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REACTIONS OF BIS(TRIPHENYLPHOSPHINE)IMINIUM PENTACARBONYLMANGANATE(-I) WITH GROUP IV HALIDES

D. Neil Duffy and Brian K. Nicholson*
School of Science, University of Waikato, Hamilton, N.Z.

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SUMMARY

Bis(triphenylphosphine)iminium pentacarbonylmanganate(-I) [PPNMn(CO)$_5$] has been shown to be a convenient alternative to NaMn(CO)$_5$ in the synthesis of alkyl, germyl or stannyl derivatives of Mn(CO)$_5$. Reactions of PPNMn(CO)$_5$ with halosilanes follow an anomalous route to give Mn(CO)$_4$Cl$_2^-$ as a major manganese containing product.

INTRODUCTION

The versatile synthetic reagent Mn(CO)$_5^-$ is usually obtained in solution as the Na$^+$ salt by reduction of the dimer Mn$_2$(CO)$_{10}$ with sodium amalgam in ether solvents [1,2]. The resulting solutions are generally used without further purification which may lead to complications arising from incomplete reduction, formation of polynuclear anionic species or incorporation of mercury-containing by-products. The solid salt NaMn(CO)$_5$ is not readily isolated in a pure state, which leads to difficulties when accurately known stoichiometries are required, or when Mn(CO)$_5^-$ is required in solvents other than the ethers commonly used for the reduction. Furthermore, extensive ion-pairing is known to occur in solutions of NaMn(CO)$_5$ [3,4] which may have a profound effect on reactivity patterns [5].

A possible way of overcoming these problems is via the ionic salt PPNMn(CO)$_5$ [PPN$^+$≡(Ph$_3$P)$_2$N$^+$]. Ruff [6] and others [7] have shown that the PPN$^+$ cation is useful for isolating otherwise reactive anions as pure, relatively air-stable salts and this stabilising effect can apparently be partially carried over into solution [8]. Furthermore the PPN^+ cation is non-polarising and is unlikely to perturb the reactivity of $Mn(CO)_5^-$ by ion-pairing interactions [5]. Despite the attractions of this system there has apparently been only one report [9] of the use of $PPNMn(CO)_5$ in salt-elimination reactions. To explore this potential utility we have investigated the reactions of $PPNMn(CO)_5$ with some Group IV halides.

RESULTS AND DISCUSSION

General Properties of $PPNMn(CO)_5$

Pure samples of $PPNMn(CO)_5$ can be readily isolated in >75% yield, based on $Mn_2(CO)_{10}$ used, following the procedure described by Ruff [6] for $PPNCo(CO)_4$. The resulting salt forms pale-yellow crystals that can be manipulated in air for short periods without decomposition, although visible darkening occurs after several days. Stored at -30°C under nitrogen the solid is unchanged after a year.

$PPNMn(CO)_5$ is very soluble in THF and CH_2Cl_2, sparingly so in benzene and Et_2O and insoluble in saturated hydrocarbon solvents. In CH_2Cl_2 or THF solution $PPNMn(CO)_5$ gives two ν_{CO} bands in the infrared spectrum at 1892 cm^{-1} and 1854 cm^{-1} $[A_2''+E']$ characteristic of free D_{3h} $Mn(CO)_5^-$ unperturbed by ion-pairing [3,4]. As a suspended solid in nujol the E' band is split into two (1856 cm^{-1}, 1839 cm^{-1}) presumably due to lowering of local symmetry by crystal packing effects.

Reactions of $PPNMn(CO)_5$ with alkyl, germyl and stannyl halides

Results of reactions of $PPNMn(CO)_5$ with $PhCH_2Br$, R_3SnCl and Me_3GeCl are compared in Table 1 with those obtained in similar reactions using $NaMn(CO)_5$. It is apparent that $PPNMn(CO)_5$ is reacting in the same manner as $NaMn(CO)_5$ (eqn. 1).

$$RX + M^+ + Mn(CO)_5^- \rightarrow RMn(CO)_5 + MX \qquad \text{........ (1)}$$

$[M^+ = Na^+ \text{ or } PPN^+;\ RX = PhCH_2Br, Ph_3SnCl, Bu_3SnCl, Me_3GeCl]$

Thus $PPNMn(CO)_5$ is a suitable reagent in Et_2O or CH_2Cl_2 for salt elimination reactions with carbon, germanium or tin halides. However it offers no real advantages in routine syntheses over $NaMn(CO)_5$ which normally gives uncomplicated reactions with these Group IV halides. Nevertheless the ease of handling of $PPNMn(CO)_5$ simplifies the experimental procedure, especially if several similar derivatives are required, and the successful application in CH_2Cl_2 suggests $PPNMn(CO)_5$ is the reagent of choice if non-ether solvent systems are required.

Table 1 Reactions of $PPNMn(CO)_5$ with C, Ge and Sn halides

Halide	Solvent	Product	Yield	Literature*
$PhCh_2Br$	Et_2O	$PhCH_2Mn(CO)_5$	74%	70% (ref 10)
Bn_3SnCl	Et_2O	$Bu_3SnMn(CO)_5$	80%	52% (ref 11)
$PhCH_2Br$	CH_2Cl_2	$PhCH_2Mn(CO)_5$	63%	-
Ph_3SnCl	CH_2Cl_2	$Ph_3SnMn(CO)_5$	60%	-
Me_3GeCl	CH_2Cl_2	$Me_3GeMn(CO)_5$	-	-

*Reported yields in similar reactions using $NaMn(CO)_5$

Reactions of $PPNMn(CO)_5$ with silicon halides

In contrast to the systems involving other Group IV halides, reaction of $PPNMn(CO)_5$ with Me_3SiCl, Me_3SiBr or Ph_3SiCl was unsatisfactory as a route to species with Si-Mn bonds. In each case a major manganese containing product was $Mn(CO)_4X_2^-$ [X=Cl or Br] as the PPN^+ salt. In an attempt to elucidate the mechanism of formation of this product the interaction of Me_3SiCl with $PPNMn(CO)_5$ was studied in detail. When the reagents were mixed together in CH_2Cl_2 a rapid reaction occurred and after 10 minutes infrared examination showed no $Mn(CO)_5^-$ was present in solution, the major feature in the carbonyl stretching region being a broad band at 2010 cm^{-1} arising from an, as yet, unidentified species. After an hour at room temperature a band at 1930 cm^{-1} (from $Mn(CO)_4Cl_2^-$) is reasonably intense and after 24 hours this is the dominant product. Attempts to work up the system after 15 minutes to identify the initial product met with little success. Addition of hexane to remove ionic species led to varying amounts of PPNCl, $PPNMn(CO)_4Cl_2$ and

$PPNMn(CO)_5$ being precipitated with small amounts of $Mn_2(CO)_{10}$, $Me_3SiMn(CO)_5$ (<2%) and $ClMn(CO)_5$ remaining in solution.

In an analogous manner Me_3SiBr and $PPNMn(CO)_5$ in CH_2Cl_2 gave $PPNMn(CO)_4Br_2$ as the main product. Similarly Ph_3SiCl gave $Mn(CO)_4Cl_2^-$ in a slower, less clean reaction and it is noteworthy (vide infra) that no $Mn_3(CO)_{14}^-$ was detected in the system at any stage.

Reaction between Me_3SiCl and $PPNMn(CO)_5$ in Et_2O is slow because of the heterogeneous nature of the system but again $Mn(CO)_4Cl_2^-$ was the major product after 24 hours at room temperature, with very little ether-soluble metal-carbonyl containing product.

Unusual reactions of metal-carbonyl anions with chlorosilanes are well documented [12,13,14]; indeed $Fe(CO)_2Cp^-$ is the only anion that consistently gives silyl derivatives under normal conditions [1,2,15]. Only in the absence of solvent [14] or with a non-polar solvent such as hexane [16] do coupling reactions between $NaMn(CO)_5$ and silicon chlorides occur successfully. In a detailed study of the reaction between $NaMn(CO)_5$ and Ph_3SiCl in THF Curtis [12] showed that $Mn_3(CO)_{14}^-$ was the major metal-containing product, with the formation of $Ph_3SiOSiPh_3$ accounting for the silicon group. A mechanism involving silicon attack at a coordinated carbonyl group was proposed, and similar explanations have accounted for products found in cobalt carbonyl systems [13]. In contrast, no $Mn_3(CO)_{14}^-$ was encountered in the reactions of $PPNMn(CO)_5$ with silicon halides in the present study, suggesting that the counter ion present has an important influence on the reaction pathway.

The route to formation of $Mn(CO)_4Cl_2^-$ remains unclear. A possible intermediate is $Me_3SiMn(CO)_5$ since it was shown independently to react with PPNCl to give $Mn(CO)_4Cl_2^-$ as a major product. (In contrast, soluble halides lead to a reversible dissociation of the Sn-Mn bond in $Ph_3SnMn(CO)_5$ [17].) However infrared evidence suggests that $Me_3SiMn(CO)_5$ is not the rapidly formed initial product. Similarly no appreciable amounts of $ClMn(CO)_5$ were detected at any stage, although this too reacts with PPNCl to give $Mn(CO)_4Cl_2^-$ under mild conditions. Although the details remain unresolved it can be concluded that $PPNMn(CO)_5$ is no more useful than $NaMn(CO)_5$ in the preparation of silicon-manganese bonds. This suggests that ion-pairing effects are not responsible for the anomalous reactions previously observed.

EXPERIMENTAL

General

All reactions were carried out under oxygen free nitrogen using standard techniques. THF and Et_2O were distilled from sodium benzophenone ketyl immediately before use. Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer. $Mn_2(CO)_{10}$, Me_3SiCl, Ph_3SiCl, Ph_3SnCl and Bu_3SnCl were obtained commercially. PPNCl [6], PPNBr [6], Me_3SiBr [18], $Me_3SiMn(CO)_5$ [14], $ClMn(CO)_5$ [19] and $BrMn(CO)_5$ [19] were prepared using methods available in the literature.

Preparation of $PPNMn(CO)_5$

This was carried out using the method of Ruff and Schlientz [6]. $Mn_2(CO)_{10}$ (2.0g, 5.1 mmol) in THF (25 cm^3) was stirred for 90 minutes with excess 1% sodium amalgam. A solution of PPNCl (5g, 8.7 mmol) in CH_2Cl_2 (25 cm^3) was added and after 15 minutes precipitated NaCl was filtered off using a glass sinter. The filtrate was evaporated to dryness under vacuum leaving a yellow residue which was recrystallised from CH_2Cl_2/Et_2O to give $PPNMn(CO)_5$ (5.5g, 75%) as pale yellow crystals.

Reaction of $PPNMn(CO)_5$ with $PhCH_2Br$

A solution of $PPNMn(CO)_5$ (0.7g, 0.95 mmol) in CH_2Cl_2 (10 cm^3) was treated with $PhCH_2Br$ (0.29g, 1.7 mmol) and the mixture was stirred for 12 hours. Hexane (10 cm^3) was added to precipitate PPNBr. The filtrate was evaporated to dryness and the residue sublimed (30°C/0.1 mm) on to a cold finger to give $PhCH_2Mn(CO)_5$ (0.18g, 63%) [10]. A similar reaction in Et_2O gave $PhCH_2Mn(CO)_5$ in 74% yield.

Reaction of $PPNMn(CO)_5$ with Ph_3SnCl

$PPNMn(CO)_5$ (0.45g, 0.6 mmol) and Ph_3SnCl (0.3g, 0.6 mmol) were stirred together in CH_2Cl_2 (10 cm^3) for an hour. After the addition of hexane (20 cm^3) the mixture was filtered and solvents were evaporated to give $Ph_3SnMn(CO)_5$ (0.19g, 60%) [20].

Similar reactions of $PPNMn(CO)_5$ with Bu_3SnCl (in Et_2O) or Me_3GeCl (in CH_2Cl_2) gave $Bu_3SnMn(CO)_5$ (80%) [11] or $Me_3GeMn(CO)_5$ [21].

Reaction of $PPNMn(CO)_5$ with Me_3SiCl

A] $PPNMn(CO)_5$ (0.7g, 0.95 mmol) and Me_3SiCl (0.17g, 1.5 mmol) were stirred for 12 hours in Et_2O (50 cm^3). The solid present was filtered off, and after recrystallisation from CH_2Cl_2/Et_2O/hexane was shown to be $PPNMn(CO)_4Cl_2$ by comparison with an authentic sample. The original filtrate was evaporated to dryness to leave a small residue containing $Mn_2(CO)_{10}$ and $ClMn(CO)_5$ (by i.r.).

B] $PPNMn(CO)_5$ (0.72g, 1 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and to this was added Me_3SiCl (0.17g, 1.5 mmol). After 10 minutes an infrared spectrum showed a strong band at 2010 cm^{-1} with weaker peaks at 2120 cm^{-1}, 2053 cm^{-1} and 1930 cm^{-1} and complete absence of absorptions at 1892 cm^{-1} and 1854 cm^{-1} from $Mn(CO)_5^-$. After an hour the peak at 1931 cm^{-1} began to dominate the spectrum. Removal of solvent after 24 hours left a residue which was recrystallised from CH_2Cl_2/Et_2O to give $PPNMn(CO)_4Cl_2$ (0.25g).

C] The reaction in B was repeated except that hexane (20 cm^3) was added after 15 minutes to precipitate ionic products. The yellow precipitate formed was found (by i.r.) to be a mixture of $PPNMn(CO)_5$, $PPNMn(CO)_4Cl_2$ and PPNCl. The filtrate was evaporated to dryness and sublimation of the residue gave $Me_3SiMn(CO)_5$ (0.005g, 2%).

D] The reaction in B was repeated except that solvent was removed in vacuum after 15 minutes. The residue was a mixture of $PPNMn(CO)_5$ and $PPNMn(CO)_4Cl_2$, with no $Me_3SiMn(CO)_5$ being detectable.

Reaction of PPNCl with $Me_3SiMn(CO)_5$

A mixture of PPNCl (0.55g, 1 mmol) and $Me_3SiMn(CO)_5$ (0.12g, 0.5 mmol) in Et_2O (15 cm^3) was stirred at room temperature for 24 hours. The solid present was identified as $PPNMn(CO)_4Cl_2$ and infrared examination of the supernatant showed that no $Me_3SiMn(CO)_5$ remained.

Preparation of PPNMn(CO)$_4$Cl$_2$

This was prepared by a modification of literature methods [22,23]. $Mn(CO)_5Cl$ (0.2g, 0.85 mmol) and PPNCl (0.44g, 0.8 mmol) were dissolved in 1,1,2,2-tetrachloroethane and the mixture heated to 50°C for 3 hours. Petroleum ether (150 cm^3) was added to precipitate the product which was recrystallised from dichloromethane/petroleum ether to give creamy-white crystals of $PPNMn(CO)_4Cl_2$ (0.34g, 56%) ν_{CO} (CH_2Cl_2) 2088(w), 2023(s), 1982(w), 1931(s) cm^{-1}.

Similarly PPNBr and $BrMn(CO)_5$ in tetrachloroethane at 60°C for 4 hours gave, after work-up as described above, $PPNMn(CO)_4Br_2$ in 80% yield as orange crystals ν_{CO} (CH_2Cl_2) 2087(w), 2011(s), 1980(m), 1931(s) cm^{-1}

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