

## Ring-opening Hydroformylation of $\alpha$ -Cyclopropylstyrene by $\text{HMn}(\text{CO})_5$ , and Structure of a Novel $\text{Mn}_2(\text{CO})_9(\eta^1\text{-Aldehyde})$ Complex

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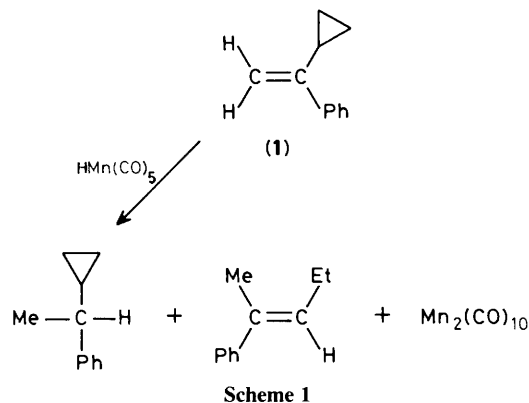
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An  $\eta^1$ -aldehyde complex,  $\text{Mn}_2(\text{CO})_9[\text{Me}(\text{Ph})\text{C}=\text{CHCH}_2\text{CH}_2\text{CHO}]$ , was isolated from the reaction of  $\alpha$ -cyclopropylstyrene with wet  $\text{HMn}(\text{CO})_5$ ; the crystal structure of this unusual compound confirmed the  $\eta^1$  ( $\sigma$ ) bonding of the aldehyde oxygen as an equatorial ligand on  $\text{Mn}_2(\text{CO})_9$ .

Dinuclear elimination reactions constitute the product-forming step in many hydrogenation and hydroformylation reactions. Several studies<sup>1</sup> have revealed details about the mechanisms of formation of aldehydes from reactions of metal alkyls with metal hydrides, but the intermediacy of aldehyde complexes<sup>2</sup> in these reactions has not been previously established. We have found that aldehyde complexes are formed from the reaction of manganese alkyls with

$\text{HMn}(\text{CO})_5$ . This communication reports the synthesis and structure of the first dinuclear  $\eta^1(\sigma)$ -aldehyde complex, which was isolated from an intriguing ring-opening/hydroformylation of  $\alpha$ -cyclopropylstyrene by  $\text{HMn}(\text{CO})_5$ .

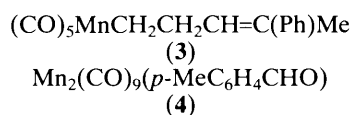
We recently reported that several metal carbonyl hydrides react with  $\alpha$ -cyclopropylstyrene (**1**) to give both ring-opened and unrearranged hydrogenation products.<sup>3</sup> The reaction of (**1**) with excess of dry  $\text{HMn}(\text{CO})_5$  in benzene proceeds



analogously and produces  $\alpha$ -cyclopropylethylbenzene in high yield, along with trace amounts of *E*-2-phenylpent-2-ene (Scheme 1). The second-order kinetics,<sup>†</sup> inverse isotope effect ( $k_{\text{HMn}}/k_{\text{DMn}} \sim 0.4$ ) and insensitivity of the reaction to CO (1 atm) are consistent with a mechanism involving sequential hydrogen atom transfers from  $\text{HMn}(\text{CO})_5$  to the organic substrate.

In contrast, the reaction of *wet*<sup>4</sup>  $\text{HMn}(\text{CO})_5$  with (1) results in an unprecedented ring-opening/hydroformylation, and orange air-sensitive crystals of (2) have been isolated in up to 70% yield (Scheme 2). Spectroscopic data<sup>‡</sup> suggested that (2) was a dimanganese  $\eta^1$ -aldehyde complex. This was confirmed by X-ray diffraction;<sup>§</sup> an ORTEP drawing is shown in Figure 1. The C=O bond length of (2) [1.216(9) Å] is similar to that observed in free aldehydes. This stands in marked contrast to  $\eta^2$ -aldehyde and  $\eta^2$ -ketone complexes, where a substantial lengthening of this bond is generally observed upon co-ordination.<sup>2</sup> While there is some precedent<sup>5</sup> for the  $\eta^1(\sigma)$ -bonding of aldehydes, almost all previously reported aldehyde complexes exhibit  $\eta^2(\pi)$ -bonding. The manganese carbonyls of (2) are staggered, and the aldehyde ligand occupies an equatorial site. The Mn–Mn distance of (2) [2.878(2) Å] is slightly shorter than that reported for  $\text{Mn}_2(\text{CO})_{10}$  [2.9038(6) Å].<sup>6</sup>

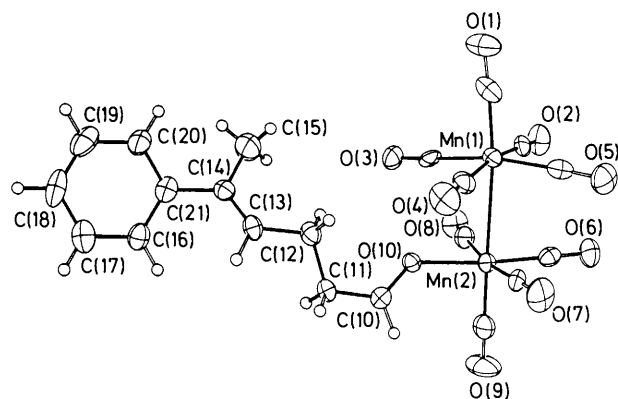
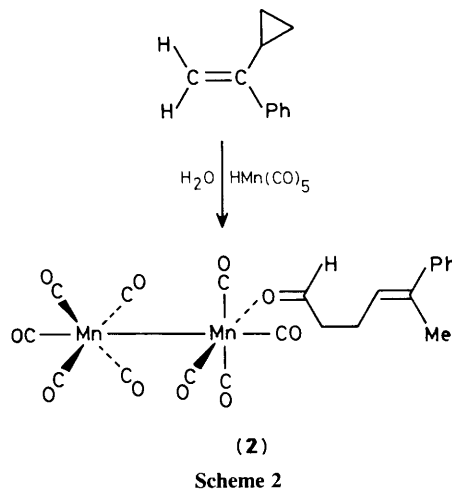
An intermediate observed by <sup>1</sup>H n.m.r. spectroscopy in the synthesis of (2) has been identified as  $(\text{CO})_5\text{MnCH}_2\text{CH}_2\text{CH}=\text{C}(\text{Ph})\text{Me}$  (3). This complex was independently synthesized and shown to react with dry  $\text{HMn}(\text{CO})_5$  to give (2).



<sup>†</sup> Kinetics determined by <sup>1</sup>H n.m.r. spectroscopy at 25 °C.  $-d[(1)]/dt = k[(1)][\text{HMn}(\text{CO})_5]$ ;  $k = 7.4(5) \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

<sup>‡</sup> Selected spectral data associated with aldehyde ligand of (2): <sup>1</sup>H n.m.r. ( $\text{C}_6\text{D}_6$ )  $\delta$  8.47; <sup>13</sup>C n.m.r. ( $\text{CD}_3\text{C}_6\text{D}_5$ ,  $-40^\circ\text{C}$ )  $\delta$  215.7; i.r. (hexane) 1675  $\text{cm}^{-1}$ .

<sup>§</sup> Crystal data for (2):  $\text{C}_{21}\text{H}_{14}\text{Mn}_2\text{O}_{10}$ , monoclinic,  $P2_1/n$ ,  $a = 13.147(5)$ ,  $b = 9.054(3)$ ,  $c = 19.468(6)$  Å,  $\beta = 98.51(2)^\circ$ ,  $U = 2292(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.554 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 11.01 \text{ cm}^{-1}$ . Of 3587 data collected (Nicolet R3M diffractometer,  $T = 293 \text{ K}$ ,  $4^\circ \leq 2\theta \leq 50^\circ$ ), 3169 were independent, and 1813 with  $F_o \geq 3\sigma(F_o)$  were used in refinement. With all non-hydrogen atoms anisotropic, hydrogen atoms idealized isotropic contributions and the phenyl ring constrained to planar, hexagonal geometry:  $R(F) = 6.18\%$ ,  $R_w(F) = 6.22\%$ , GOF = 1.461,  $\Delta(\rho)_{\text{max}} \text{ max} = 0.51 \text{ e \AA}^{-3}$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** Structure of (2). Selected bond distances (Å) and angles (°): Mn(1)–Mn(2) 2.878(2); Mn(2)–O(10) 2.098(5); Mn(2)–C(6) 1.783(9); Mn(2)–C(9) 1.799(10); Mn(2)–C(8) 1.857(9); Mn(2)–C(7) 1.842(10); O(10)–C(10) 1.216(9); C(10)–C(11) 1.473(11); C(11)–C(12) 1.512(12); C(12)–C(13) 1.506(12); C(13)–C(14) 1.309(14); Mn(2)–O(10)–C(10) 130.6(6); O(10)–C(10)–C(11) 123.4(8).

The recognition that (2) was formed in a reaction involving a metal hydride and a metal alkyl suggested a more generalized synthetic route to aldehyde complexes. We have isolated ( $\eta^1$ -tolualdehyde) $\text{Mn}_2(\text{CO})_9$  (4) in 80% yield from the reaction of  $(\text{CO})_5\text{Mn}(p\text{-MeC}_6\text{H}_4)$  with  $\text{HMn}(\text{CO})_5$  in dry hexane at room temperature; toluene was a minor product of this reaction. An analogous reaction between  $\text{MeMn}(\text{CO})_5$  and  $\text{HMn}(\text{CO})_5$  gave  $\text{Mn}_2(\text{CO})_9(\text{MeCHO})$  (92% n.m.r. yield) but this complex is less stable than (4) and has not been isolated in pure form.

Displacement of the weakly bound aldehyde ligand of (4) by CO, MeCN, or  $\text{PPh}_3$  proceeds rapidly ( $<1$  min) at room temperature and produces  $\text{Mn}_2(\text{CO})_9\text{L}$  (L = CO, MeCN,  $\text{PPh}_3$ ) and *p*-tolualdehyde. Metal hydrides can also displace the aldehyde ligand; the new cluster  $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Ru}(\mu\text{-H})\text{Mn}_2(\text{CO})_9$  was isolated from the reaction of  $\text{HRu}(\text{CO})_2(\text{C}_5\text{H}_5)$  with (4). An analogous reaction of  $\text{HRe}(\text{CO})_5$  with (4) produced  $(\text{CO})_5\text{Re}(\mu\text{-H})\text{Mn}_2(\text{CO})_9$ . We suggest that aldehyde complexes similar to (4) may be previously unrecognized intermediates in the hydroformylation of alkenes. However, the facile displacement of the  $\eta^1$ -aldehyde ligand in these manganese complexes suggests that observation of similar cobalt aldehyde complexes would probably be precluded at the temperatures and pressures utilized in catalytic hydroformylations.

While we can account for the formation of (2) from (3), the unusual reaction of (1) with wet  $\text{HMn}(\text{CO})_5$  to give (3) raises a number of mechanistic questions. Further studies are in progress to address these points.

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