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NEW SYNTHETIC APPROACHES TO $Mn_2(CO)_{10-n}L_n$ DERIVATIVES (L = PHOSPHINES): THEIR CATALYTIC ACTIVITY IN THE HOMOGENEOUS HYDROGENATION OF DIPHENYLACETYLENE AND THE CRYSTAL STRUCTURE OF $Mn_2(CO)_9(PPh_2H)$

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Abstract—Novel $Mn_2(CO)_{10-n}L_n$ complexes have been investigated as hydrogenation catalysts and a representative member has been structurally characterized.

We are investigating the behaviour of carbonyl clusters, and in particular that of phosphine-substituted and phosphido-bridged derivatives as homogeneous hydrogenation catalysis.[1] We have studied the behaviour of $Mn_2(CO)_{10}$ (**1**), $Mn_2(CO)_9(PPh_2H)$ (**2**), $Mn_2(\mu\text{-H})(\mu\text{-PPhH})(CO)_8$ (**3**), $Mn_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)$ (**4**) and $Mn_2(\mu\text{-PPh}_2)_2(CO)_8$ (**5**) in the hydrogenation of diphenylacetylene.

Phosphine-substituted dimanganese derivatives are generally obtained by thermal or photochemical activation of the CO's, generally in non-selective processes; indeed it is believed that Mn—Mn bond cleavage occurs and that the phosphine-substituted fragments recombine in a random fashion.[3]

We have attempted the synthesis of $Mn_2(CO)_{10-n}L_n$ derivatives by labilization of CO's with Me_3NO[4] in relatively mild conditions (L = PPh_3, PPh_2H, $PPh_2CH{=}CH_2$, $PPh_2PC{\equiv}CPPh_2$). Heating $Mn_2(CO)_{10}$ with a 1–5 molar excess of ligand in hexane or heptane, in the presence of dry Me_3NO for 2 min, leads to mixtures containing 30–40% of $Mn_2(CO)_9L$, about 5–10% of $Mn_2(CO)_8L_2$ (one or two isomers) and about 50% of unreacted carbonyl (which was re-used).

The complexes were identified by spectroscopy and, in particular, by ^{31}P NMR; for **2** a sharp singlet at δ 51.12 was observed. However, for the other monosubstituted complexes sharp singlets centred at δ 50–60 and a broad peak at δ 20–30 was found (but for PPh_3, a sharp singlet at δ 29.52, a broad peak at δ 74.62 ppm). This should indicate

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Table 1

Complex	Reaction time[a]	Conversion[a]	Selectivity to:		
			cis-stilbene	*trans*-stilbene	*trans–cis* ratio[b]
1	1–27	5.0–12.5	24.0–22.4	76.0–77.6	3.2–3.5
2	1–48	5.1–11.9	15.7–21.0	84.3–79.0	5.4–3.8
3	1–76	14.2–21.3	28.9–27.2	71.1–72.8	2.5–2.7
4[c]	48	50.4	20.2	79.8	3.9
5	1–48	5.8–15.4	25.9–27.3	74.1–72.7	2.9–2.7

[a] Minimum and maximum value; 1 atm H_2.
[b] Initial and final value.
[c] Under 34 atm pressure of H_2.

that mostly equatorial, monosubstituted complexes are obtained.

Thus, apparently, the use of Me_3NO gives, in most cases, stereospecific substitution of one equatorial CO, a statistically favoured process. In order to confirm the structure of **2**, a suitable crystal of **2** was selected for an X-ray diffraction study. Crystal data: $C_{21}H_{11}Mn_2O_9P$, $M = 548.16$, monoclinic space group $C2/c$, $a = 24.038(8)$, $b = 14.645(6)$, $c = 16.328(6)$ Å, $\beta = 125.58(2)°$, $Z = 8$, $d_{calc} = 1.559$ g cm^{-3}, μ(Mo-K_α) $= 11.50$ cm^{-1}. Of 4409 reflections collected on an Enraf–Nonius CAD-4 diffractometer (Mo-K_α) ($3 < \theta < 24°$), 1548, having $I > 2\sigma(I)$, were used in the refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were clearly located and refined isotropically. Final R and R_w values were 0.0363 and 0.0436, respectively. Atomic coordinates have been deposited with the Director, Cambridge Crystallographic Data Centre. The structure of **2** is shown in Fig. 1. The Mn—Mn distance of 2.910(2) Å, is practically identical to that found in $Mn_2(CO)_{10}$.[5]

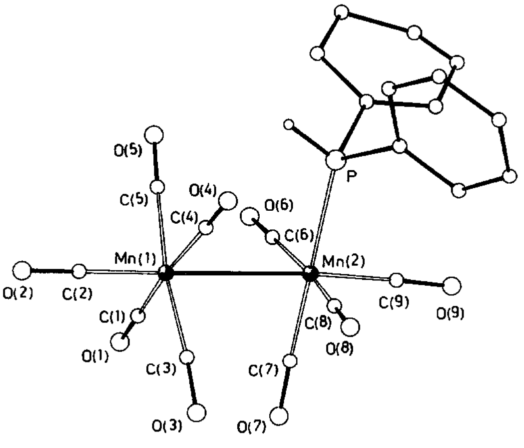

Fig. 1. View of the molecular structure of $Mn_2(CO)_9(PPh_2H)$.

Monosubstituted derivatives, characterized as axial, were obtained with PPh_3, PBu_3, $P(OPh)_3$, $AsPh_3$, $PPhMe_2$ (X-ray structure),[6] $AsPhMe_2$, PPh_2Me and PF_3; only with PH_3 was an equatorial derivative observed.[7] A few X-ray structures for axial,[6] diaxial[8] and diequatorial[8] complexes have been reported; thus **2** is the first confirmed example of equatorial substitution.

Some preliminary results in homogeneous hydrogenation of diphenylacetylene are given in Table 1.

Worthy of note are the high *trans–cis* stilbene ratios observed; identification of the organometallic species in the hydrogenation solutions is in progress in order to gain better insight into the reaction mechanisms.

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