

Preliminary communication

THERMOLYSIS AND PHOTOLYSIS OF $(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{CH}_2\text{OH}$: A RETRO FISCHER-TROPSCH STEP

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Summary

The new hydroxymethyl osmium complex $(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{CH}_2\text{OH}$ has been prepared and its conversion to $(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{H}$, CO, and H_2 either thermally (half life 3 h at 174°C) or by UV irradiation has been studied. Deuterium labelling experiments established that a methylene hydrogen of the hydroxymethyl ligand becomes the hydride hydrogen of the product, and a mechanism is proposed for this process.

Surface-bound hydroxymethyl and α -hydroxyalkyl groups are plausible intermediates in the hydrogenation of carbon monoxide catalyzed by transition metals [1–3], and there has accordingly been much interest in discrete complexes having CH_2OH or $\text{CH}(\text{R})\text{OH}$ ligands. Very few have actually been characterized: $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ [4–6], $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{NO})(\text{CO})\text{CH}_2\text{OH}$ [5], *cis*-(Ph_3P)₂(OC)₂Os(H)CH₂OH [7], and the cyclic phosphine derivatives (OC)₄MPPPh₂(*o*-C₆H₄CHOH) (M = Mn, Re) [8]. We briefly report here a new hydroxymethyl compound $(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{CH}_2\text{OH}$ (1) with observations on its conversion to the hydride $(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{H}$ (2) [9] which afford some insight into the stability of hydroxymethyl complexes generally.

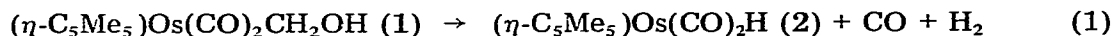
Reduction of $[(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_3][\text{BF}_4]$ [9] (70 mg, 0.14 mmol) with NaBH_4 (11 mg, 0.29 mmol) in THF/ H_2O (10 ml THF and 0.2 ml H_2O) at -30°C for 20 min afforded, after removal of solvent and pentane extraction, 50 mg (86%) of 1 as an air stable colorless solid, m.p. $63\text{--}66^\circ\text{C}$ (dec.). IR ($\nu(\text{CO})$, pentane, cm^{-1}) 1995s, 1932s; ^1H NMR (dimethylsulfoxide-*d*₆, δ) 1.98 (s, 15H), 3.73 (t, *J* 4.88 Hz, 1H), 4.59 (d, *J* 4.88 Hz, 2H). A satisfactory microanalysis was obtained.

When a solution of 1 (2.4×10^{-2} M in THF-*d*₈ or cyclohexane-*d*₁₂) was irradiated* in an NMR tube and the reaction monitored by ^1H NMR, clean for-

*Hanovia 140 Watt medium pressure mercury lamp, Pyrex filtration.

mation of **2** [9] was observed. Conversion was complete in about 4 h, and peak intensities of product **2** ($C_5Me_5/Os-H = 15/1$) indicated that no deuterium from the solvent had been incorporated. The same reaction was carried out using a standard breakseal apparatus, and mass spectrometric analysis of the gaseous products indicated the presence of both CO and H_2 .

The same conversion (eq. 1) may be carried out thermally. When **1** was refluxed in *n*-decane (b.p. $174^\circ C$) for 20 h, **2** was formed in high yield ($>95\%$)

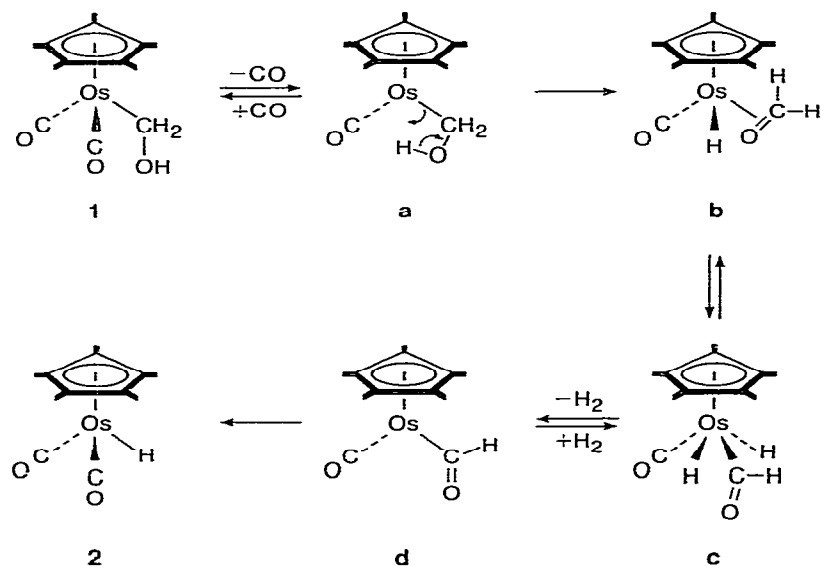


as the only carbonyl containing product. Disappearance of **1** was monitored by IR at this temperature, and a good first order rate plot was obtained for the conversion ($k = 9.0 \times 10^{-5} \text{ sec}^{-1}$, ΔG_{447}^\ddagger 34.8 kcal mole $^{-1}$).

To probe more closely the mechanism of this β -elimination reaction, deuterium labelled derivatives of **1** were prepared and photolyzed. $(\eta-C_5Me_5)Os(CO)_2CD_2OD$ (**3**) was first prepared (in the same manner as **1**, employing 2 mol $NaBD_4$ in $THF-d_8/D_2O$ (100/1) at $-30^\circ C$); when **3** was irradiated in protio-THF, only $(\eta-C_5Me_5)Os(CO)_2D$ formed (1H and 2H NMR monitoring; $\delta(Os-D) -13.997$; $\delta(Os-H) -14.00$ [9]).

Finally, the methylene labelled complex $(\eta-C_5Me_5)Os(CO)_2CD_2OH$ (**4**) was prepared in essentially quantitative yield from **3** by exchange with H_2O (1 h, $25^\circ C$, CH_2Cl_2/H_2O). Irradiation of **4** in $THF-d_8$ afforded 94% $(\eta-C_5Me_5)Os(CO)_2D$ and 6% **2** based on 1H NMR integration. The gaseous products consisted of HD and CO, with small amounts of H_2 and D_2 .

A plausible pathway for the reaction consistent with these facts is shown in Scheme 1. The observed activation free energy of 35 kcal mol $^{-1}$ in the thermal reaction is consistent with loss of a CO ligand to form the 16 electron intermediate **a** as the rate determining step [10]. The conversion of **a** to **b** dif-



SCHEME 1

fers from the β -hydride shift of metal alkyls [11] only insofar as O—H, rather than C—H bond cleavage occurs. Conversion of the η^2 -formaldehyde intermediate **b** to the formyl hydride **c** has precedent in the work of Roper et al. [12]. Reductive elimination of H₂ then forms **d**, which rearranges to the final product **2**.

Scheme 1 requires that the hydrogen bonded to osmium in the product originate in the methylene group of **1**, as shown by the labelling experiment. We attribute the small amount of **2** formed in the irradiation of **4** to reversibility of the steps shown; since the reaction was carried essentially to completion in a sealed NMR tube, some scrambling would occur as initially formed HD was incorporated into **c** and **b**.

The reverse of eq. 1 would be vastly more interesting, although it may not be favorable thermodynamically even at high pressures of CO and H₂. While we term the reaction observed at sub-atmospheric pressure a retro Fischer-Tropsch step, it does provide, in the microscopic reverse, an interesting model system for CO reduction.

It is clear from the foregoing that β -elimination is a favored pathway for decomposition of transition metal hydroxymethyl complexes, as earlier proposed [13]. A key element in their stabilization must be to decrease the ease of ligand dissociation to form a coordinatively unsaturated intermediate analogous to **a**.

Acknowledgment

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