# The production of the species HMn(CO)₃(ligand)₂ from dimanganese decacarbonyl and triphenylphosphine or triphenyl phosphite

The reaction of $Mn_2(CO)_{10}$ with group V ligands, such as tertiary phosphines and phosphites, is known[1,2] to yield substitution products, where the CO/Mn ratio is 4 or 4.5. It is also known[3] that the use of a suitable ligand, such as $(Ph_2PCH_2)_2L'$, together with different reaction conditions, afforded compounds with lower CO/Mn ratio than before, *e.g.* paramagnetic $Mn(CO)_3L'$ or paramagnetic $Mn(CO)L'_2$. Since the latter compounds were found[4] to be reactive towards tin(II) chloride, we attempted the synthesis of similar compounds, such as $[Mn(CO)_3L_2]_n$ $[L = Ph_3P$ or $(PhO)_3P;$ $n = 1$ or 2].

A xylene solution of manganese carbonyl and of the appropriate ligand L was refluxed under nitrogen for 80 h, affording a good yield of substituted manganese carbonyl derivative. When the ligand was triphenylarsine, the product was $[Mn(CO)_4-(Ph_3As)]_n$ with a magnetic moment of 0.5–1.1 B.M. (according to different preparations)[1]. However, when either triphenylphosphine or triphenyl phosphite were reacted using the same conditions, $HMn(CO)_3(Ph_3P)_2$ and $HMn(CO)_3[(PhO)_3P]_2$, respectively, was the product*. This formulation is in agreement with analyses, osmometric molecular weights determinations (Table 1), infrared and ¹H NMR spectra (Tables 2 and 3), diamagnetism in the solid state in solution, and also with the chemical behavior.

TABLE 1

COMPOUNDS OBTAINED

| | Compound | Color and m.p. | $C^a$ | $H^a$ | $P^a$ | Mol.wt.$^a$ | Purification |
|---|---|---|---|---|---|---|---|
| (I) | $HMn(CO)_3(Ph_3P)_2{}^c$ | cream-white 237–9°(dec.) | 70.44 70.50 | 4.52 4.05 | 9.35 8.98 | 671$^b$ 664 | benzene pet. ether |
| (II) | $HMn(CO)_3[(PhO)_3P]_2$ | white 87–88°(dec.) | 61.21 61.66 | 4.12 4.08 | 8.21 8.16 | 810$^b$ 760 | EtOH |
| (III) | *trans*-$[BrMn(CO)_3(Ph_3P)_2]$ | yellow 186–8° | 62.66 62.98 | 4.06 4.03 | | | benzene pet. ether |
| (IV) | *trans*-$\{BrMn(CO)_3[(PhO)_3P]_2\}$ | yellow 154–7° | 55.70 55.78 | 3.46 3.57 | | | $C_6H_6$/EtOH pet. ether |
| (V) | *trans*-$[IMn(CO)_3(Ph_3P)_2]$ | orange 157–9° | 58.60 59.20 | 3.61 3.79 | | | benzene pet. ether |
| (VI) | *trans*-$\{IMn(CO)_3[(PhO)_3P]\}$ | orange 147–9°$^d$ | 52.30 52.80 | 3.78 3.40 | | | $C_6H_6$/EtOH pet. ether |

$^a$ Found/calculated. $^b$ Osmometry in benzene; similar results at different concentrations. $^c$ Manganese: found 8.29, calcd. 7.91%. $^d$ lit.[8] 152°.

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* In the absence of the NMR data cited above, we had previously proposed[5] that these complexes should be formulated $[Mn(CO)_3L_2]_2$.

The compounds reacted with iodine or bromine in $CCl_4$ or $CHCl_3$, yielding hydrogen halide and $XMn(CO)_3L_2$[6] (Table 1), to which a structure with two *trans* P ligands was assigned on the basis[7] of the IR spectrum (Table 2). The compounds

TABLE 2

INFRARED DATA[a]

| Compound | | | | | |
|---|---|---|---|---|---|
| (I) | (nujol) | 1912 s | 1898 s, | 1827 vw | |
| | (CH₂Cl₂) | 1919 s | | | |
| (II) | (nujol) | 2100 w, | 1964 s, | 1942 vs, | 1914 sh |
| | (CH₂Cl₂) | 2090 w, | 1963 s | | |
| (III) | (CH₂Cl₂) | 2035 w, | 1955 vs, | 1919 s | |
| (IV) | (CH₂Cl₂) | 2058 w, | 1987 vs, | 1935 s | |
| (V) | (CH₂Cl₂) | 2028 w, | 1953 vs, | 1916 s | |
| (VI) | (CH₂Cl₂) | 2056 w, | 1991 vs, | 1948 s | |

[a] Perkin–Elmer 237 grating instrument.

TABLE 3

¹H NMR DATA[a]

| Compound | ppm above TMS | J(P–H) (cps) | Solvent |
|---|---|---|---|
| (I) | 7.4 (triplet) | 29 ± 6 | CDCl₃ |
| (II) | 8.2 (triplet) | 50 | C₆D₆ |

[a] Varian 100 A instrument.

TABLE 4

ELECTRIC DIPOLE MOMENTS[a]

| Compound | $w_2 \cdot 10^{-3}$ | $\Delta\varepsilon_{12} 10^{-3}$ | $\Delta v_{12} 10^{-3}$ | $\alpha_0$ | $\beta$ |
|---|---|---|---|---|---|
| (I) | 9.99 | 7.6 | − 7.49 | 0.76 | −0.75 |
| | 6.52 | 5.1 | | 0.78 | |
| | 8.89 | | − 0.67 | | −0.75 |

$P_{200} = 0.267 \pm 0.05$; $P_M = 178$; $P_E = 183.2$; $\mu = 0$ Debye

| | | | | | |
|---|---|---|---|---|---|
| (II) | 7.61 | 13.3 | − 3.00 | 1.66 | −0.39 |
| | 26.60 | | − 12.1 | | −0.45 |
| | 9.20 | 15.0 | | 1.63 | |

$P_{200} = 0.522 \pm 0.05$; $P_M = 395.9$; $P_E = 204.5$; $\mu = 3.06$ Debye; $\mu_{20\%} = 2.7$ Debye

[a] The Halverstadt-Kumler formula[12] was used. Dielectric constants of benzene solutions were measured on a WTW Dipolmeter DM01. Electronic polarization was calculated using the value given in the literature[13].

reacted very slowly with carbon tetrachloride, some *trans*-$ClMn(CO)_3L_2$ being formed; the latter compound also was formed by prolonged action of boiling alcoholic hydrogen chloride on the hydride. Further, the reported properties of $HMn(CO)_3L_2$

prepared by two other independent syntheses[8,9] are similar to those of the compounds reported here.

Although the origin of the hydride is not yet clear, we have shown that it does not come from the ligand, as it happens in the equilibrium between $[Ru(C_{10}H_8) \cdot (Me_2PCH_2CH_2PMe_2)]$ or $[Ru(Me_2PCH_2CH_2PMe_2)_2]$ and the corresponding hydrides[10]. Indeed, the $^1H$ NMR spectra of our compounds showed hydride formation when $(C_6D_5)_3P$ was employed. When di-n-butyl ether or diglyme were used as solvents, the reaction did not yield any stable compound.

The generally high stability of two phosphorus atoms in a *trans* configuration across the metal atom may be the reason for this surprising hydrogen abstraction. Indeed, in the same reaction and under the same conditions, but with a chelating diphosphine, no hydrogen abstraction was observed, although the corresponding $HMn(CO)_3(Ph_2PCH_2CH_2PPh_2)$ is known[11]. Additional work is in progress.

*Experimental*

All the reactions were carried out initially under nitrogen; evaporation was always carried out under reduced pressure (20–50 mm). Analytical and other data are given in the Tables.

$HMn(CO)_3(Ph_3P)_2$ (I). Dimanganese decacarbonyl (1.0 g) and triphenylphosphine (3.1 g) were dissolved in xylene (30 ml). The solution was maintained at 130–140° for 80 h. The colour of the solution changed to orange and at the end it was yellow. On cooling yellow-white crystals (1.7 or 1.9 g) precipitated; sometimes black powder also was present. Addition of excess petroleum ether to the mother liquor gave a second crop (0.2 g). The impure crystals were slightly paramagnetic; crystallization from benzene/pet. ether afforded a cream-white, diamagnetic compound (1.6 g), (I).

$HMn(CO)_3\{(PhO)_3P\}_2$ (II). Dimanganese decacarbonyl (0.5 g) and freshly distilled triphenyl phosphite (1.6 g) were dissolved in xylene (20 ml). The solution was kept 80 h at 130–140°. The pale-yellow solution was evaporated; the yellow oil was washed with pet. ether (10 ml; four times) and was dissolved in boiling ethanol (40 ml). On cooling the concentrated solution, white crystals of (II) were obtained (0.4 g).

*Reaction of* $Mn_2(CO)_{10}$ *with* $Ph_3As$. Dimanganese decacarbonyl (1.0 g) and triphenylarsine (3.7 g) were dissolved in xylene (30 ml). The solution was heated at 140° for 80 h. Orange-red crystals were left on evaporation; hexane crystallization gave orange crystals of $Mn(CO)_4(Ph_3As)^1$ (0.8 g) (Found: C, 55.54; H, 3.56. $C_{22}H_{15}$-$AsMnO_4$ calcd.: C, 55.80; H, 3.20.)

*Reactions of* (I) *and* (II) *with halogens*. The hydride was dissolved in slightly more than the minimum amount of $CCl_4$ or $CHCl_3$ and the stoichiometric quantity of the halogen was added, using a 0.1 N solution in $CCl_4$. After washing with water, the organic layer was evaporated to dryness and the compound was crystallized (Table I).

*Reaction of* (I) *and* (II) *with* $CCl_4$. A solution of (II) or a suspension of (I) in $CCl_4$ was boiled 1 h. After evaporation of the solvent, the IR spectrum (nujol mull) of the residue showed a weak absorption band at *ca.* 2050 cm$^{-1}$ and a stronger one at nearly 1970 cm$^{-1}$. After refluxing 3 h, the absorption at 1950–1900 cm$^{-1}$ of $HMn(CO)_3L_2$ disappeared and the absorption at *ca.* 2050w, 1970 vs, and 1950 s of *trans*-$ClMn(CO)_3L_2$ were present.

Reactions of (I) and (II) with alcoholic HCl. An alcoholic suspension of (I) or of (II) did not react with alcoholic HCl at room temperature. After 1 h refluxing pale yellow crystals were filtered. The IR spectrum (nujol mull) of the product derived from (I) had absorption maxima at 2042 w, 1970 vs, 1956 s. The IR spectrum of the product obtained from (II) had maxima at 2050 w, 1974 vs, 1925 s.

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