Inorganica Chimica Acta, 49 (1981) 99–105
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The Coordination Chemistry of Manganese.
Part VII. The Preparation and Spectroscopic Characterisation of some Manganese(II) Complexes of Triphenylphosphine of Unusual Stoicheiometry, $Mn(PPh_3)X_2$

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Received September 3, 1980

Novel manganese(II) complexes of triphenylphosphine, $Mn(PPh_3)X_2$ (X = Cl, Br, I, NCS), have been isolated and studied by a number of spectroscopic techniques. The basic structure in the solid state is pseudotetrahedral and the complexes may be oligomeric. The $Mn(OPPh_3)(NCS)_2$ complex, synthesised for comparative purposes, differs from $Mn(PPh_3)(NCS)_2$ in a number of important ways.

Introduction

The coordination chemistry of manganese(II) is not well developed, for two reasons, both arising from the $3d^5$ electronic configuration: firstly, there is no ligand field stabilisation for a high-spin $3d^5$ species and, secondly, because of the complexity of the interpretation of electronic properties resulting from five unpaired electrons (electronic and e.p.r. spectra). Moreover, of interest here is the fact that manganese(II) is recognised as a class 'a' acceptor and as such is not expected for form strong bonds with heavy group 5 donors such as phosphorus (III) ligands.

Our first interest in Mn(II)–PR_3 complexes was an investigation of the 'MnX_2/EPh_3' (E = P, As) [1–4] system, and we showed that reaction of apparently anhydrous manganous halides with PPh_3, $AsPh_3$, $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2AsPh_2$ (dae) and *cis*-$Ph_2PCHCHPPh_2$ (vpp) gave very low yields (5–15%) of only $Mn(OEPh_3)_2X_2$, $Mn(OPPh_2)_2$, Mn(ligand $O_2)X_2$ (ligand O_2 = $dpmO_2$, $dpeO_2$, $daeO_2$, $vppO_2$) [5]. Indeed we went on to show that using strictly anhydrous manganese(II) salts it was possible to stabilise even Mn^{II}–As and Mn^{II}–Sb bonds in the complexes $[Mn(ligand)_2X_2]$ (ligand = *o*-phenylenebis(dimethylarsine) and *o*-phenylene(dimethylarsine)(dimethylstibine); X = Cl, Br, I) [2].

We have since then thoroughly investigated methods of obtaining anhydrous MnX_2 species, having found that greater care is necessary to achieve this than in the cases of other MX_2 salts we have worked with in this laboratory. Moreover, we have found that the *anhydrous* MnX_2 species appear to no longer be typical class 'a' acceptor species and that it is possible to isolate a wide range of $Mn(PR_3)X_2$ complexes [6] even from tetrahydrofuran (THF) solution. Rather surprisingly we found that $Mn(THF)_2X_2$ will react with $PPhMe_2$ in THF to form $Mn(PPhMe_2)X_2$, a displacement of hard oxygen donor THF ligands by a soft phosphine donor [1].

The $Mn(PR_3)X_2$ are unique compounds. For example, they react almost instantaneously with molecular oxygen to form highly coloured dioxygen adducts, $Mn(PR_3)X_2\cdot O_2$. The binding is reversible and the equilibrium

$$Mn(PR_3)X_2 \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} Mn(PR_3)X_2\cdot O_2$$

is pO_2 dependent, *e.g.* $Mn(PPhMe_2)Br_2$ binds dioxygen even at very low pO_2, whereas $Mn(PBu^n_3)(NCS)_2\cdot O_2$ rapidly loses dioxygen at $pO_2 < 150$ torr [6]. In the solid state or at temperatures $\leqslant 0$ °C dioxygen binding and release can occur without deterioration of the $Mn(PR_3)X_2$ molecule. We have made a detailed examination by mass spectroscopy of the O_2 molecule before and after binding to $Mn(PR_3)X_2$; mixtures of $^{16}O_2/^{18}O_2$ absorbed retain their identity on desorption from the solids or the complexes in solution in THF [7]. Absorption in solution is always followed by quantitative gas burette measurements, and by a Toepler apparatus in the solid state. We have been aided in obtaining solution isotherms with dioxygen by the fact that the $Mn(PR_3)X_2$ species are highly coloured and we can follow dioxygenation spectrophotometrically, and

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have recently shown that both the K_{O_2} and $P^{O_2}_{1/2}$ (pO_2 at which 50% of the binding sites are dioxygenated) for $Mn(PBu^n_3)Br_2$ in 1,2-dichloroethane indicate that this complex is a remarkably close analogue of myoglobin in this solvent [8]. However, these $Mn(PR_3)X_2$ complexes have the ability to reversibly chemically bind a number of other small molecules, *e.g.* carbon monoxide, sulphur dioxide and the adsorption of molecular hydrogen is also being investigated.

We are now embarking on a full systematic disclosure of the details of our system. We begin here with a description of the synthesis and properties of $Mn(PPh_3)X_2$ (X = Cl, Br, I, NCS). When we began this investigation in 1972 it was our initial aim to prepare $Mn(PPh_3)_2X_2$, but as previously stated only $Mn(OPPh_3)_2X_2$ and $Mn(OPPh_2)_2$ were isolable. As our understanding of the factors necessary to stabilise $Mn^{\underline{II}}PR_3$ bonds developed we were surprised to find that, apart from their ability to coordinate reversibly small molecules, the stoicheiometry of the complexes are of the 1:1 MnX_2/PR_3 type. We have thus been able to isolate a large number of $Mn(PR_3)X_2$ complexes, and recently have obtained the 'parent' $Mn(PPh_3)X_2$ (X = Cl, Br, I, NCS) species. So far these latter complexes show no ability to coordinate small molecules, but nonetheless we feel that they are of interest for a number of reasons, *viz.* the unusual 1:1 Mn:PPh_3 stoicheiometry, and because they are inactive towards dioxygen, despite the fact that they belong to the same family of active complexes.

In preparation is an account of the dioxygen-active $Mn(Pamyl_3)X_2$ complexes [9]. It is the overall aim of our work to produce complexes which are specific binders of one small molecule under a particular set of conditions, thus being useful in the gas separation industry. We have accumulated sufficient evidence so far for us to believe that this is a realisable goal.

Results and Discussion

We stress that the preparation of the $Mn(PPh_3)X_2$ complexes is critically dependent on the use of anhydrous solvents, manganese(II) salts and synthesis conditions. Our own approach has been developed over a number of years. (Following the methods outlined in the Experimental section results in almost quantitative yield, but careless workers will experience difficulty.) Once isolated the complexes are quite robust and insensitive to all but very moist conditions.

We have made a careful study of the conditions necessary to completely dehydrate the manganese(II) salts used in our investigations, and the chief point to be stressed is that removal of the last *ca.*

TABLE I. Analytical Data and Some Physical Properties.

Complex	Colour	M. Pt. (°C)	μ_{eff} (μ_B)	%Mn[a]	%C	%H	%P	%Hal	%N	%S
$Mn(PPh_3)Cl_2$	Pink	96	5.8	14.5(14.4)	55.5(55.5)	3.6(3.9)	8.1(8.0)	18.5(18.3)		
$Mn(PPh_3)Br_2$	Pink	78	5.5	11.7(11.7)	45.5(45.2)	3.4(3.1)	6.7(6.5)	33.9(33.5)		
$Mn(PPh_3)I_2$	Pink-Orange	194	5.4	9.9(9.8)	37.8(37.8)	3.0(2.6)	5.7(5.4)	44.7(44.4)		
$Mn(PPh_3)(NCS)_2$	Light yellow	70	5.2	12.7(12.9)	55.3(55.3)	3.7(3.5)	7.3(7.1)		6.8(6.5)	14.9(14.7)
$Mn(OPPh_3)(NCS)_2$[b]	V. pale yellow	226	5.5	12.8(12.4)	52.1(53.3)	3.6(3.3)	6.9(6.9)		6.2(6.2)	14.7(14.2)

[a] Found (Calc.). [b] Oxygen analysis by difference: 3.7% (Calc. 3.6%).

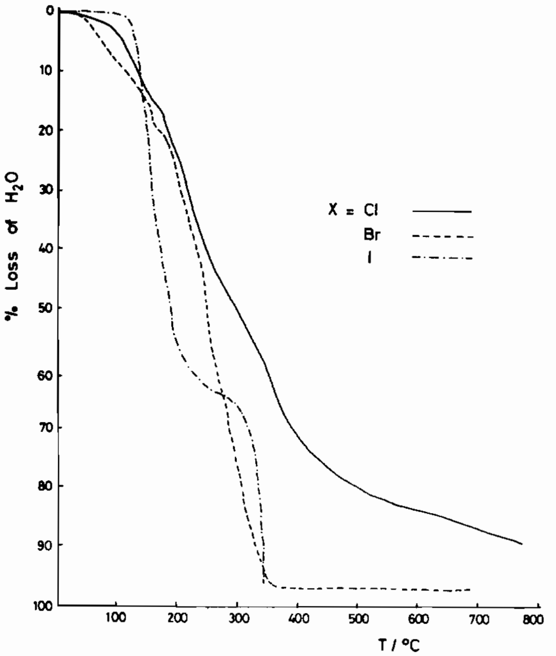

Fig. 1. T.G.A. Traces of pre-analysed $Mn(H_2O)_4X_2$. X = Cl ———; Br ------; I —.—.—.

$0.5H_2O/Mn$ is difficult to achieve without decomposing the salt. Figure 1 contains TGA traces for the $Mn(H_2O)_4X_2$ (X = Cl, Br, I) species. We observed decomposition prior to complete dehydration at ~750 °C for the chloride, at ~500 °C for the bromide, and at ~300 °C for the iodide. Painstaking investigations of a large number of dehydration-without-decomposition methods, which will be the subject of another publication, have enabled us to develop the methods detailed in the Experimental section.

The successful isolation of these $Mn(PPh_3)X_2$ (X = Cl, Br, I, NCS) complexes, Table I, is entirely dependent on producing *anhydrous* MnX_2 species, and it is clear from this and other [1, 2] studies that heavy Group VB donor ligands can form quite stable adducts of typical class 'a' acceptors under the right conditions. It is noteworthy that the usual stoicheiometry $M(PPh_3)_xX_2$ (M = Fe [10], Co [11], Ni [12, 13]; x = 2, 3, 4) for 1st row divalent T.M. complexes is not obtained for M = Mn; even with excess of PPh_3 we only obtain the 1:1 $Mn(PPh_3)X_2$ complexes. It may be said here that we believe that the startling ability of the $Mn(PR_3)X_2$ ($R_3 \neq Ph_3$) to coordinate small molecules is due to three factors: the oxidation state of the manganese, the $3d^5$ configuration, and the ostensible coordination unsaturation about the metal. For example, we find no activity with other $3d^5$ species, *e.g.* iron(III) [14] we have examined, and we do have evidence for Mn–X–Mn bond breaking and bond making in successive dioxygenation cycles [5]. Based on the $Mn(PR_3)X_2$ formulation two variables are possible, R and X. Clearly for R = Ph in the complexes $Mn(PPh_3)X_2$ we observe one extreme in our search for structure/reactivity relationships, for in this case we observe no chemical reactivity towards small molecule reversible coordination. In drawing preliminary conclusions about the structure of the $Mn(PPh_3)X_2$ complexes we have made use of a number of spectroscopic techniques, the results of which are listed below.

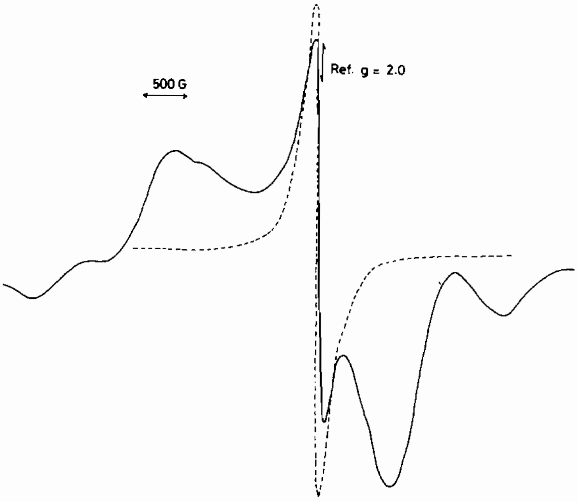

Fig. 2. Electron paramagnetic spectra of $Mn(PPh_3)(NCS)_2$. ----- in dichloromethane at room temperature; ——— in tetrahydrofuran at room temperature.

The electronic paramagnetic resonance spectra of both $Mn(PPh_3)Cl_2$ and $Mn(PPh_3)Br_2$ in the solid state and in dichloromethane solution exhibit a broad band at g_{eff} *ca.* 2; no fine structure is observed. In tetrahydrofuran the chloro complex also produces a band at g_{eff} *ca.* 2, as does the bromo complex, but with the latter deterioration of the spectrum begins after 15 minutes and after 45 minutes no spectrum persists. In the solid state and in dichloromethane solution $Mn(PPh_3)I_2$ exhibits lines at g_{eff} *ca.* 4 and *ca.* 2, together with other lines. Comparison of these spectra with the published graphs of Dowsing and Gibson [15] suggests that for this complex D is *ca.* 0.09 cm^{-1} and λ is *ca.* 0.333, suggesting a tetrahedral environment in both physical states. In tetrahydrofuran no e.p.r. spectrum is observed. The e.p.r. spectra of $Mn(PPh_3)(NCS)_2$ in the solid state and in dichloromethane solution are characterised by a broad band at g_{eff} ca. 2, and no fine structure is observed, Fig. 2. However, in tetrahydrofuran solution the thiocyanato complex exhibits an e.p.r. spectrum with lines at g_{eff} *ca.* 6, *ca.* 4 and *ca.* 2, together with other lines at $g_{eff} < 2$, Fig. 2. Comparison with the published graphs of Gibson and Dowsing [15] suggests that

TABLE II. Electronic and Infrared Spectra of the Complexes.

	Electronic Reflectance spectra (nm)[a]				Infrared Spectra (cm^{-1})[b]				
	$4T_1(G) \leftarrow {}^6A_1$	$4T_2(G) \leftarrow {}^6A_1$	$4A_1,4E(G) \leftarrow {}^6A_1$	$4T_2 \leftarrow {}^6A_1$	ν(Mn–P)	ν(Mn–X)	ν(CN)	ν(Mn–N)	ν(Mn–S)
$Mn(PPh_3)Cl_2$	525	445	418	400	421	326, 232			
$Mn(PPh_3)Br_2$	528	450	422	400(sh)	420	229, 192			
$Mn(PPh_3)I_2$	530	480	430	400	417				
$Mn(PPh_3)(NCS)_2$[c]	516	475	446	366	418		2140	256	304
$Mn(OPPh_3)(NCS)_2$[d,e,f]							2100, 2075	254	300

[a] Diffuse reflectance spectra; assignments based essentially on t_d symmetry. [b] Nujol/HCB mulls. [c] δ(NCS) 408 cm^{-1}. [d] δ(NCS) 420 cm^{-1}. [e] Electronic reflectance bands at 434, 366 nm. [f] ν(P=O) 1140 cm^{-1} (free $OPPh_3$ exhibits ν(P=O) at 1180 cm^{-1}).

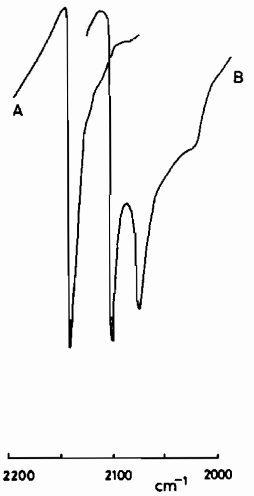

Fig. 3. Mull infrared spectra in the CN stretching region. A) $Mn(PPh_3)(NCS)_2$; B) $Mn(OPPh_3)(NCS)_2$.

for this complex in THF D is 0.08 cm^{-1} and λ is 0.00, suggesting an octahedral environment about manganese in tetrahydrofuran.

The infrared spectra as Nujol mulls are listed in Table II. We have found that comparing spectra of the anhydrous MnX_2 salt, triphenylphosphine (or $OPPh_3$), and the $Mn(PPh_3)X_2$ complex has allowed us to make assignments [16] with some degree of certainty. In particular there is a large body of evidence for bridging anions in these complexes, *e.g.* $Mn(PPh_3)(NCS)_2$ shows evidence for only bridging Mn–NCS–Mn moieties by exhibiting a single, strong, sharp ν(CN) at 2140 cm^{-1}, Fig. 3. However, for the bromo and chloro derivatives there is evidence for both bridging and terminal Mn–X linkages. The ν(Mn–P) absorption is clearly identifiable in all the PPh_3 complexes, but is absent in $Mn(OPPh_3)(NCS)_2$ and in PPh_3 itself.

The diffuse reflectance spectra are listed in Table II, and may be assigned on the basis of a ${}^6A_1$ ground state and essentially t_d symmetry according to the suggestions of Figgis [17]. Significantly, the spectrum of $Mn(OPPh_3)(NCS)_2$ does not exhibit the same type of spectrum (see below). It is predicted that all complexes of metals with a ${}^6A_1$ ground term should show magnetic moments very close to the spin-only value, 5.92 μ_B, and are independent of temperature [18]. Table I lists the room temperature magnetic moments of the complexes, and for $Mn(PPh_3)X_2$ these decrease in the order Cl > Br > I > NCS, suggesting that the bridging Mn–X–Mn moieties lead to some significant spin-pairing in this order. The low value of the thiocyanato complex is in keeping with our recognition of only Mn–NCS–Mn groups.

In suggesting structures for the $Mn(PPh_3)X_2$ (X = Cl, Br, I) we bear in mind the infrared spectral evidence for Mn–X and Mn–X–Mn links (X = Cl, Br) and so in the solid state these complexes are at least dimeric [6]. However, it is pertinent to refer to the recent work of Churchill on the $3d^{10}$ ostensibly coordinatively unsaturated $Cu(PR_3)X$ systems [19–22], which have tetrameric cubane or stepped structures. It is likely, we feel, that the $Mn(PR_3)X_2$ complexes are oligomeric to a degree dependent on R and X. We are continually trying to obtain crystals suitable for X-ray analysis, but have not so far obtained any. The $Mn(PPh_3)(NCS)_2$ complex contains only bridging –NCS– groups and so, presumably has a different structure to the halo derivatives.

We synthesised $Mn(OPPh_3)(NCS)_2$ for two reasons: first, to see if the 1:1 ligand:manganese stoicheiometry was restricted to phosphine ligands only (we have previously isolated a series of $Mn(OPPh_3)_2X_2$ complexes [5]), and, second, to show that PPh_3 and $OPPh_3$ complexes are recognisably different. We chose the thiocyanate derivative as the one most likely to accentuate infrared spectral differences. Figure 3 dramatically shows the difference in the ν(CN) region between $Mn(PPh_3)(NCS)_2$ and $Mn(OPPh_3)(NCS)_2$; the profile of the former shows only bridging –NCS– groups, whereas that of the latter contains evidence for both Mn–SCN and Mn–NCS terminal linkages [23, 24] (the presence of a band assignable to δ(SCN) at 420 cm^{-1} is strong additional evidence for Mn–SCN links [25]). Moreover, whilst a ν(Mn–P) is discernible for $Mn(PPh_3)(NCS)_2$ it is absent for $Mn(OPPh_3)(NCS)_2$, and the latter additionally shows a strong ν(P=O) band at 1140 cm^{-1} (absent in the former), shifted from the free ligand value at 1180 cm^{-1}. None of the complexes reported here are sufficiently soluble for molecular weight measurements, but are all non-conductors in *ca.* 10^{-3} *M* 1,2-dichloroethane solution. It may be that $Mn(OPPh_3)(NCS)_2$ is a genuine three-coordinate complex, similar to $Cu(PPh_3)_2Br$ [26], since we find no evidence for any dissociative interactions.

Experimental

Drying of Reagents is of crucial importance in the synthesis of these $Mn(PR_3)X_2$ complexes:

Tetrahydrofuran (BDH reagent grade) is initially dried for ~24 h over $CaCl_2$ and then transferred to a 3 l still equipped with a 2ft Vigereaux column and reflux/distillation still head, and fitted with a dinitrogen bleed system to prevent bumping. After passing a rapid N_2 stream through the THF for ~10 min, several 3/4″ lumps of potassium metal are added, followed by several grams of benzophenone. The THF is allowed to reflux under N_2 for ~24 h after which time the THF solution turns deep blue/purple (due to the formation of potassium benzophenone/ketyl). The THF is then ready for distillation into dry N_2 filled flasks, and is used immediately (never stored). The THF in the still occasionally loses its purple colour either due to the introduction of dioxygen or moisture. The former causes the potassium benzophenone ketyl to oxidise (yellow-brown colouration) and can be remedied by turning up the N_2 flow rate to the still, followed by addition of more benzophenone and potassium metal (if all silver balls of metal have disappeared from the surface of the liquid). *Important*: THF stills should not be continuously refilled due to the danger of peroxide build-up. When most of the THF has been distilled the residue can be disposed of with ethyl acetate followed after 1 h by ethanol.

Toluene is dried in a similar manner, but sodium can replace potassium if desired. The toluene is distilled into N_2-filled dry flasks, and may be stored over 4A molecular sieves.

Chlorinated hydrocarbons are distilled from P_4O_{10} under a dinitrogen atmosphere. The first 10% of the distillate is discarded, and the remaining distillate may be stored over 4A molecular sieves.

Manganese(II) Iodide. Commercially available as $MnI_2(H_2O)_4$ (Ross Chemicals, Devon), this contains 18.9% water. Under an argon atmosphere at ~120 °C approx. $3.5H_2O$ is lost after 6 h, and the remaining $0.5H_2O$ can be removed at 200–220 °C in *ca.* 2 h, but at this temperature there is almost always decomposition of the salt. Thus, a general method we employ is: $MnI_2(H_2O)_4$ (50 g) is ground to a fine powder and placed in a round bottom flask (250 cm^3) equipped with a vacuum stop cock. Initial drying *in vacuo* at 80 °C (flask placed in oil bath) for 7 h is followed by removal to a dry box where, under an argon atmosphere, the solid cake is reground to a fine powder) and drying *in vacuo* at 100 °C is continued for 2 h, after which the oil bath temperature is gradually raised to 120 °C and held there for 4 h.

Manganese(II) Bromide is commercially available as $MnBr_2(H_2O)_4$ from BDH Ltd. and contains 25.1% water. Heating under an argon atmosphere for 4 h removes almost all the water; the compound rapidly decomposes >400 °C. The method of dehydration we employ is as follows: finely ground $MnBr_2(H_2O)_4$ (50 g) is treated as above by heating *in vacuo* at 150 °C for 7 h, the cake finely ground, reheated to 150 °C for 2 h and then gradually heated to 180 °C and maintained at this temperature for 5 h.

Manganese(II) Chloride is commercially available as $MnCl_2(H_2O)_4$, containing 36.4% water, from BDH Ltd. Under an argon atmosphere most of the water is lost at 350 °C, but absolutely anhydrous material is only obtained after prolonged heating at 400 °C.

Our method is as follows: Finely ground $MnCl_2(H_2O)_4$ (50 g) was heated *in vacuo* at 200 °C for 6 h, the cake finely ground, and then further heated *in vacuo* at 220 °C for 6 h.

Manganese(II) Thiocyanate is prepared (see below) as $Mn(NCS)_2(H_2O)_4$ and loses almost all the water by heating under argon to 180 °C; final dehydration occurs at ~280 °C without apparent decomposition. We obtain anhydrous material in the following manner: The finely ground $Mn(NCS)_2(H_2O)_4$ (50 g) was heated *in vacuo* at 180 °C for 7 h, reground, and finally heated *in vacuo* at 280 °C for 5 h. *Important.* No manganese(II) salt is used by us in our work which gives a Karl Fischer analysis for water of >0.2% within 7 days of use. After 7 days, even if stored under the most stringent anhydrous conditions, the material is reanalysed to ensure the water content is less than 0.2%.

Preparation of Manganese(II) Thiocyanate

Barium(II) isothiocyanate dihydrate* (1157 g, 4 mol) was dissolved in distilled water, the solution made up to 2.0 l, and assayed for Ba^{2+}. A 2 l solution of manganese(II) sulphate tetrahydrate (East Anglia Chemicals Ltd.) in distilled water was similarly prepared and assayed for SO_4^{2-}. In a typical experiment assays indicated equivalent volumes of solutions to be 1990 cm³ $Ba(NCS)_2 \equiv 1922$ cm³ $MnSO_4$. To the barium isothiocyanate solution (1990 cm³), in a 10 l round bottom flanged flask equipped with a mechanic stirrer under a dinitrogen atmosphere, was added a further 2 l distilled water. The manganese(II) sulphate solution (1920 cm³) was diluted by the addition of 1 l distilled water and added rapidly to the stirred barium salt solution, resulting in the rapid precipitation of barium(II) sulphate. The mixture was then stirred for 4 h, after which it was allowed to settle overnight. The clear pale pink supernatant liquor was tested for excess Ba^{2+} or SO_4^{2-} by treating aliquots with $MnSO_4$ and $Ba(NCS)_2$ solutions. Any ppt. formed indicates excess ions and these must be accurately estimated and the appropriate quantity of the deficient solution added, stirred and re-tested until the tests are negative. The clear pale pink solution was then decanted and the barium(II) sulphate slurry was centrifuged (1800 rpm/20 min) and the clear pale pink centrifugate added to the bulk of the decanted solution; this was finally filtered through a Whatman filter tube (size 1A) to remove the last traces of suspended solids. The solution was concentrated using a rotatory evaporator until the first signs of a solid were noticed as a pale yellow ring on the flask. The solution changed in colour during this time from pale pink, through blue to green as the concentration increased. After cooling the solution in an ice-bath the mass of pale green crystals which separated were shown to be $Mn(NCS)_2(H_2O)_4$ by elemental and Karl Fischer analyses.

Preparation of the Complexes, $MnLX_2$ ($L = PPh_3$, $OPPh_3$)

The apparatus usually employed is a round bottom 250 cm³ flask equipped with a side-arm containing a ground glass tap. This is dried *in vacuo* stored under argon, and subsequently dried by the application of a Bunsen flame prior to use. Typically the *anhydrous* MnX_2 salt (4.0 mmol) is added to the flask, the flask is evacuated, and the magnetic stirrer allowed to break up any lumps by stirring at high speed for *ca.* 2 h, after which general practice is to gently Bunsen flame the flask to ensure no moisture contamination has occurred during handling and transfer of the stored MnX_2 to the flask. [The technique of finally powdering the MnX_2 salt and finally warming *in vacuo* does appear to be beneficial to clean reaction products.] After cooling to room temperature a 60:40 mixture of freshly distilled toluene/dichloromethane (90 cm³) is added after prior degassing under dinitrogen. Once in the flask a vacuum is applied and let down under argon; this is repeated three times to ensure no dioxygen is present. Prior to the addition of the triphenylphosphine (1.05 g; 4.0 mmol) in degassed dichloromethane (35 cm³) the syringe used for the addition of the solution is heated in an oven at 130 °C for 2 h, allowed to cool in an argon atmosphere and flushed with argon before loading. On addition of the triphenylphosphine, application of a vacuum and return to ambient pressure under argon is carried out four times to further ensure no possibility of triphenylphosphine oxidation. The mixture is allowed to stir under argon at room temperature for 5 days, after which the volume of the solution is reduced to *ca.* 25 cm³ by application of a vacuum (heat is not applied). The resulting solid is separated by Schlenk techniques under argon, allowed to dry under an argon stream, taken up in dichloromethane (50 cm³), filtered in a Schlenk apparatus, the volume further reduced to *ca.* 10 cm³, and the resulting complex filtered and dried *in vacuo.* Yields are almost quantiative. [A similar method is used for the $OPPh_3$ complex preparations].

Physical Measurements

These were obtained as previously described by us [1, 2]. Thermogravimetric analyses were obtained using a Stanton Redcroft TG-750 Thermobalance in an argon atmosphere; the heating rate used was 10 °C per minute and the temperature

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*Obtained from East Anglia Chemicals Ltd., sold as the wet dihydrate, is very hygroscopic.

range was ambient–750 °C, after which all the manganese(II) salts had decomposed. Prior to TGA measurements the $Mn(H_2O)_4X_2$ species were shown to be exactly tetrahydrates by Karl Fischer analysis. Elemental analyses were performed by Dr. R. Perry and staff, Microanalytical Laboratory, UMIST, or by Dr. W. E. Hill, Chemistry Department, Auburn University, Alabama.

Acknowledgements

We are grateful to Dr. M. J. Parrott for assistance with E.P.R. interpretation and to N.R.D.C., S.R.C. and C.E.G.B. for financial support.

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