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STUDIES OF LAMBERT'S REACTION: THE FORMATION OF $[Mn_2(CO)_8(\mu\text{-}AsR_2)_2]$ COMPLEXES FROM TERTIARY ARSINES AND $[Mn_2(CO)_{10}]$ AT HIGH TEMPERATURES

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Summary

Although very bulky ligands e.g. $(o\text{-}MeC_6H_4)_3E$ or $(\alpha\text{-}C_{10}H_7)_3E$ (E = P or As) are inert, the normal photochemical or thermal reaction of tertiary phosphines or arsines, L, with $[Mn_2(CO)_{10}]$ is CO substitution with the formation of $[Mn_2(CO)_8(L)_2]$ derivatives (I). At elevated temperatures some triarylarsines, R_3As, undergo Lambert's reaction with ligand fragmentation to give $[Mn_2(CO)_8(\mu\text{-}AsR_2)_2]$ complexes (II) (R = Ph, $p\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_4$, $p\text{-}FC_6H_4$, or $p\text{-}ClC_6H_4$) even though, in the absence of $[Mn_2(CO)_{10}]$, R_3As are stable under the same conditions. Exceptional behaviour is exhibited by $(p\text{-}Me_2NC_6H_4)_3As$ which forms a product of type I; by some $HN(C_6H_4)_2AsR$ which give a product of type II as a result of loss of the non-aryl groups R = $PhCH_2$, *cyclo*-C_6H_{11}, or MeO; and by $Ph(\alpha\text{-}C_{10}H_7)_2P$ which is the only phosphine to form a product of type II, albeit in trace amounts only. The thermal decomposition of a n-butanol solution of $[Mn_2(CO)_8(AsPh_3)_2]$ in a sealed tube gives C_6H_6 and $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$, whilst in an open system in the presence of various tertiary phosphines, L, $[Mn(H)(CO)_3(L)_2]$ are obtained. It is suggested that Lambert's reaction is a thermal fragmentation of $[Mn(CO)_4(AsR_3)]^\cdot$ radicals, the first to be recognised. They lose the radical $R^\cdot$ which abstracts hydrogen from the solvent. The resulting $[Mn(CO)_4(AsR_2)]$ moiety dimerises to $[Mn_2(CO)_8(\mu\text{-}AsR_2)_2]$. The reaction is facilitated by the stability of the departing radical (e.g. $PhCH_2$ or MeO) and, as the crowding about As is relieved, by its size (e.g. Ph, *cyclo*-C_6H_{11}, $o\text{-}MeC_6H_4$, or $\alpha\text{-}C_{10}H_7$). In general, phosphine-substituted radicals $[Mn(CO)_4(PR)_3]^\cdot$ do not undergo this decomposition, probably because the P—C bonds are much stronger than As—C.

Introduction

Thermal and photochemical promotion of the reactions of manganese carbonyl, $[Mn_2(CO)_{10}]$ with tertiary phosphines, L, results in CO-substitution to give $[Mn_2(CO)_9L]$ or $[Mn_2(CO)_8L_2]$, which have structures based on that of the parent carbonyl. The actual stereochemistry of these compounds depends on the size of L; the most common disubstituted isomer is illustrated as I in Fig. 1 [1]. Under more extreme thermal reaction conditions of longer times, higher temperatures, and larger amounts of L, $[Mn(H)(CO)_3(L)_2]$ are obtained [1]. Trialkylarsines and Ph_3As react similarly in the photochemical reaction [1]. However, Lambert found that in the thermal reaction Ph_3As gives a third product, $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$, which predominates at higher temperatures. Its probable structure is illustrated as II, (R = Ph), in Fig. 1 [2].

Although it has been known for twenty years, Lambert's reaction has been neglected and its importance has not been appreciated. An exception has been its recent utilization in the preparation of substituted phosphole [3] and arsole [4] derivatives of manganese. Consequently we decided that a reinvestigation of the reaction would be opportune, especially in the light of the work by Poë and others who have shown that the CO substitution reactions of $[Mn_2(CO)_{10}]$ are probably not simple, but proceed to a large extent via radicals resulting from Mn—Mn bond fission [5,6]. However, the persistently low yields of the reaction and the extensive decomposition which accompanied it has meant that we were unable to carry out the kinetic studies which had been our original objective.

Experimental

Tertiary arsines were prepared from an arsenic(III) halide, $HN(C_6H_4)_2AsCl$ [7] or $AsCl_3$, and the appropriate Grignard reagent [9]. Other chemicals were purchased.

Unless it is stated otherwise, reactions were carried out in the dark and under an atmosphere of nitrogen in solvents which had been purified by distillation from calcium hydride prior to use.

IR spectra were run on a Perkin-Elmer 337 spectrometer equipped with a Hitachi-Perkin-Elmer readout recorder. They were calibrated with DCl and H_2O vapour [8], and peak positions are accurate to within ±1 cm^{-1}. ^1H NMR

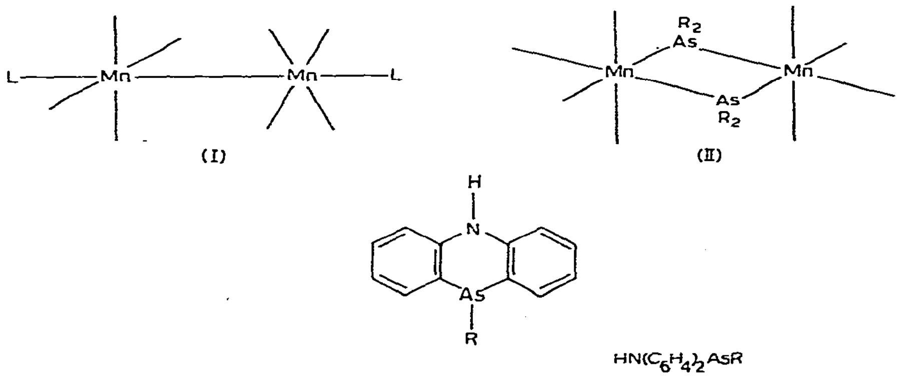

Fig. 1. The structures of $[Mn_2(CO)_8(L)_2]$ (I), $[Mn_2(CO)_8(\mu\text{-}AsR_2)_2]$ (II), and $HN(C_6H_4)_2AsR$. CO ligands have been omitted for the sake of clarity.

spectra were recorded on a Perkin-Elmer R12B spectrometer using Me_4Si as an internal standard. Analyses were determined in the Analytical Laboratory of University College, Dublin.

Photochemical reactions of [$Mn_2(CO)_{10}$] with tertiary phosphines and arsines

Solutions of [$Mn_2(CO)_{10}$] (1 g) and the ligand L (mole ratio 1 : 2.5) in cyclohexane (100 ml) were irradiated at room temperature with a Philips HPR 125 W lamp. The reactions were monitored by IR spectroscopy and were stopped when all of the [$Mn_2(CO)_{10}$] had been consumed (12—24 h). The precipitates were filtered off and recrystallized from benzene/hexane mixtures to give analytically pure, orange crystals of [$Mn_2(CO)_8(L)_2$] (I) in 60—80% yields for L * = $Ph(C_6H_{11})_2P$ (171—172°C), $Ph_2(C_6H_{11})P$ (168—170°C), Ph_3P (208—209°C), (p-$MeC_6H_4)_3P$ (194—196°C), (p-$ClC_6H_4)_3P$ (dec. 204°C), $^iPr_3As$ (dec. 162°C), Ph_3As (162—163°C), (p-$MeC_6H_4)_3As$ (dec. 194°C), (p-$ClC_6H_4)_3As$ (dec. 148°C), (p-$FC_6H_4)_3As$ (138—142°C), (p-$MeOC_6H_4)_3As$ (dec. 170°C), (p-$Me_2NC_6H_4)_3As$ (dec. 202°C), $HN(C_6H_4)_2AsMe$ (dec. 155°C), $HN(C_6H_4)_2AsEt$ (dec. 172°C), $HN(C_6H_4)_2AsPr^i$ (dec. 178°C), $HN(C_6H_4)_2AsBu^s$ (dec. 150°C), $HN(C_6H_4)_2AsPh$ (dec. 167°C), and $HN(C_6H_4)_2AsC_6H_4OMe$-p (dec. 139°C).

Thermal reactions of [$Mn_2(CO)_{10}$] with tertiary phosphines and arsines

Solutions (50 ml) of [$Mn_2(CO)_{10}$] (1 g) and the tertiary phosphine or arsine, L (mole ratio 1 : 2), where heated in (a) n-butanol at reflux for 7—12 h, (b) toluene at reflux for 8 h, (c) xylene at 120°C for 8 h, (d) xylene at reflux for 8 h, (e) n-octane at reflux for 6 h, (f) decalin at reflux for 4 h, or (g) diglyme at reflux for 4 h. On cooling the reactions mixtures, yellow-orange solids precipitated, contaminated with large amounts of black solids. These were recrystallized from benzene/hexane mixtures to give analytically pure crystalline products in 16—34% yield. These were of class I, [$Mn_2(CO)_8(L)_2$] for L = Ph_3P, (p-$ClC_6H_9)_3P$, (p-$Me_2NC_6H_4)_3As$ and $HN(C_6H_4)_2AsPr^i$; and of class II, [$Mn_2(CO)_8(\mu$-$AsR_2)_2$], when L = R_3As = Ph_3As (dec. 260°C), (p-$MeC_6H_4)_3As$ (129—132°C), (p-$MeOC_6H_4)_3As$ (112—115°C), (p-$ClC_6H_4)_3As$ (dec. 194°C), and (p-$FC_6H_4)_3As$ (dec. 180°C). The class II complex [$Mn_2(CO)_8\{\mu$-$As(C_6H_4)_2NH\}_2$] (dec. 145°C) was obtained from L = $HN(C_6H_4)_2AsR$ in boiling xylene solution when R = α-$C_{10}H_7$ (34%, 4 h), o-$MeOC_6H_4$ (26%, 5 h), Ph (25%, 5 h) p-$MeOC_6H_4$ (25%, 5 h), $PhCH_2$ (18%, 7 h), PhO (17%, 6 h), Pr^i (13%, 7 h), MeO (12%, 7 h) and *cyclo*-C_6H_{11} (<1%, 10 h); the yields of purified products and the reaction times are enclosed in the parentheses. There was spectroscopic evidence for the formation of a complex of class II in trace amounts only as the sole carbonyl-containing product from the reaction where L = $Ph(\alpha$-$C_{10}H_7)_2P$.

When the reaction between [$Mn_2(CO)_{10}$] and Ph_3As in boiling xylene was carried out under an atmosphere of CO rather than N_2, it was slowed down. The yield of [$Mn_2(CO)_8(\mu$-$AsPh_2)_2$] was unchanged.

In these thermal reactions a black precipitate was always formed. It was filtered off and found to be insoluble in water and various organic solvents, but

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* Melting points are quoted in parentheses in °C with dec. = decomposition. They were measured in sealed tubes.

soluble in dilute hydrochloric acid. Its Mn content was ca. 60% (atomic absorption spectroscopy). In the $[Mn_2(CO)_{10}]/Ph_3As$ reaction in xylene, this black precipitate contained ca. 40% of the manganese in the mixture.

If a solution of Ph_3As (0.5 g) in xylene (50 ml) was boiled for 8 h, the original arsine was recovered unchanged.

Thermal decomposition of $[Mn_2(CO)_8(AsPh_3)_2]$

$[Mn_2(CO)_8(AsPh_3)_2]$ (1 g, 0.95 mmol) in n-butanol (20 ml) was sealed in an evacuated Carius tube and heated to 120°C for 5 h. After cooling, the tube was opened. The precipitated orange crystals of $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ were filtered off and purified as before (yield 30%). A GLC analysis of the yellow filtrate showed that it contained 1.1 mmol of C_6H_6.

Thermal reaction of $[Mn_2(CO)_8(AsPh_3)_2]$ with tertiary phosphines and arsines

Solutions of $[Mn_2(CO)_8(AsPh_3)_2]$ (0.25 g) and R_3P (mole ratio 1 : 5; R = Ph, $p\text{-}MeC_6H_4$, or $p\text{-}ClC_6H_4$) in n-butanol (10 ml) were heated to reflux. The reaction was monitored by IR spectroscopy, and when all of the $[Mn_2(CO)_8(AsPh_3)_2]$ had been consumed (4—6 h) the hot mixture was filtered and cooled. The deposited cream crystals were recrystallized from pentane/benzene mixtures to give $[Mn(H)(CO)_3(PR_3)_2]$ in 30—40% yield for R = Ph (dec. 205°C), $p\text{-}MeC_6H_4$ (253—254°C) and $p\text{-}ClC_6H_4$ (191—195°C).

Under the same conditions, $(o\text{-}MeC_6H_4)_3P$ and $(p\text{-}ClC_6H_4)_3As$ gave $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ only.

If n-butanol was replaced by xylene, identical results were obtained.

Reaction of $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ with Ph_3P

A solution of $[Mn_2(CO)_8(AsPh_2)_2]$ (0.25 g) and Ph_3P (mole ratio 1 : 5) in n-butanol were heated to reflux for 7 h. On cooling it gave red crystals (dec. 172°C) for which C = 61.1% and H = 3.7%.

All of the products, or close relatives of them, have been reported previously. Consequently, although we have characterised them by analyses (C, H, N, or Cl), IR spectroscopy, and ^1H NMR spectroscopy, these data may be found elsewhere [1], and we have not tabulated them here. Typical $\nu(CO)$ frequencies are quoted in the Results and Discussion section.

Results and discussion

The two types of dinuclear complexes which we have isolated from reactions of tertiary phosphines or arsines with decacarbonyldimanganese are yellow-orange, air-stable crystalline solids. They have structures I and II (Fig. 1). They may be distinguished by their analyses and IR spectra in the 1900—2100 cm^{-1} region, e.g. for $[Mn_2(CO)_8(AsPh_3)_2]$ of class I $\nu(CO)$ = 1953 (10) and 1982 (0.7) cm^{-1}, for $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ of class II $\nu(CO)$ = 1953 (8.5), 1981(sh), 1991 (10) and 2045 (8.8) cm^{-1}, and for $[Mn_2(CO)_8\{\mu\text{-}As(C_6H_4)_2NH\}_2]$ of class II $\nu(CO)$ = 1965 (7.3), 1978 (10), 1983(sh) and 2042 (9.4) cm^{-1}. Spectra were measured in carbon disulphide solution with relative peak heights in parentheses (sh = shoulder). They have been discussed in detail in refs. 1 and 10.

The only products isolated from the photochemical reactions of tertiary phosphines or arsines, L, with $[Mn_2(CO)_{10}]$ were $[Mn_2(CO)_8(L)_2]$ derivatives of class I. There was spectroscopic evidence for the formation of the closely related $[Mn_2(CO)_9(L)]$ [1], but not for compounds of class II. No carbonyl-containing products could be detected in reactions involving $(o\text{-}MeC_6H_4)_3P$ or $(o\text{-}MeC_6H_4)_3As$ even though all of the $[Mn_2(CO)_{10}]$ disappeared. The large size of these ligands may prevent CO substitution.

The thermal reaction of the ligands L with $[Mn_2(CO)_{10}]$ (mole ratio 2 : 1 in a refluxing solvent) gave no isolable products for L = $(o\text{-}MeC_6H_4)_3P$ in n-butanol, $(\alpha\text{-}C_{10}H_7)_3P$ (n-butanol), $(o\text{-}MeC_6H_4)_3As$ (n-butanol), $(o\text{-}ClC_6H_4)_3As$ (xylene), or $(\alpha\text{-}C_{10}H_7)_3As$ (xylene or n-hexanol). This again is probably a steric effect. Other phosphines gave $[Mn_2(CO)_2(L)_2]$ derivatives of class I, but in much lower yields than from the photochemical reactions. The exception was $Ph(\alpha\text{-}C_{10}H_7)_2P$ which formed as its sole product in xylene solution a derivative of type II. It was observed in trace amounts only and was identified by its IR spectrum in the 1800—2100 cm^{-1} region [$\nu(CO)$ = 1946 (4.7), 1982 (8.5), 1992 (10) and 2049 (5.4) cm^{-1}, c.f. $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ above].

The organo-derivatives of 5,10-dihydrophenarsazines, L = $HN(C_6H_4)_2AsR$ (Fig. 1), gave no isolable products when heated with $[Mn_2(CO)_{10}]$ (mole ratio 2.5 : 1) in refluxing n-butanol for 12 h if R = Me or Et, but if R = Pr^i the $[Mn_2(CO)_9(L)]$ and $[Mn_2(CO)_8(L)_2]$ derivatives of class I were obtained. Under the same conditions related ligands where R = Ph or $p\text{-}MeOC_6H_4$ gave only $[Mn_2(CO)_8(\mu\text{-}As(C_6H_4)_2NH)_2]$ of class II. The same product was obtained in boiling xylene for R = $\alpha\text{-}C_{10}H_7$, $o\text{-}MeC_6H_4$, Ph, $p\text{-}MeOC_6H_4$, $PhCH_2$, PhO, Pr^i, MeO and *cyclo*-C_6H_{11}.

Of the triarylarsines, only $(p\text{-}Me_2NC_6H_4)_3As$ gave a product of class I (yield 18%) in high boiling solvents. All others that we investigated formed products of class II. Monitoring these reactions by IR spectroscopy showed that intermediates were present in the mixtures, but not in large amounts. Consequently they could not be identified unambiguously. The reaction yields were solvent dependent; for example Ph_3As gave $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ in yields of 16% from diglyme (b.p. 196°C), 20% from dekalin (b.p. 195°C), 21% from n-butanol (b.p. 113°C) and 25% from xylene (b.p. 139°C). Similar results were obtained using n-octane, toluene or n-hexanol as reaction solvents. Other $(p\text{-}XC_6H_4)_3As$ also formed $[Mn_2(CO)_8\{\mu\text{-}As(C_6H_4X\text{-}p)_2\}_2]$ in yields comparable to the above when X = MeO, Me, Cl or F.

Current evidence suggests that both the photochemical and thermal CO substitution reactions of $[Mn_2(CO)_{10}]$ proceed largely or completely with scission of the Mn—Mn bond [5,6,11 and refs. therein]. The $[Mn(CO)_5]^{\bullet}$ radicals thus formed undergo rapid replacement of CO by the incoming ligand L. The resultant $[Mn(CO)_4(L)]^{\bullet}$ moieties recombine to give $[Mn_2(CO)_9(L)]$ and $[Mn_2(CO)_8(L)_2]$ with, eventually, complete conversion to the latter. The $[Mn_2(CO)_8(L)_2]$ also undergo reversible Mn—Mn bond fission. At the same time the $[Mn(CO)_5]^{\bullet}$ and, presumably, $[Mn(CO)_4(L)]^{\bullet}$ radicals may decompose either by reaction with adventitious oxygen or water or by a thermal process involving loss of all CO and L ligands.

It is possible to account for Lambert's reaction in the context of these ideas if it is assumed that the $[Mn(CO)_4(AsR_3)]^{\bullet}$ radicals undergo another thermal reaction at elevated temperatures. In this, homolytic fission of an As—R bond gives a coordinatedly unsaturated $[Mn(CO)_4(AsR_2)]^{\cdot}$ fragment which dimerises to II, and a $R^{\cdot}$ radical, which abstracts a hydrogen atom from the solvent to give RH. This mechanism accounts for the formation of C_6H_6 and $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_3]$ from Ph_3As and $[Mn_2(CO)_{10}]$ [2], and for the low product yields. These last are a consequence of the high temperatures necessary to bring about Lambert's reaction. Elevated temperatures in their turn accelerate the competing thermal decomposition of the $[Mn(CO)_5]^{\cdot}$ and $[Mn(CO)_4(AsR_3)]^{\cdot}$ radicals which result in the total loss of their ligands.

The thermal decomposition of $[Mn_2(CO)_8(AsPh_3)_2]$ to $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$ and C_6H_6 in a sealed tube is also explicable using the above mechanism if it is assumed that the $[Mn(CO)_4(AsPh_3)]^{\cdot}$ radicals arise from homolytic cleavage of their dimer. However it does not mean that $[Mn_2(CO)_8(AsPh_3)_2]$ is necessarily an intermediate in the direct reaction of $[Mn_2(CO)_{10}]$ and Ph_3As. The $[Mn(CO)_4(AsPh_3)]^{\cdot}$ radicals may decompose thermally to $[Mn(CO)_4(AsPh_2)]$ before they are able to dimerise.

The yields of $[Mn_2(CO)_8\{\mu\text{-}As(C_6H_4)_2NH\}_2]$ are a function of the group R which leaves $HN(C_6H_4)_2AsR$. Monitoring studies using IR spectroscopy suggest that these yields reflect the ease of the reaction. This would not be surprising as there are two reaction competing for the ultimate fate of the manganese carbonyl; Lambert's reaction and total decomposition. To a crude approximation, the latter acts as an internal clock for the former. Consequently the formation of $[Mn_2(CO)_8\{\mu\text{-}As(C_6H_4)_2NH\}_2]$ would be expected to be more rapid in those reactions in which its yields are greatest. The times that the reactions require for completion are also consistent with this proposition. The yields and hence reaction rates decline along the series $R = \alpha\text{-}C_{10}H_7(\alpha\text{-naphthyl}) > o\text{-}MeC_6H_4 \sim Ph \sim p\text{-}MeOC_6H_4 > PhCH_2 \sim PhO > Pr^i \sim MeO$. Reaction times increase along the above series. As the aryl radicals produced would be of the σ-type they are not particularly stabilized by resonance. They and the Pr^i group probably owe their places in the above series to their bulk. Their departure would relieve the crowding about the arsenic atom in the $[Mn(CO)_4(AsR_3)]^{\cdot}$ radicals, an effect which would be greater for the more bulky R. On the other hand, $PhCH_2^{\cdot}$ and $PhO^{\cdot}$ are stabilized by resonance, and consequently they have a high position in the series even though they are not particularly bulky.

Generally, Lambert's reaction does not occur with triarylphosphines even though $[Mn(CO)_4(PR_3)]^{\cdot}$ radicals are formed [1,5,6, and 11], and would be expected to be more crowded about phosphorus than arsenic for a given combination of organo groups R. The probable reason is that the P—C bond dissociation energy (71 kcal/mol in Ph_3P and 65 kcal/mol in Me_3P [12]) is much greater than the As—C bond dissociation energy (60 kcal/mol in Ph_3As and 52 kcal/mol in Me_3As [13]). $Ph(\alpha\text{-}C_{10}H_7)_2P$ is exceptional, but here steric effects must be very important.

It is worth pointing out that if a ligand is too bulky, e.g. $(o\text{-}MeC_6H_4)_3E$ or $(\alpha\text{-}C_{10}H_7)_3E$ (E = P or As), it is unable to coordinate to manganese (cf. the photochemical reaction). As such ligands do not undergo Lambert's reaction, this is unlikely to proceed by a route which does not involve prior coordination of the ligand to manganese. Furthermore, in the absence of $[Mn_2(CO)_{10}]$, Ph_3As is stable in boiling xylene, etc., and may be recovered unchanged from it. Consequently, a reaction of the arsine prior to coordination to the metal is also an unlikely reaction pathway.

The thermal reaction of [$Mn_2(CO)_8(AsPh_3)_2$] with a large excess of R_3P to give [$Mn(H)(CO)_3(PR_3)_2$] parallels the similar reactions of [$Mn_2(CO)_{10}$] or [$Mn_2(CO)_8(PR_3)_2$] [1]. It provides an example of yet another class of reactions of the [$Mn(CO)_4(AsPh_3)$]$^\cdot$ radical, as it is clear that replacement of Ph_3As by a more nucleophilic phosphine takes place more readily than loss of $Ph^\cdot$. Equally, those ligands which would be expected to replace Ph_3As more slowly because they are too bulky, e.g. (o-$MeC_6H_4)_3P$, or insufficiently nucleophilic, e.g. R_3As, do not prevent the conversion of I to II. If the formation of [$Mn(H)(CO)_3$-$(PR_3)_2$] took place with the prior conversion of I to II, the product would be expected to be analogous to that obtained from the reaction of [$Mn_2(CO)_8$-$(\mu$-$AsPh_2)_2$] with Ph_3P (see below). As it is not, such a scheme is ruled out. Consequently we suggest that the reaction of an excess of R_3P with [$Mn_2(CO)_8$-$(L)_2$] (L = tertiary phosphine or arsine) proceeds with arsine displacement to give [$Mn(CO)_4(PR)_3$]$^\cdot$ and then [$Mn(CO)_3(PR_3)_2$]$^\cdot$ radicals. These last, being unable to dimerise for steric reasons in most instances, abstract a hydrogen atom from the reaction solvent to give [$Mn(H)(CO)_3(PR_3)_2$] cf. refs. 6 and 14.

The product from the [$Mn_2(CO)_8(\mu$-$AsPh_2)_2$]/Ph_3P reaction does not appear to be a hydride, even though its C and H analyses are close to those anticipated for [$Mn(H)(CO)_4(PPh_3)$] (C, 61.4; H, 3.7%). Furthermore its IR spectrum in chloroform shows ν(CO) frequencies (with relative peak heights in parentheses) at 1949 (10), 1990 (8.2) and 2048 (7.8) cm^{-1}. In this solvent [$Mn(H)(CO)_4$-(PPh_3)] would be expected to form [*cis*-$MnCl(CO)_4(PPh_3)$] for which $\nu(CO) =$ 1953, 2007, 2027 and 2093 cm^{-1} [15]. The analysis is close to those expected for either [$Mn(CO)_4(AsPh_2)(PPh_3)$] (C, 62.1; H, 3.8%) or [$Mn_2(CO)_6(\mu$-$AsPh_2)_2$-$(PPh_3)_2$] (C, 62.7; H, 4.0%). Either formulation is consistent with the IR spectrum but we were unable to characterise the compound more completely.

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