Notes

On the Synthesis of Dimethylphenylphosphine Complexes of Manganese(II) Halides

Denys A. Wickens* and Gillian Abrams
BOC Group Technical Center, 100 Mountain Avenue, Murray Hill, NJ 07974, U.S.A.

The preparation of complexes of the formula $MnX_2(PMe_2Ph)$ (X = Cl, Br, I, or NCS) is described in detail since it has been the subject of controversy. The identity of the compounds was established by a combination of chemical analysis and effective separation from unreacted tertiary phosphine. Notes on the analogous tri-n-propylphosphine complexes are included. Some observations on the reactions with dioxygen are given.

Although previous workers[1-4] have reported the synthesis and discussed the properties of tertiary phosphine complexes of manganese(II) halides, insufficient experimental detail was provided to duplicate their results. Probably for this reason other workers[5,6] have been unable to duplicate both the synthesis of the compounds and the reversibility[7] of their reaction with dioxygen. The problem in the synthesis occurs because solvents in which the manganese halide–tertiary phosphine system is highly soluble enable the precipitation of the solvated manganese halide (only) on reduction in the solution volume.

Experimental

Infrared spectra were recorded for KBr discs using a Perkin-Elmer 597 spectrophotometer. An inert atmosphere was assured by preparing the discs in a nitrogen glove-box, with spectra measured by supporting the disc between caesium iodide windows separated by a Viton O-ring to provide a miniature gas-tight chamber. Nitrogen was obtained by cryogenic boil-off (BOC Ltd.) and typically contained <0.5 p.p.m. dioxygen and <0.5 p.p.m. water. Toluene was refluxed over sodium–benzophenone, diethyl ether over sodium wire, and tetrahydrofuran (thf) over potassium–benzophenone before use and then freshly distilled. It was found that the colour of the refluxing thf was dependent on the quantity of potassium added, and extra metal was needed to achieve a purple colour, rather than royal blue. Karl Fischer water analysis typically gave values of the order of 20 p.p.m. (thf) or less (toluene, ether).

Phosphines were vacuum distilled and tested for purity by gas chromatography. Manganese(II) halides (John Ross Chemicals) supplied as tetrahydrates were dried to 0.05% (w/w) water under vacuum in a rotary evaporator at final temperatures of 160 (iodide), 200 (bromide), or 250 °C (chloride). It was necessary to use an indented (Morton) flask and to grind the material so as to pass through a 125-mesh sieve before final drying; slow intermediate heating is advisable. Dry manganese(II) iodide was found to be stable only in the absence of oxygen. All manipulations were carried out under nitrogen in a glove-box.

Dimethylphenylphosphinemanganese(II) *Bromide.*—Manganese(II) bromide (6.67 g, 3 mmol) was added to diethyl ether (200 cm^3) with dimethylphenylphosphine (4.4 cm^3, 3.1 mmol) with stirring. After 16 h a white and flocculent solid was obtained. Isolation was by gravity filtration through a no. 1 sinter, followed by pumping off the residual solvent (Found: Br, 46.55; Mn, 15.9; P, 8.40. $C_8H_{11}Br_2MnP$ requires Br, 45.3; Mn, 15.6; P, 8.80%). Yield 80—90%. Use of larger amounts of reactants leads to a suspension too thick to stir.

Dimethylphenylphosphinemanganese(II) *Chloride.*—Using diethyl ether (200 cm^3), manganese(II) chloride (9.95 g, 7.9 mmol), and dimethylphenylphosphine (13.3 cm^3, 9.5 mmol) as above, the product was substantially contaminated with unreacted manganese halide even after addition of more solvent to aid stirring (Found: Cl, 37.25; Mn, 23.1; P, 9.65. $C_8H_{11}Cl_2MnP$ requires Cl, 26.85; Mn, 20.8; P, 11.75%).

Dimethylphenylphosphinemanganese(II) *Iodide.*—Using diethyl ether (400 cm^3), manganese(II) iodide (8.2 g, 2.7 mmol), and dimethylphenylphosphine (3.8 cm^3, 2.7 mmol) as above, followed by solvent removal *in vacuo* to *ca.* 20—30 cm^3, a 20—50% yield could be achieved (Found: C, 21.8; H, 2.40, I, 55.95; Mn, 12.15; P, 6.65. $C_8H_{11}I_2MnP$ requires C, 21.5; H, 2.45; I, 57.0; Mn, 12.3; P, 6.65%). Successful reaction only occurred if enough diethyl ether was initially present for complete dissolution of all solids; the material crystallizes with approximately 0.66 molecules of diethyl ether per manganese (based on density measurements). Ether is lost from both crystal forms (one is blue cubes, the other straw-coloured needles) on removal from the mother-liquor.

Results and Discussion

The syntheses described above are the most successful tried: use of toluene as solvent led to greatly increased reaction times and lower purities (Table). When dichloromethane was added to the toluene[8] the reaction time was comparable to that with ether, but inorganic chloride could be detected in the isolated solids, presumably resulting from solvent quaternization of phosphine to phosphonium chloride. The i.r. spectra of the complexes are too similar to those of the unreacted phosphine to draw any real conclusions. Proof that the materials were truly compounds and not mixtures came from the physical appearance of the filterable material (colourless and flocculent changing from a fine pink dust) and from *X*-ray powder patterns, which could be related in the case of $MnI_2(PMe_2Ph)$ to a single-crystal study.[9] Recrystallization of the bromide or chloride complexes is not possible because the material is virtually insoluble in non-co-ordinating solvents, and co-ordinating solvents gave only solvated manganese halides on volume reduction (acetone, thf, and ethyl acetate were tried).

The method described in the Experimental section is effective

Table. Analytical data for the complexes synthesized[a] and experimental details

			Reaction		Analysis[b] (%)		
Halide	Phosphine	Solvent	Temperature (°C)	Time	Mn	P	X
$MnBr_2$	PMe_2Ph	Toluene	Ambient	14 d	13.9 (15.6)	7.95 (8.80)	47.75 (45.3)
$MnBr_2$	PMe_2Ph	Toluene	40	3 d	13.85 (15.6)	7.60 (8.80)	46.55 (45.3)
$MnBr_2$[c]	PMe_2Ph	Toluene	70—80	5 d	14.25 (15.6)	6.20 (8.80)	57.45 (45.3)
$MnBr_2$	PMe_2Ph	Ether	Ambient	16 h	15.9 (15.6)	8.40 (8.80)	46.55 (45.3)
$MnCl_2$[c]	PPr_3	Ether	Ambient	16 h	26.3 (19.2)	6.55 (10.85)	33.5 (24.8)
$MnBr_2$	PPr_3	Ether	Ambient	20 h	14.4 (14.65)	7.65 (8.25)	41.6 (42.6)
MnI_2	PPr_3	Ether	Ambient	2 d	11.15 (11.7)	6.75 (6.60)	50.7 (54.15)
$Mn(NCS)_2$[c]	PPr_3	Ether	Ambient	20 h	16.1 (16.6)	8.30 (9.35)	34.1 (35.1)

[a] Values for $MnCl_2(PMe_2Ph)$ and $MnI_2(PMe_2Ph)$ are given in equivalent detail in the Experimental section. [b] Calculated values are given in parentheses. [c] Analyses indicate appreciable contamination with unreacted halide.

for dimethylphenylphosphine and tri-n-propylphosphine complexes (Table), but is not a general synthesis route. Attempts to produce tri-n-butylphosphine complexes led only to manganese halide contaminated with 10—20% complex. Soxhlet extraction of manganese(II) iodide with ether–tri-n-butylphosphine gave a homogeneous solution, but reduction in volume resulted in a pink precipitate largely composed of manganese halide. Manganese(II) thiocyanate was also tested and some preparations were quite effective with dimethylphenylphosphine, but others were not. Phosphorus analyses ranged from 0.5 to 9.0%; $Mn(NCS)_2(PMe_2Ph)$ requires P, 10.0%.

The reaction of these materials with dioxygen was studied using an absorption balance (bromide and iodide complexes) as well as volumetrically for thf solutions (iodide complex only). On exposure to dioxygen the solids became intensely coloured, but absorption as monitored by weight change was slow; a slow loss of phosphine under vacuum made accurate work impossible. No reversibility could be detected within these limitations. Pale yellow solutions of $MnI_2(PMe_2Ph)$ in thf were cooled during gas absorption measurements and became red in colour. This colour change, which faded irreversibly at (constant) 0 °C, could be reversed by warming cold solutions under vacuum. Several such cycles could be achieved but even saturated solutions revealed oxygen absorptions only about 5% greater than that of the blank. The irreversible uptake at 0 °C was *ca.* 0.6 mol of dioxygen per mol of complex.

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References

1 W. Richter, R. Kummer, and R. Platz, G.P. 2 927 934/1981.
2 K. B. Yatsimirskii, U. I. Bratushko, and N. I. Ermokhina, *Teor. Eksp. Khim*, 1982, **18**, 367.
3 C. A. McAuliffe, H. Al-Khateeb, M. H. Jones, W. Levason, K. L. Minten, and F. P. McCullough, *J. Chem. Soc., Chem. Commun.*, 1979, 736.
4 C. A. McAuliffe, *J. Organomet. Chem.*, 1982, **228**, 255.
5 R. M. Brown, R. E. Bull, M. L. H. Green, P. D. Grebenitz, J. J. Martin-Polo, and D. M. P. Mingos, *J. Organomet. Chem.*, 1980, **201**, 437.
6 M. L. H. Green, *J. Organomet. Chem.*, 1982, **228**, 263.
7 C. A. McAuliffe, W. Levason, and F. P. McCullough, U.S.P. 4 215 452/1981.
8 A. Hossieny, A. G. Mackie, C. A. McAuliffe, and K. L. Minten, *Inorg. Chim. Acta*, 1981, **49**, 99.
9 B. Beagley, J. C. Briggs, A. Hosseiny, W. E. Hill, T. J. King, C. A. McAuliffe, and K. L. Minten, *J. Chem. Soc., Chem. Commun.*, 1984, 305.

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