

# Dinuclear Derivatives of $\text{Mn}_2(\text{CO})_{10}$ with the Ligand Tri(1-cyclohepta-2,4,6-trienyl)phosphane, $\text{P}(\text{C}_7\text{H}_7)_3$ , and their Oxidative Cleavage

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The photo-induced reaction of  $\text{Mn}_2(\text{CO})_{10}$  with the olefinic phosphane  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**; [P] if coordinated to a metal) leads stepwise to the axially substituted derivatives  $ax\text{-}\{\text{Mn}_2(\text{CO})_9[\text{P}]\}$  (**2**) and  $ax,ax\text{-}\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$  (**3**). Oxidative cleavage of **3** by halogens gives  $cis\text{-}\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}]\}$  ( $\text{X} = \text{Cl}$  (**4a**),  $\text{Br}$  (**4b**),  $\text{I}$  (**4c**)), whereas oxidation of **3** with  $\text{NOBF}_4$  provides a route to the salt  $\{\text{Mn}(\text{CO})_4[\text{P}]\}\text{BF}_4$  (**5**) which is also accessible by halide abstraction from **4b** by  $\text{AgBF}_4$ . The reactivity of the bromo complex **4b** has been studied, and analogues such as  $cis\text{-}\{\text{Mn}(\text{R})(\text{CO})_4[\text{P}]\}$  ( $\text{R} = \text{Me}$  (**4d**),  $\text{Fc}$  (**4e**) and  $\text{N}(\text{tPr})_2$  (**4f**)) have been prepared. The displacement of a carbonyl ligand from **4b** by iodide leads to  $mer\text{-}\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}]\}$  (**6c**) and by **1** to  $mer,trans\text{-}\{\text{Mn}(\text{Br})(\text{CO})_3[\text{P}]_2\}$  (**7b**). The complexes  $mer\text{-}\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]\}$  (**6a-c**) are obtained by splitting the dimers,  $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\mu\text{-X})_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), with  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**). The cation in **5** and the halogeno compounds **6a-c** contain [P] (**1**) as a chelating four-electron ligand which uses one cyclohepta-2,4,6-trienyl substituent for  $\pi$ -complexation. The coordinated double bond in **6c** can be displaced by phosphites  $\text{P}(\text{OR})_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) to give  $fac\text{-}\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{OR})_3]\}$  (**8c**).

The structures of the new complexes **2-8** have been assigned on the basis of their carbonyl stretching absorption patterns in the IR spectra and by their NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ). Single-crystal X-ray structure analyses have been carried out for **3** and **6c**.

**Key words:** Manganese, Olefinic Phosphanes, Carbonyl-manganese Complexes