

## Bridging Ligands formed by Decarbonylation of Keten and by Decarboxylation of Diketen and Vinylene Carbonate at Triosmium Clusters

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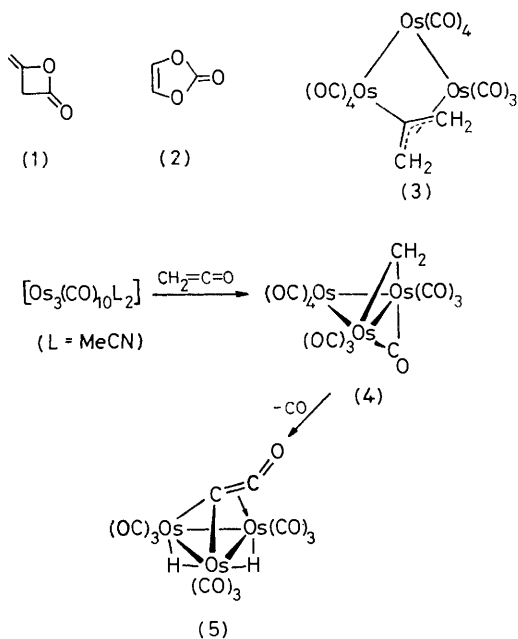
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The compound  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  reacts with keten to give  $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2)]$  by C=C bond cleavage while diketen undergoes decarboxylation to give the  $\mu^2$ -allene compound  $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$  and vinylene carbonate undergoes decarboxylation to give the  $\mu^3$ -formylmethylidene compound  $[\text{Os}_3(\text{CO})_{10}(\text{CHCHO})]$ .

A currently important area of research is the synthesis and reactivity of  $\text{C}_1$  ligands such as C, CH,  $\text{CH}_2$ , CHO, COH, CHOH,  $\text{CH}_2\text{O}$ , and  $\text{CH}_2\text{OH}$  as well as the more familiar  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  ligands. Some or all of these are implicated in Fischer-Tropsch chemistry and in the reduction of CO to give oxy-organics. An even wider range of  $\text{C}_2$  ligands formally or actually formed by coupling of these  $\text{C}_1$  ligands must also be

considered. In attempting to synthesise some of these ligands we have found that keten, diketen (**1**), and vinylene carbonate (**2**) react with the more reactive of triosmium clusters such as  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]^1$  and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]^2$  to give clusters containing fragments of the organic starting materials.

We planned to synthesise the ketendiyl (ketenylidene) compound  $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{C}=\text{O})]$  by oxidative addition of

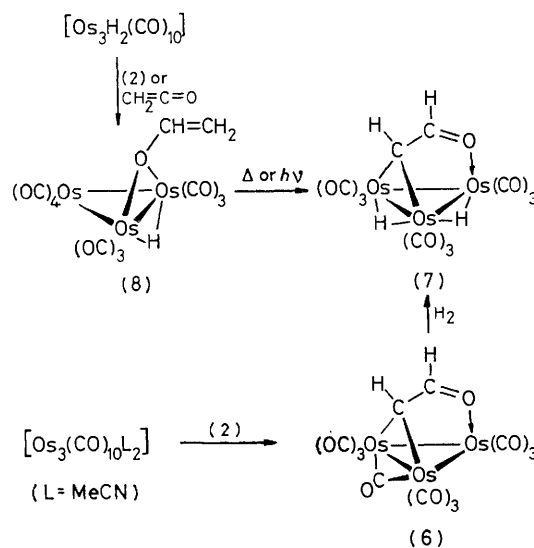


keten at a triosmium cluster as in the formation of  $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{CH}_2)]$  from ethylene.<sup>3</sup> However, allowing  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  to react with keten in dichloromethane at room temperature rapidly gave the red compound  $[\text{Os}_3(\text{CO})_{11}(\text{CH}_2)]$  (4) (49%) and  $[\text{Os}_3(\text{CO})_{11}(\text{C}_3\text{H}_4)]$  (3) (12%).<sup>†</sup> The allene compound (3) is probably derived from allene which is an impurity in keten formed by cracking (1) at 550 °C. Rather than cleaving a C–H bond of keten to give  $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-CH}=\text{C}=\text{O})]$  the C=C bond of keten is broken. Compound (4) was previously prepared by acidifying  $[\text{Os}_3(\text{CO})_{11}(\text{CHO})]^-$  or by treating  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$  with diazomethane.<sup>4,5</sup> Interestingly the keten group which was cleaved in the formation of (4) is reformed on heating (4) in refluxing heptane (2 h) to give (5) in excellent yield (Scheme 1).<sup>6</sup>

At one stage we considered that (3) might have been formed from some diketene (1) that had escaped decomposition in the cracking to keten, but, since  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  does not react with (1) at room temperature, compound (3) is not formed in this way. However, the bis-acetonitrile compound with an excess of (1) in refluxing benzene (3 h) does give compound (3) (18%). This decarboxylation reaction suggested a route to  $\mu^3$ -ligands by decarboxylation of cyclic carbonates. Thus the bis-acetonitrile compound reacts in refluxing dichloromethane (18 h) with an excess of (2) to give the formylmethylidene compound (6)<sup>‡</sup> (65%) (Scheme 2). Compound (6) is closely related to (4), containing a  $\mu$ -CO and a  $\mu$ -alkylidene group, and moreover (4) and (6) are isomeric but these do not interconvert at temperatures lower than those at which they convert into other compounds. While compound (4) readily converts into (5) (Scheme 1), its isomer (6) is much more thermally robust and only at 125 °C (reflux-

<sup>†</sup> Allene reacts with  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$  to give (3); the X-ray structure shows a  $\eta^1, \eta^3$ -bonding mode across the open edge of the metal triangle (J. Lewis, personal communication).

<sup>‡</sup> Compound (6):  $\nu(\text{CO})$  (cyclohexane) 2102w, 2059s, 2020m, 2006w, 1988w, 1863w, and 1500vw  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  10.68 (d) and 3.43 (d) ( $J$  4.0 Hz). Compound (7):  $\nu(\text{CO})$  (cyclohexane) 2112m, 2084s, 2056s, 2027s, 2014ms, 2002s, 1983ms, 1953vw, and 1500s  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\delta$  11.59, (d), 4.39 (d) ( $J$  4.0 Hz),  $-12.55$  (d),  $-14.42$  (d) ( $J$  2.0 Hz).



ing octane) does it slowly convert with associated decomposition into the dihydride (7)<sup>‡</sup> with no indication of any compound (5) being formed. The source of the extra two hydrogen atoms was not established but, since yields of (7) are relatively low (38% after 1.5 h in refluxing octane), all the hydrogen atoms in (7) could have originated from (6). Better yields of (7) (76%) were obtained by allowing (6) to react with  $\text{H}_2$  (1 atm) in refluxing cyclohexane for 45 min. We reported earlier that (7) is formed in extremely low yield on thermolysis of (8),<sup>§</sup> itself formed from  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  and keten.<sup>7</sup> We have since found that the reaction of  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  with (2) is a better route to (8) (70%) (Scheme 2).

Compound (7) has a very similar  $\nu(\text{CO})$  i.r. spectrum to that of the oxocyclohexadienediyl complex  $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}_6\text{H}_4\text{O})]$  formed from phenol<sup>8</sup> and by analogy the structures of (7) and also (6) are drawn as shown. The X-ray structure of (6) will be determined shortly.

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<sup>§</sup> Compound (7) by this route was reported as a mixture of isomers,<sup>8</sup> but since only a few mg were obtained the analysis of the weak  $^1\text{H}$  n.m.r. spectra is doubtful. Only a single isomer of (7) was obtained from (6) or from u.v. photolysis of (8).