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Preliminary communication

Unexpected formation of hydrido-hydroxy derivatives as direct products in the reactions of the unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L\text{–}L)]$ $(L\text{–}L = Ph_2PCH_2PPh_2, (EtO)_2POP(OEt)_2)$ with carbon dioxide

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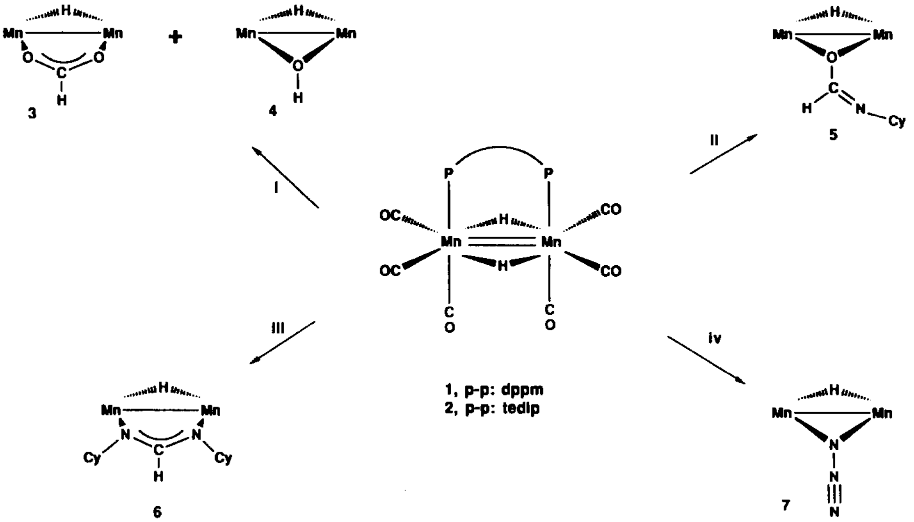
Abstract

The unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = $Ph_2PCH_2PPh_2$, dppm, **1**; $(EtO)_2POP(OEt)_2$, tedip, **2**) react with carbon dioxide (at 50 atm) or with formic acid to yield not only the expected hydridoformate complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}O_2CH)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **3a**; tedip, **3b**) but also the hydridohydroxo-derivatives $[Mn_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **4a**; tedip, **4b**). The complexes **4** do not seem to arise from decomposition of **3** or to be products of the reaction of **1** and **2** with water. The hydrides **1** and **2** also react under mild conditions with several heterocumulenes (cyclohexylisocyanate, dicyclohexylcarbodiimide and trimethylsilylazide) to afford $[Mn_2(\mu\text{-}H)(\mu\text{-}OC(H)\text{=}NCy)(CO)_6(\mu\text{-tedip})]$ (**5**), $[Mn_2(\mu\text{-}H)(\mu\text{-}CyNC(H)NCy)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **6a**; tedip, **6b**) and $[Mn_2(\mu\text{-}H)(\mu\text{-}N_3)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **7a**: tedip, **7b**), respectively.

There is current interest in the interaction of small molecules and metal clusters. For instance, the reactivity of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ towards small unsaturated organic molecules have been thoroughly investigated [1]. We have found that the unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (**1**) and $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})]$ (**2**) also react with a range of small molecules [2]. We report now the preliminary results of the reactions of **1** and **2** with carbon dioxide, formic acid, and several heterocumulenes.

At atmospheric pressure the complexes **1** and **2** are inert towards carbon dioxide, but at 50 atm they react at room temperature with CO_2 to give a mixture of two complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}O_2CH)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **3a**; tedip, **3b**) and $[Mn_2(\mu\text{-}H)(\mu\text{-}OH)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **4a**; tedip, **4b**) (i in Scheme 1) roughly in a 2:1 ratio. The same products, in the same proportion, are obtained treating **1** and **2** with an aqueous solution of formic acid, as shown by the $^{31}P\{^1H\}$ NMR spectra of the final reaction mixtures. All attempts made to separate **3** and **4** by fractional crystallization failed. However when the mixture was chromatographed on an alumina column (activity IV) only the hydridohydroxo-



Scheme 1. (i) CO_2, 50 atm., toluene, r.t., 4 days or HCOOH, toluene, r.t. 90 m. (ii) CyNCO, toluene, r.t., 24 h. (iii) CyNCNCy, t.h.f., r.t., 2 h. (iv) Me_3SiN_3, toluene, r.t. 10 h.

complex **4** could be eluted. Complexes **3**, which could not be isolated, apparently decompose into **4** on the column, as **4** were obtained by yields higher than 50%.

Complexes **3** and **4** have been characterized spectroscopically [3], the presence of the formate ligand in **3** being identified mainly by the ^{13}C NMR resonances at 178 ppm, $J(HC) = 210$ Hz, and the IR, $\nu(CO_2)$ absorptions of the bridging *O,O'*-bonded carboxylate at ca. 1568 and 1430 cm^{-1} [3]. The structure of complexes **3** is further supported by the X-ray determination of the structure of the related $[Mn_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(CO)_6(\mu\text{-dppm})]$ [4], which also possesses an *O,O'*-bonded carboxylate bridge, and of which the $^{31}P\{^1H\}$ NMR spectrum exhibits a single peak at 56.5 ppm, very close to the $^{31}P\{^1H\}$ NMR resonance at 55.3 ppm of complex **3a**.

Although **3a,b** decompose into **4a,b** in the chromatography column, (probably a consequence of the alumina), **3** do not transform into **4** in solution. Monitoring the reaction of **1** with CO_2 by ^{31}P NMR spectroscopy indicates that the **3**/**4** ratio is roughly the same throughout the reaction. Moreover, proportion of **3** to **4** in the mixture was not altered for 3 days by the addition of water or by bubbling N_2. Incidentally, the compounds **4a,b** do not react with formic acid to generate **3a,b**. On the other hand, the complexes **4** do not seem to arise from a direct reaction of **1** and **2** with water, as the unsaturated manganese dihydrocomplexes do not react with H_2O at room temperature. The formation of **4** as a direct product of the reaction of **1** and **2** with CO_2 (or with formic acid) and not as a result of the decomposition of **3** is particularly significant as hydridohydroxo-complexes have been proposed to be intermediates in the decomposition of mononuclear metalloformates into metal carbonyl derivatives [5].

The reaction of **1** and **2** with carbon dioxide is also interesting, because no reaction of an unsaturated dihydrocomplex with CO_2 has yet been reported. Furthermore, the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with CF_3COOH does not give any bridging carboxylate derivative, but complexes containing monodentate trifluoroacetate and three hydrido-ligands [6]. This retention of hydride seems to suggest that the hydrido ligands in **1** or **2** are more prone to be loss than they are in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which may depend on the weakness of the Mn–H bond.

At room temperature, **2** reacts in the dark with cyclohexylisocyanate (ii in Scheme 1), and **1** and **2** react with dicyclohexylcarbodiimide (iii in Scheme 1), to give the insertion products $[Mn_2(\mu\text{-}H)\{\mu\text{-}OC(H){=}NCy\}(CO)_6(\mu\text{-tedip})]$ (**5**) and $[Mn_2(\mu\text{-}H)\{\mu\text{-}CyNC(H)NCy\}(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **6a**; tedip, **6b**), respectively. Treatment of **1** with OCNCy in the dark gives a complex mixture, in which $[Mn_2(CO)_8(\mu\text{-dppm})]$, $[Mn_2(CO)_6(\mu\text{-dppm})_2]$, and $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$ have been identified. The structures of **5** and **6** are supported by their spectroscopic data [3], primarily by the $^{13}C\{^1H\}$ NMR resonances at 174.9 (**5**), 168.6 (**6a**) and 170.8 ppm (**6b**), assigned to carbon nuclei joined to a single H atom. For compound **5** the pattern of the IR $\nu(CO)$ absorptions precludes an *N*,*O*-bonded N-cyclohexylformamido-bridge.

At room temperature **1** and **2** react with trimethylsilylazide to yield the hydrido-azido-complexes $[Mn_2(\mu\text{-}H)\{\mu\text{-}N_3\}(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm, **7a**; tedip, **7b**) (iv in Scheme 1), which have been characterized spectroscopically [3]. Since we were not able to obtain suitable single crystals for an X-ray diffraction study, the dispositions of the azide ligand in complexes **7** remain unclear. However, the IR absorption at 2080 cm^{-1} suggests that N_3 should be linear and bridging as shown in Scheme 1.

The formation of complexes **5**–**7** is somewhat surprising, as the reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with isocyanates, carbodiimides, or azides lead to other type of products [1]. This seems to confirm that the unsaturated dihydrides **1** and **2** possess their own particular reactivity pattern, different from that observed in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ [2].

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3 All compounds (except **3a** and **3b**, which were not isolated) gave satisfactory microanalyses (C, H, N). Selected spectroscopic data for the new compounds. **3a**: $\nu(CO)$ (toluene): 2041s, 2015s, 1959m, 1944m and 1923vs; $\nu(CO_2)$ (KBr): 1565m, 1440m cm^{-1}. ^1H NMR ($CDCl_3$, δ in ppm, J in Hz, 22 °C). $\delta(Mn_2(\mu\text{-}H))$: −16.3 (t, $J(PH) = 27$, 1H). $^{31}P\{^1H\}$ NMR. $\delta(Mn\text{–}P)$: 55.3 (s, 2P). ^{13}C NMR. $\delta(OC(H)O)$: 178.3 (d; $J(CH) = 210$, 1C). **3b**: $\nu(CO)$ (toluene): 2060s, 2030s, 1960s, 1955m and 1927vs; $\nu(CO_2)$ (KBr): 1570m, 1422m cm^{-1}. ^1H NMR. $\delta(Mn_2(\mu\text{-}H))$: −18.3 (t, $J(PH) = 33$, 1H). $^{31}P\{^1H\}$ NMR. $\delta(Mn\text{–}P)$: 163.9 (s, 2P). ^{13}C NMR. $\delta(OC(H)O)$: 178.8 (d, $J(CH) = 210$, 1C). **4a**: $\nu(OH)$ (KBr): 3582s; $\nu(CO)$ (toluene): 2028s, 1998s, 1940m and 1911vs cm^{-1}. ^1H NMR. $\delta(Mn_2(\mu\text{-}OH))$: −1.4 (t, $J(PH) = 6$, 1H), $\delta(Mn_2(\mu\text{-}H))$: −10.9 (t, $J(PH) = 21$, 1H). $^{31}P\{^1H\}$ NMR, $\delta(Mn\text{–}P)$: 47.2 (s, 2P). **4b**: $\nu(OH)$ (KBr): 3570s; $\nu(CO)$ (toluene): 2050s, 2020s, 1962s, 1945s and 1930vs cm^{-1}. ^1H NMR. $\delta(Mn_2(\mu\text{-}OH))$: −2.2 (br, 1H), $\delta(Mn_2(\mu\text{-}H))$: −12.3 (t, $J(PH) = 31$, 1H). $^{31}P\{^1H\}$ NMR. $\delta(Mn\text{–}P)$: 159.7 (s, 2P). **5**: $\nu(CO)$ (toluene): 2051s, 2023s, 1956s, 1930s and 1918vs; $\nu(N{=}C)$ (toluene): 1708m cm^{-1}. ^1H NMR. $\delta(Mn_2(\mu\text{-}H))$: −19.7 (t, $J(PH) = 32$, 1H). $^{31}P\{^1H\}$ NMR. $\delta(Mn\text{–}P)$: 165.7 (s, 2P). $^{13}C\{^1H\}$ NMR (using standard DEPT experiments). $\delta(OC(H){=}N)$: 174.9 (s, 1C). **6a**: $\nu(CO)$ (THF): 2024vs, 1994m, 1940s, 1922m and 1904m cm^{-1}. ^1H NMR. $\delta(Mn_2(\mu\text{-}H))$: −17.9 (t, $J(PH) = 35$, 1H).

^{31}P{^{1}H} NMR. δ(Mn–P): 53.2 (s, 2P). ^{13}C{^{1}H} NMR (using standard DEPT experiments): δ(NC(H)N): 168.6 (s, 1C). **6b**: ν(CO) (THF): 2045s, 2015s, 1951vs, 1940s and 1912vs cm^{-1}. ^{1}H NMR. δ(Mn$_2$(μ-H)): -21.1 (t, J(PH) = 35, 1H). ^{31}P{^{1}H} NMR. δ(Mn–P): 166.1 (s, 2P). ^{13}C{^{1}H} NMR (using standard DEPT experiments). δ(NC(H)N): 170.8 (s, 1C). **7a**: ν(N$_3$) (toluene): 2082; ν(CO) (toluene): 2030s, 2010s, 1957s, 1938sh and 1924vs cm^{-1}. ^{1}H NMR. δ(Mn$_2$(μ-H)): -13.3 (t, J(PH) = 17, 1H). ^{31}P{^{1}H} NMR. δ(Mn–P): 48.9 (s, 2P). **7b**: ν(N$_3$) (toluene): 2082; ν(CO) (toluene): 2050s, 2030s, 1970s, 1950m and 1928vs cm^{-1}. ^{1}H NMR. δ(Mn$_2$(μ-H)): -14.8 (t, J(PH) = 17, 1H). ^{31}P{^{1}H} NMR: δ(Mn–P): 160.0 (s, 2P).

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