Preliminary communication

# Hydride to carbene migration in the CpMH{=C(OEt)Ph}(CO)$_2$ (M = Mo, W) system and subsequent rearrangement of the consequent products to $\eta^3$-benzyl complexes. X-Ray crystal structure of the $\eta^3$-benzyl CpW(CO)$_2${$\eta^3$-C$_6$H$_5$CH(OEt)}

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## Abstract

Addition of acetic acid to solution of the anions [CpM{=C(OEt)Ph}(CO)$_2$]$^-$ (M = Mo or W) affords the crystallographically characterized (M = W) $\eta^3$-benzyl complexes CpM{$\eta^3$-C$_6$H$_5$CH(OEt)}(CO)$_2$. These reactions involve hydride to carbene migration within the primary products CpMH{=C(OEt)Ph}-(CO)$_2$ to form CpM{$\eta^2$-CH(Ph)OEt}(CO)$_2$, the O–M bond in which is cleaved intramolecularly by the Ph group to give the $\eta^3$-benzyl species.

## Introduction

Migration of hydride to carbene or alkylidene [1] is important in the context of bond formations and in the sense that it is a fundamental process. We have discovered a few isolable complexes L$_n$MH(=CR$^1$R$^2$) which undergo this process [2] but there are many other systems in which the existence of the complex L$_n$MH(=CR$^1$R$^2$) is assumed or inferred rather than observed [1].

Our approach to complexes of the type L$_n$MH(=CR$^1$R$^2$) involves reduction of iodo metal carbenes L$_n$MI(=CR$^1$R$^2$) to form the carbene anions [3] [L$_n$M(=CR$^1$R$^2$)]$^-$ followed by protonation. This approach is successful for the formation of a number of isolable or identifiable hydride complexes such as CpMH{=C(CH$_2$)$_3$NMe}(CO)$_2$ and CpMH{=C(NHEt)Ph}(CO)$_2$ (M = Mo or W) [4,5].

The carbene anions [M{=C(OEt)Ph}(CO)$_2$]$^-$ (**1** and **2**) are available through the reduction of the iodo metal carbene complexes CpMI{=C(OEt)Ph}(CO)$_2$] (**3** and **4**). Addition of acetic acid to the carbene anions **1** or **2** at −78°C followed by warming to ambient temperature results in the unstable new complexes **5** and **6**. These complexes are very sensitive and not isolable. They decompose on chro-
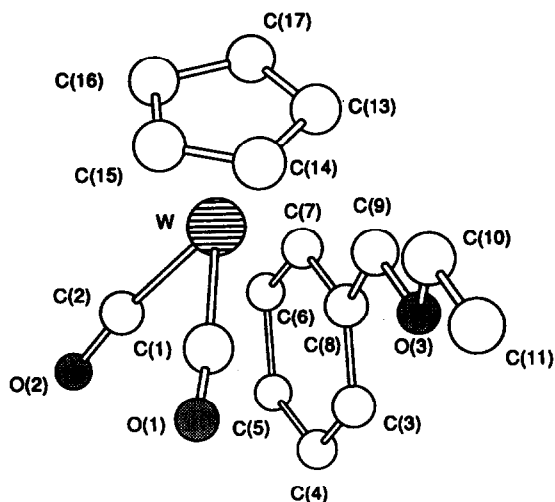
Fig. 1. Molecular structure of CpW{$\eta^3$-C$_6$H$_5$CH(OEt)}(CO)$_2$ (**8**). Selected bond lengths (Å) and angles (°): W(1)–C(1) 1.950(28), W(1)–C(2) 1.949(29), W(1)–C(7) 2.399(19), W(1)–C(8) 2.391(28), W(1)–C(9) 2.212(31), C(1)–W(1)–C(2) 75.2(12), C(7)–C(8)–C(9) 113.3(10), O(3)–C(9)–C(8) 113.1(17).

matography and rearrange (over a few minutes for **5**, 5 h for **6**) at ambient temperature to fluxional $\eta^3$-benzyl complexes **7** and **8** *.

Therefore, **5** and **6** are only partially characterized **. Complex **8** is isolated in 41% yield and, wishing to determine the OEt orientation, is characterized by X-ray crystallography. Its molecular structure is illustrated in Fig. 1 and shown an *endo* configuration. This is similar to the situation in, for instance, CpMo(CO)$_2$($\eta^3$-CH$_2$C$_6$H$_4$Me-$p$) [6]. The attachment of the benzyl is asymmetric with the distance

* **8**: CpW{$\eta^3$-C$_6$H$_5$CH(OEt)}(CO)$_2$. Found: [$M^+$], 440; C, 43.66; H, 3.66. C$_{16}$H$_{16}$WO$_3$ calc. [$M^+$], 440; C, 43.75; H, 3.66. IR $\nu$(CO)(cyclohexane): 1954s, 1939m, 1885s, 1863m cm$^{-1}$. $^1$H NMR [10] $\delta$(250 MHz, toluene-$d_8$, $-40$°C, $J$ in Hz): 7.61 {m, 1H, $J$(HH) [H$^2$ 1.8, H$^3$ 0.9, H$^5$ 8.8, H$^7$ 0.7], H$^6$}; 6.79 {m, 1H, $J$(HH) [H$^2$ 1.0, H$^3$ 8.7, H$^5$ 6.3, H$^6$ 1.2, H$^7$ 0.2], H$^4$}; 6.69 {m, 1H, $J$(HH) [H$^2$ 5.8, H$^4$ 8.7, H$^5$ 1.2, H$^6$ 0.9, H$^7$ < 0.1], H$^3$}; 6.53 {m, 1H, $J$(HH) [H$^2$ 0.4, H$^3$ 1.2, H$^4$ 6.3, H$^6$ 8.8, H$^7$ 0.5], H$^5$}; 4.58 (s, 5H, Cp); 4.03 {m, 1H, $J$(HH) [H$^2$ 0.5, H$^3$ < 0.1, H$^4$ 0.2, H$^5$ 0.5, H$^6$ 0.7], H$^7$}; 3.65 [d of q, 1H, $J$(HH) 8.7, 7.0, OCH$_2$]; 3.35 [d of q, 1H, $J$(HH) 8.7, 7.0, OCH$_2$]; 1.41 [t, 3H, $J$(HH) 7, OCH$_2$Me]; traces of a minor isomer that exchanges with **8** are also detected, 4.27 (s, 5 H, Cp); $^{13}$C NMR $\delta$(62.9 MHz, acetone-$d_6$, $-50$°C): 231.8 (CO), 231.6 (CO), 135.5 (Ph), 127.5 (Ph), 126.9 (Ph), 122.3 (Ph), 98.5 (C1), 90.9 (Cp), 80.2 (C$^2$ or C$^7$), 67.6 (OCH$_2$), 52.1 (C$^2$ or C$^7$), 15.5 (OCH$_2$Me). *Crystal data.* $M = 440.10$; crystallises from Et$_2$O/hexane as red blocks; crystal dimensions 0.25 × 0.15 × 0.15 mm. Orthorhombic, $a = 13.606(27)$, $b = 10.553(10)$, $c = 10.265(15)$ Å, $U = 1474(4)$ Å$^3$; $D_c = 1.983$ g cm$^{-3}$, $Z = 4$, space group $Pna2_1$ ($C_{2v}^9$, No. 33); Mo-$K_\alpha$ radiation ($\bar{\lambda} = 0.71069$ Å), $\mu$(Mo-$K_\alpha$) = 80.09 cm$^{-1}$, $F(000) = 839.75$. X-Ray data (3.5 < $2\theta$ < 50°) were collected on a Nicolet R3 diffractometer by the $\omega$-scan method. The 1176 independent reflections for which $|F|/\sigma(|F|)$ > 3.0 were corrected for Lorentz and polarisation effects, and for absorption. The structure was determined by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Thermal anisotropy was permitted only for tungsten. The final value of $R$ was 0.0587. Unit weights were used throughout the refinement.

** For instance, compound **6**: IR $\nu$(CO) (THF): 1921s, 1821s cm$^{-1}$. $^1$H NMR (on a solution generated photochemically from **8** and still containing **8** $\delta$(250 MHz, C$_6$D$_6$, 20°C): 4.84 (s, 5H, s, Cp); 4.76 (s, 1H, CH); 3.08 (m, 2H, OCH$_2$); 0.68 (t, 3H, $J$(HH) 7, OCH$_2$Me); phenyl signals not assigned due to overlaps with bands of **8**.

to the exocyclic carbon atom being much the shortest. The angle between the plane of the allylic fragment and the cyclopentadienyl ring is 95°. The IR spectra of 7 and 8 show four bands in cyclohexane and NMR measurements suggest that this is a consequence of isomers generated by benzyl rotation. The ratio of *endo* to *exo* isomers of 8 at $-40°C$ in toluene-$d_8$ is 93:7. Some other $\eta^3$-benzyl complexes are known and the NMR [7] and IR [8] spectra of 7 and 8 are related to these.

The context of the chemistry and results from other studies suggests that the primary protonation products of the anions 1 and 2 are the hydrides 9 and 10. These are likely to exist as a mixture of *cis* and *trans* isomers as shown. Neither hydride is detectable at ambient temperature. A fast hydride to carbene migration proceeds to produce 5 and 6 respectively. The phenyl group displaces the ether oxygen–metal linkage to produce the $\eta^3$-benzyl complexes 7 and 8. We see that the complexes 5 and 6 are kinetic products while 7 and 8 are the thermodynamic products.
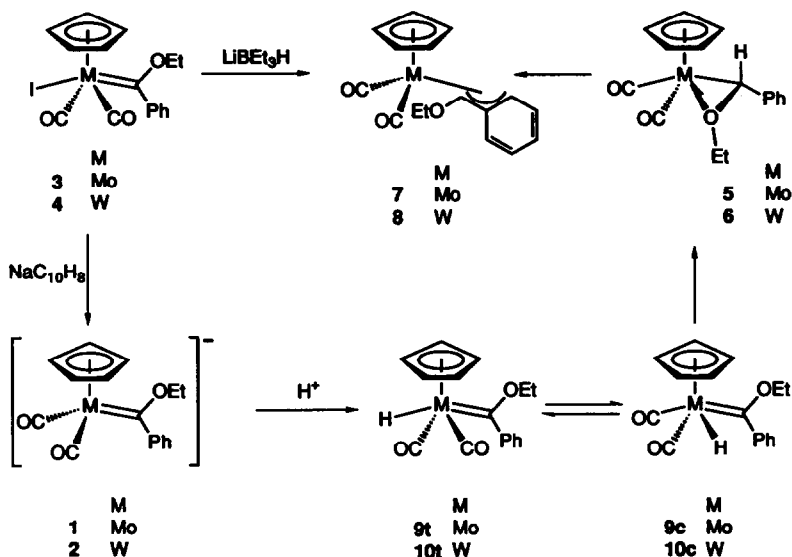


Complexes 7 and 8 are also formed by attack of LiBEt$_3$H on complexes 3 and 4 respectively. In these reactions it is felt that nucleophilic attack directly on the carbene atom and iodide loss leads to 5 and 6, which rearrange to 7 and 8 as above. This parallels the known reaction of CpMoI{=C̅(CH$_2$)$_3$Ȯ}(CO)$_2$ with LiBEt$_3$H which affords the complex CpMo{$\eta^2$-C̅H(CH$_2$)$_3$Ȯ}(CO)$_2$ [9].

Rather surprisingly, the 6 → 8 rearrangement is partially photochemically reversible. Photolysis of THF solutions containing 8 (Hanovia, 125 W mercury) for 15 min gives a solution whose IR spectrum shows bands due to 8 in addition to two bands that correspond exactly with those of 6. This experiment allows acquisition of NMR data for 6. The $^1$H NMR spectrum after photolysis reinforces the identity of this product as 6 **. The signals assigned to 6 diminish in favour of those of 8 over 5 h in both the IR and NMR spectra as the reaction reverses thermally.

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