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ARSENITES AND ANTIMONITES AS LIGANDS TOWARD π-CYCLOPENTADIENYLMANGANESE TRICARBONYL

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SUMMARY

π-Cyclopentadienyldicarbonylmanganese(I) complexes of methyl, ethyl, butyl and phenyl arsenites and antimonites have been prepared for comparison with the analogous phosphite systems. The carbonyl IR spectra suggest that the order of decreasing electron density on the manganese atom is $Sb(OR)_3 \gtrsim P(OR)_3 > As(OR)_3$, and $E(O\text{-alkyl})_3 > E(O\text{-aryl})_3$ where $E = P$, As, and Sb.

INTRODUCTION

Arsenites and antimonites[1], unlike phosphites[2], have been used only infrequently as ligands toward metal carbonyls. Because the nature of metal–ligand bonding is greatly influenced by the residue attached to the ligand, there is ample reason to extend the study of $P(OR)_3$ ligand systems to $As(OR)_3$ and $Sb(OR)_3$. As a Lewis acid, the π-cyclopentadienylmanganese dicarbonyl moiety was chosen because of the diagnostic characteristics of the carbonyl IR bands[3].

RESULTS AND DISCUSSION

Strohmeier and Müller[4] prepared π-$C_5H_5Mn(CO)_2P(OR)_3$ ($R = CH_3$, C_2H_5, n-C_4H_9, and C_6H_5) by photolysis of $C_5H_5Mn(CO)_3$ in tetrahydrofuran (THF) solution. The $C_5H_5Mn(CO)_2THF$ complex is unstable at room temperature and in the presence of a variety of ligands, L, decomposes to $C_5H_5Mn(CO)_2L$. In this project monosubstituted products having $L = P(OR)_3$, $As(OR)_3$ and $Sb(OR)_3$ ($R = CH_3$, C_2H_5, n-C_4H_9, and C_6H_5) were prepared in a similar manner. In most arsenites and antimonites, yellow solids were obtained which decompose before melting. Except for the triphenyl phosphite derivative, the phosphite adducts are oils[4]. Complete carbonyl IR spectra have recently been reported for the methyl and phenyl phosphite systems[5]. Only the symmetric carbonyl IR mode was reported previously in the ethyl and butyl phosphite compounds[4], and they were reprepared here in order to complete the assignment. $C_5H_5Mn(CO)_2L$ systems show two carbonyl bands, a symmetric mode (A') and an antisymmetric mode (A''). A decrease in the frequency of these two bands compared with $C_5H_5Mn(CO)_3$ is thought to result from an increase in negative charge on Mn[6]. This apparent charge migration can result from decreased π-acidity or increased σ-donor ability of L compared with CO. From the IR frequencies alone, however, the σ–π bonding between Mn and L must be considered together and cannot be separated with certainty. It should be mentioned that an even more fundamental consideration is the uncertain validity of *d* orbital use for transmitting π-electron density onto the main group element atom. Spectral data are frequently consistent with *d* orbital involvement, but one cannot rule out alternative explanations[7].

It is evident from Table 1 that the amount of electron density on the manganese atom decreases in the order $Sb(OR)_3 \gtrsim P(OR)_3 > As(OR)_3$. Such a sequence is not found in the analogous $C_5H_5Mn(CO)_2E(C_6H_5)_3$ compounds (E = P, As, and Sb), where the trend follows the polarizability of E, $SbR_3 > AsR_3 > PR_3$[8]. The trialkoxide systems will not necessarily mimic the triphenyl analogues in either σ-donor or π-acceptor character, however. First, the highly electronegative oxygen atoms attached directly to the metalloid atom could contract the high energy metalloid orbitals and make π-bonding between Mn and L different from the R_3E complexes[9]. This effect was invoked, for example, to account for the anomalous trend in CO frequencies of $Cl_3MCo(CO)_4$ systems, where M = Si, Ge, and Sn[10]. Secondly, the σ-donor ability of the central atom will also be affected by the electronegativity of the oxygen atoms, and by the variations in angles between the substituents on the metalloid atom. These variables make detailed σ–π comparisons between $E(OR)_3$ and ER_3 compounds hazardous. Comparisons within a series of like substituents, where the number of variables is reduced, is more reasonable.

TABLE 1

IR SPECTRA (cm^{-1}) OF π-$C_5H_5Mn(CO)_2 \cdot E(OR)_3$ COMPOUNDS[a]

E	*R* = CH_3		C_2H_5		*n*-C_4H_9		C_6H_5	
	A'	*A''*	*A'*	*A''*	*A'*	*A''*	*A'*	*A''*
P	1954 s[b]	1891 s[b]	1949 s	1886 s	1948 s	1886 s	1970 s[b]	1909 s[b]
As	1969 s	1907 s	1962 s	1904 s	1962 s	1905 s	1978 s	1932 s
Sb			1947 s[c]	1881 s[c]	1943 s	1879 s	1964 s	1908 s

[a] Cyclohexane solvent. [b] Ref. 5. [c] Nujol mull.

In order to account for the carbonyl frequency trend here, the arsenite would have to be a poorer σ-donor and/or a better π-acceptor than the phosphite or antimonite. It is difficult to reconcile an equivalency in phosphorus and antimony σ-donor ability while arguing that arsenic is a worse σ-donor. The proton basicity of triphenylpnicogens, in fact, opposes this trend[11], although protonic acid measurements are not in general transferable to metal acceptor systems. So, although σ and π bonding between Mn and E compete in determining the metal electron density, the apparently greater electron density on Mn in $P(OR)_3$ and $Sb(OR)_3$ systems compared to $As(OR)_3$ can be understood by assuming enhanced π acidity due to improved matching of the size and energy of the arsenic π orbitals to those of manganese as a result of arsenic orbital contraction by the oxygen field. These higher energy π orbitals could be *d* orbitals, *p* orbitals, or some complex mixture of states.

In chromium, molybdenum and tungsten carbonyl compounds with $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]_3As$ as ligands the carbonyl frequencies indicate that there is more negative charge on the metal with the aminophosphine than with the arsine[12]. The same orbital contraction could be operative there although it would be valuable to have the aminostibine for comparison.

Within the alkoxides, the trend in decreasing electron density on the manganese atom is $E(O\text{-alkyl})_3 > E(O\text{-aryl})_3$. This fact has been observed on numerous occasions for E = P[2,3,8b]. It appears also to be true for E = As and Sb.

It has been shown that ^1H τ values of the ring protons correlate reasonably with $\nu(CO)$ although phosphorus donors do show some deviations[13]. Unfortunately, difficulty was encountered in recording the ^1H NMR spectra of these compounds because of their insolubility and tendency to decompose in solution.

EXPERIMENTAL

Materials

Samples of π-$C_5H_5Mn(CO)_3$ were obtained through the courtesy of Dr. G. G. Long of North Carolina State University and the Ethyl Corporation. Details of the preparation and characterization of many of the arsenites and antimonites will be published at a later date. Analyses were carried out by Chemalytics, Tempe, Arizona.

(1). *Syntheses*

The compounds were prepared using a procedure similar to that of Strohmeier and Müller[4]. In general, 1.5 g (7.5 mmole) of $C_5H_5Mn(CO)_3$ dissolved in THF (150 ml) was irradiated with a 100 watt UV lamp at 366 nm for five hours in an inert atmosphere while the solution was kept near Dry-Ice temperature. A stoichiometric amount of ligand was added to the resulting red solution of $C_5H_5Mn(CO)_2THF$. After warming to 60° for 20 min, the solvent was removed with vacuum and the remaining solid, except as indicated below, was placed in a vacuum sublimation apparatus at 40° to remove the unreacted $C_5H_5Mn(CO)_3$. Further purifications were effected as follows:

π-Cyclopentadienyldicarbonyl(trimethyl arsenite)manganese(I) $C_5H_5Mn(CO)_2As(OCH_3)_3$. The yellow-brown residue was extracted with CH_2Cl_2. The yellow powder remaining was collected and dried in vacuum; yield 11%; dec. point 115±10°. (Found: C, 34.50; H, 3.96. $C_{10}H_{14}O_5AsMn$ calcd.: C, 34.90; H, 4.07%.)

π-Cyclopentadienyldicarbonyl(triethyl arsenite)manganese(I) $C_5H_5Mn(CO)_2As(OC_2H_5)_3$. The yellow residue was dissolved in ethanol and filtered into high boiling petroleum ether. The yellow powder which precipitated was collected and dried in vacuum; yield 24%; dec. point 110±10°. (Found: C, 40.66; H, 5.26. $C_{13}H_{20}O_5AsMn$ calcd.: C, 40.43; H, 5.18%.)

π-Cyclopentadienyldicarbonyl(tributyl arsenite)manganese(I) $C_5H_5Mn(CO)_2As(OC_4H_9)_3$. The yellow oil remaining after the initial solvent removal was dissolved in hexane and the solution filtered. The hexane was removed and the resulting oil heated to 80–100° under vacuum to sublime off the unreacted $C_5H_5Mn(CO)_3$. The oil was again dissolved in hexane and passed through a 25 cm chromatography column packed with acid-washed Al_2O_3. The last yellow layer to appear contained the desired compound; yield 17%, b.p. 190° (dec.). (Found: C, 48.26; H, 7.01. $C_{19}H_{32}$-

O_5AsMn calcd.: C, 48.51; H, 6.87%.) The ^1H NMR spectrum in CS_2 is in accordance with that expected. The τ value for the C_5H_5 protons is 5.52 relative to TMS.

π-Cyclopentadienyldicarbonyl(triphenyl arsenite)manganese(I) $C_5H_5Mn(CO)_2As(OC_6H_5)_3$. After the initial solvent removal the dark brown-red oil was dissolved in heptane and filtered into ethanol. The yellow crystals thus formed were further purified by dissolving in CH_2Cl_2 and filtering into cold ethanol. The yellow crystalline product was dried in vacuum; yield 46%; m.p. 129–130°. (Found: C, 65.60; H, 3.59. $C_{25}H_{20}O_5AsMn$ calcd.: C, 65.62; H, 3.81%.) The ^1H NMR spectrum in CS_2 shows the C_5H_5 protons at a τ value of 6.07 relative to TMS. The integrated intensity of the C_5H_5 protons to those of the phenyl ring is 1/3.

π-Cyclopentadienyldicarbonyl(triethyl antimonite)manganese(I) $C_5H_5Mn(CO)_2Sb(OC_2H_5)_3$. The yellow powder was dissolved in CH_2Cl_2 and filtered into ethanol. Upon cooling a yellow powder precipitated which was filtered and dried in vacuum; yield 19%; dec. point 105 ± 10°. (Found: C, 36.34; H, 4.40. $C_{13}H_{20}O_5SbMn$ calcd.: C, 36.06; H, 4.66%.)

π-Cyclopentadienyldicarbonyl(tributyl antimonite)manganese(I) $C_5H_5Mn(CO)_2Sb(OC_4H_9)_3$. The yellow brown solid was dissolved in hot CH_2Cl_2 and filtered into ethanol. Upon cooling a yellow powder precipitated. The compound was further purified by extracting with hot ethanol and evaporating the ethanol to dryness; yield 22%; dec. point, 95 ± 10°. (Found: C, 43.98; H, 6.45. $C_{19}H_{32}O_5SbMn$ calcd.: C, 44.12; H, 6.25%.)

π-Cyclopentadienyldicarbonyl(triphenyl antimonite)manganese(I) $C_5H_5Mn(CO)_2Sb(OC_6H_5)_3$. The brown yellow powder was extracted with ethanol, filtered, and the filtrate evaporated to dryness. The yellow oil resulting was dissolved in CH_2Cl_2 and passed through a chromatography column containing activated alumina. The second layer to appear was the desired product; yield 9%; m.p. 119–121°. (Found: C, 51.57; H, 3.68. $C_{25}H_{20}O_5SbMn$ calcd.: C, 51.20; H, 3.50%.)

The phosphite complexes were prepared as before[4] and their physical and chemical properties were in agreement with those previously reported[4,5].

(2). *IR spectra*

The IR spectra were recorded using a Perkin–Elmer 180 spectrometer. Samples were run in Fisher Spectroscopic Grade cyclohexane in 1.0 mm NaCl cells. The carbonyl bands are estimated to be accurate to ±1 cm^{-1}.

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