O)ML_z]$ $\{ML_z = Mo(CO)_2YCp, Mo(CO)_2YCp^*$ and $Mo(CO)Y(PMe_3)Cp$; $Y = PPh_3$ or $CO\}$ were obtained. Similarly, the reaction of $[Cp(CO)_2Fe\{(CH_2)_3\}Mo(CO)_2(PMe_3)Cp]$ with CO gave only $[Cp(CO)_2Fe\{(CH_2)_3C(O)\}Mo(CO)_2(PMe_3)Cp]$. Hydrolysis of the bimetallic compound, $[Cp(CO)_3W(CH_2)_3C(O)Mo(CO)(PPh_3)(PMe_3)Cp]$, gave the carboxypropyl compound $[Cp(CO)_3W\{(CH_2)_3COOH\}]$. Thermolysis of the compound $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3(PMe_3)Cp]$ gave cyclopropane and propene, indicating that β-elimination and reductive processes had taken place.

Keywords: Halogenoalkyl; Heterobimetallic; Tungsten; Molybdenum; Iron; Tertiary phosphines; Nitropropyl

1. Introduction

When compared to halogenomethyl transition metal compounds, longer-chain halogenoalkyl compounds have been comparatively little studied [1]. Indeed, only those of platinum [2], ruthenium [3], iron [4], tungsten [5,6] and recently molybdenum [6] have been studied in any detail. The application of some of these compounds in organic synthesis has been described [1], but few reaction studies on these compounds have been reported. Importantly, compounds of the type $[L_yM\{(CH_2)_nX\}]$ (L_yM = transition metal and its associated ligands, $n \geqslant 1$, X = halogen) are known precursors of cyclic carbene complexes [1] as well as homo- and heterodinuclear alkanediyl compounds [1,7,8]. Heterobimetallic alkanediyl compounds are proposed to be good precursors or models for catalytic intermediates. It is believed that their study may lead to improved understanding of processes such as the Fischer–Tropsch, olefin polymerization, catalytic oxidation, hydrogenation and hydroformylation reactions, as well as of CO activation [9,10]. With the growing global supply of linear paraffins and the limited supply of traditional industrial feedstocks, the study of the activation of alkanes is also gaining importance [11]. Information on the nature of the chemical activities of heterodinuclear metal functionalized

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paraffins is therefore of interest. Few of these complexes are known and therefore few reaction studies have been carried out on them.

We have previously reported the synthesis of the halogenoalkyl compounds $[Cp(CO)_3W\{(CH_2)_nX\}]$ (Cp = η^5-C_5H_5; $n = 3$–6; X = Br, I) and $[Cp(CO)_2(PPhMe_2)Mo\{(CH_2)_nX\}]$ ($n = 3,4$) [6], and the heterobimetallic alkanediyl compounds $[Cp(CO)_3W\{(CH_2)_3\}ML_y]$ $\{ML_y = Mo(CO)_3Cp$, $Mo(CO)_3Cp^*$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$), $Mo(CO)_2(PMe_3)Cp\}$ [8] and $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ [12], and now report on reaction studies carried out on some of these compounds.

2. Results and discussion

2.1. Reactions of $[Cp(CO)_3W\{(CH_2)_nX\}]$ ($n = 3$–5; X = Br, I)

The compound $[Cp(CO)_3W\{(CH_2)_3Br\}]$ (**1**) was reacted with silver nitrate in acetonitrile at room temperature to give an orange product. Significant effervescence was noted on the addition of the $AgNO_3$ and the analytical data obtained for the product implied a mixture of $[Cp(CO)_3W\{(CH_2)_3ONO_2\}]$ (**1a**) and $[Cp(CO)_3W\{(CH_2)_3NO_2\}]$ (**1b**). Repeating the reaction at 0 °C in the dark with $[Cp(CO)_3W\{(CH_2)_4Br\}]$ (**2**) gave $[Cp(CO)_3W\{(CH_2)_4ONO_2\}]$ (**2a**) only (Eq. (1a)). Apart from the elemental analysis data, the key diagnostic feature was intense IR peaks at 1622 and 1280 cm^{-1}, assignable to the symmetric and asymmetric N=O stretching of a covalent nitrate, respectively [13]. The reaction of $[Cp(CO)_3W\{(CH_2)_4Br\}]$ with $AgNO_2$ at 0 °C in the dark gave the yellow nitrobutyl compound $[Cp(CO)_3W\{(CH_2)_4NO_2\}]$ (**2b**) (Eq. (1b)), according to the elemental analysis data and the absence of a peak in its IR spectrum in the region indicative of an organo-nitrate compound [14]. Both **2a** and **2b** are relatively stable and were fully characterized. In contrast, the reaction of **1** at 0 °C in the dark with $AgNO_3$ and $AgNO_2$, respectively, gave products which were significantly less stable. Thus compound **1a** is pyrophoric in the solid state with even traces of oxygen, whilst **1b** is unstable in solution at room temperature. The difference in the physical properties of functionalized propyl transition metal compounds, when compared to longer alkyl chain compounds, has been postulated to be due to an interaction between the metal and the functional group at the end of the propyl chain [4,6]

$$\underset{\mathbf{1}\ (n{=}3),\ \mathbf{2}\ (n{=}4)}{[Cp(CO)_3W\{(CH_2)_nBr\}]} + AgNO_3 \rightarrow \underset{\mathbf{1a}\ (n{=}3),\ \mathbf{2a}\ (n{=}4)}{[Cp(CO)_3W\{(CH_2)_nONO_2\}]} + AgBr \tag{1a}$$

$$[Cp(CO)_3W\{(CH_2)_nBr\}] + AgNO_2 \rightarrow \underset{\mathbf{1b}\ (n{=}3),\ \mathbf{2b}\ (n{=}4)}{[Cp(CO)_3W\{(CH_2)_nNO_2\}]} + AgBr \tag{1b}$$

The ^1H NMR spectra of **2a** and **2b** showed a significant downfield shift of ca. 1 ppm due to the CH_2NO_2 and CH_2ONO_2 protons versus the CH_2Br protons of the starting material [8]. In the ^{13}C NMR spectra the carbon attached to these protons was very deshielded, and found at 72.9 and 75.0 ppm, respectively, compared to 8.16 ppm for the starting material [8], reflecting the strong electronegativity of the nitro and nitrato groups.

Neither **1**, $[Cp(CO)_3W\{(CH_2)_3I\}]$ (**3**), nor $[Cp(CO)_3W\{(CH_2)_4I\}]$ (**4**) reacted with sodium cyanide or potassium cyanide in acetonitrile. However, the reaction of silver cyanide with compound **3** in acetonitrile gave the compound $[Cp(CO)_3W\{(CH_2)_3CN\}]$ (**3a**) (Eq. (2))

$$\underset{\mathbf{3}}{[Cp(CO)_3W\{(CH_2)_3I\}]} + AgCN \rightarrow \underset{\mathbf{3a}}{[Cp(CO)_3W\{(CH_2)_3CN\}]} + AgI \tag{2}$$

A sharp peak at 2244 cm^{-1}, characteristic of $\nu(CN)$ was observed in the infrared spectrum [13]. The ^1H NMR spectrum showed peaks around 3.10 ppm (CH_2CN) and 1.7 pm (CH_2CH_2CN) in the upfield region (Table 1). The reaction proceeded slowly, as found by monitoring by ^1H NMR spectroscopy over several days (for the disappearance of the CH_2I peak) and did not reach completion. The ^{13}C NMR spectrum showed a peak at 119 ppm, which is attributable to the cyano group [13].

A change of reaction medium had a significant effect on the reaction. Hence, the reaction of AgCN with **3** in an equi-volume mixture of nitrogen saturated water and tetra-

Table 1
IR, yields and ^1H NMR data from the reaction studies of some of the tungsten halogenoalkyl compounds

Compound	IR $\nu(CO)$[a] (cm^{-1})	Yield (%)	Cp[b]	α-CH_2	CH_2L	CH_2CH_2L	β-CH_2	γ-CH_2
$[Cp(CO)_3W\{(CH_2)_3CN\}]$	2012sb, 1914sb	95	5.38s	1.44m	3.10t, 7.2[c]	1.70m		
$[Cp(CO)_3W\{(CH_2)_4CN\}]$	2011sb, 1912sb	92	5.38s	1.46m	3.42t, 7.2	1.84m	1.64m	
$[Cp(CO)_3W\{(CH_2)_3NO_2\}]$	2011sb, 1912sb	97	5.36s	1.49m	4.43t, 6.6	1.71m		
$[Cp(CO)_3W\{(CH_2)_4NO_2\}]$	2011ss, 1912sb	97	5.38s	1.46m	4.38t, 7.1	1.99m	1.62m	
$[Cp(CO)_3W\{(CH_2)_4ONO_2\}]$	2011ss, 1912sb	63	5.38s	1.46m	4.44t, 6.6	1.71m	1.62m	
$[Cp(CO)_3W\{(CH_2)_4N_3\}]$	2011ss, 1912sb	98	5.38s	1.45m	3.42t, 6.7	1.85m	1.67m	
$[Cp(CO)_3W\{(CH_2)_5N_3\}]$	2010ss, 1910sb	95	5.35s	1.51m	3.16t, 6.7	1.82m	1.37m	1.47m

[a] Measured in CH_2Cl_2 sb = strong broad, ss = strong sharp.

[b] ^1H NMR spectra measured in $CDCl_3$ relative to TMS ($\delta = 0.00$ ppm), s = singlet, m = multiplet, t = triplet; α-CH_2 refers to the CH_2-group α to tungsten, etc.

[c] *J* values are given in Hz.