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REACTIONS OF CYCLIC ARSINES WITH IRON AND MANGANESE CARBONYLS

PATRICIA S. ELMES AND B. O. WEST
Department of Chemistry, Monash University, Clayton, Victoria, 3168 (Australia)
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SUMMARY

The cyclic arsines $(AsCH_3)_5$, $(AsC_2H_5)_5$ and $(AsC_6H_5)_6$ react with iron pentacarbonyl to yield products of general formula $[Fe(CO)_3]_2(AsR)_4$.

Dimanganese decacarbonyl and pentamethylcyclopentaarsine react in the presence of light at room temperature to give $Mn_2(CO)_8(AsCH_3)_5$ and at elevated temperatures to give $[Mn(CO)_3(AsCH_3)_4]_2$. Structures are proposed in which the Mn–Mn bond of $Mn_2(CO)_{10}$ is replaced by bridging arsenic chains.

INTRODUCTION

Cyclic pentaphosphines $(PR)_5$ react with Group VIA metal carbonyls[1,2] to give complexes in which the cyclic pentaphosphine ring is apparently still intact[3] and with $Fe(CO)_5$ to give binuclear derivatives $[Fe(CO)_3]_2(PR)_4$ ($R=CH_3$, C_2H_5, C_6H_5) in which a PR unit has been eliminated. The mass spectra of these latter compounds[1] showed no evidence for the existence of $(PR)_4$ cyclic phosphines in their structures. A notable difference is apparent between cyclic phosphines and arsines however in that cyclic pentaarsines react with Group VIA carbonyls[4] to give binuclear complexes in which mass spectral evidence indicates that arsine rings have been opened and the resulting chains of arsenic atoms are bridging between two metals. It is important therefore to establish the behaviour of cyclic arsines with $Fe(CO)_5$ to extend the comparison between the cyclic Group V compounds*. Furthermore in connection with the ability of cyclic arsine rings to open and form bridged compounds with metal carbonyls the reaction between a cyclic arsine and a binuclear metal carbonyl containing a metal–metal bond is of interest. Such carbonyls are claimed to facilitate the cleavage of As–As or P–P bonds in ligands[5].

RESULTS AND DISCUSSION

The cyclic arsines $(AsCH_3)_5$ and $(AsC_2H_5)_5$ react with $Fe(CO)_5$ to yield complexes $[Fe(CO)_3]_2(AsR)_4$, $R=CH_3$, C_2H_5. A single crystal X-ray study of

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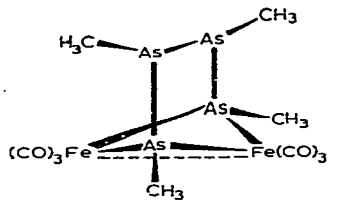
* A preliminary account[15] of the reaction of $(AsCH_3)_5$ has been published in the report of the Meeting on the Synthetic and Stereochemical Aspects of Coordination Chemistry, Nara, Japan, 1967.

the methyl derivative has conclusively demonstrated the existence of a chain, not a ring, of arsenic atoms in this complex, the end arsenic atoms bridging the two iron atoms, (I)[6]. The formal requirements of the EAN rule are met by postulating an Fe–Fe bond in the molecule. These atoms are 2.68 Å apart and are thus within the limits presently accepted for such bonds.



(I)

The ^{1}H NMR spectra of all samples of the compounds examined indicated only two kinds of alkyl groups in the molecules, thus eliminating the possibility of different isomeric forms of these complexes arising from different conformations of alkyl groups on the two central arsenic atoms. In each case the resonance peaks at lower field (Table 1) ($R=CH_3$, δ 2.32; $R=C_2H_5$, CH_3 δ 1.66 and CH_2 δ 2.81) are assumed to relate to alkyl groups attached to coordinated arsenic atoms[4,7] because of the expected deshielding of these alkyl groups.

The structure of the methyl substituted complex shows that the methyl groups attached to arsenic atoms 2 and 3 are *trans* to one another and no evidence has been obtained for a possible *cis* isomer. Structural isomerism has been observed, however, in other bridged derivatives such as $[C_5H_5FeAsR_2(CO)]_2$[8] and $[Fe(SR)(CO)_3]_2$[9,10].

The mass spectra of the alkyl arsenido compounds show peaks for the parent ions as well as those arising from the loss of CO to yield $Fe_2(AsR)_4^+$ followed by loss of R to give $Fe_2As_4^+$ and subsequently Fe_2^+. The molecular ions $As_4R_4^+$ were not observed.

The infrared spectra of the compounds show four or five sharp bands (Table 2) in the CO stretching region similar to the spectra given by other bridged iron derivatives[11].

Hexaphenylcyclohexaarsine reacts with pentacarbonyl iron to yield several products. Mass spectra indicate that the diarsenido compound $[Fe(CO)_3]_2As_2(C_6H_5)_4$ (II) is formed as well as the expected product $[Fe(CO)_3]_2(AsC_6H_5)_4$ (III) in smaller

TABLE 1

^{1}H NMR SPECTRA OF CYCLIC ARSINE COMPLEXES

Complex	δ Values				
$Fe_2(CO)_6(AsCH_3)_4$	1.50 (6H)	2.32 (6H)			
$Fe_2(CO)_6(AsC_2H_5)_4$	1.33 (6H)	1.66 (6H)	1.85 (4H)	2.81 (4H)	(J 7.5Hz)
$Mn_2(CO)_8(AsCH_3)_5$	1.39 (3H)	1.68 (3H)	1.75 (3H)	2.03 (3H)	2.08 (3H)
$Mn_2(CO)_6(AsCH_3)_8$[a]	1.48 (6H)	1.65 (6H)	2.28 (6H)	2.53 (6H)	

[a] Refer to experimental for details.

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF COMPLEXES

Complex	Medium	Frequencies (cm^{-1})				
$Fe_2(CO)_6(AsCH_3)_4$	Cyclohexane	2044 s	2008 s	1978 s	1967 s	1955 w
	Chloroform	2040 s	2005 s	1975 vs	1965 sh	
$Fe_2(CO)_6(AsC_2H_5)_4$	Cyclohexane	2042 s	2006 s	1976 s	1966 s	1954 m
$Mn_2(CO)_8(AsCH_3)_5$	Chloroform	2055 m	2030 m	1985[a]	1975[a]	1965vs br
$Mn_2(CO)_6(AsCH_3)_8$	Chloroform	2000 sh	1985 s	1924 m br	1910[a]	

[a] Inflexion.

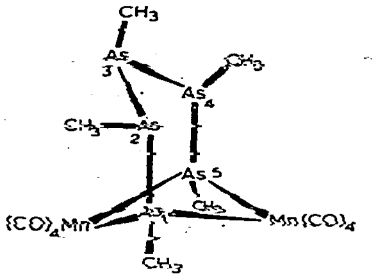
yield. The source of either $As_2(C_6H_5)_4$ molecules or $As(C_6H_5)_2$ radicals which could react with $Fe(CO)_5$ to give (II) is not clear. Although cyclic arylarsines when heated above their melting points yield aryldiarsines and arsenic[12], heating $(AsC_6H_5)_6$ alone in benzene under the conditions used for the reaction (*viz.* 150°, 24 h) did not yield any tetraphenyldiarsine and the hexaphenylcyclohexaarsine could be recovered, with its mass spectrum and melting point unaltered. Neither does (III) appear to be a precursor of (II), since the effect of heat on a mixture containing both (II) and (III) did not increase the yield of (II) but instead caused substantial decomposition of both to unidentified products. A mass spectral investigation of a mixture of products obtained from a similar reaction carried out under ultraviolet irradiation showed that $Fe_2(CO)_6(AsC_6H_5)_4$ is formed but not $Fe_2(CO)_6As_2(C_6H_5)_4$.

Reactions with decacarbonyl dimanganese

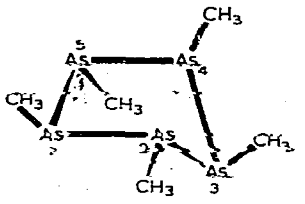
A bright yellow crystalline complex precipitates when a mixture of pentamethylcyclopentaarsine and decarbonyl dimanganese in benzene is exposed to light at room temperature. The reaction will also proceed in the dark at 80°.

The yellow compound rapidly turns red when the solvent is removed. The red compound has the empirical formula $[Mn(CO)_4]_2(AsCH_3)_5$ and the parent ion can be detected in the mass spectrum of the complex. Other species were observed indicating normal stepwise loss of CO groups to give $Mn_2(AsCH_3)_5^+$, together with a variety of binuclear and mononuclear species $Mn_2As_m(CH_3)_n$ ($m=5$–0, $n=4$–0) and $MnAs_x(CH_3)_y$ ($x=5$–0, $y=4$–0), respectively. The most intense peak is due to the rearrangement ion $MnCH_3^+$ also detected in the spectrum of $Mn_2(CO)_8P_2(CH_3)_4$[13]. The absence of the fragmentation pattern associated with $(AsCH_3)_5$ has been taken as evidence against the existence of an arsine ring in the parent compound. This evidence points to a chain of arsenic atoms bridging two Mn atoms in the complex. A possible structure is given in (IV).

The ^1H NMR spectrum of the complex showed five equally intense bands at δ 1.39, 1.68, 1.75, 2.03, and 2.08 ppm [*cf.* $(AsCH_3)_5$: δ 1.66, 1.63, 1.62[7]]. The pair of methyl groups giving the two resonances at the low field end of the sequence are taken to be those located on arsenic atoms 1 and 5 which are directly bonded to Mn atoms in (IV). The next pair of resonances is assigned to the methyls on As atoms 2 and 4 and the fifth resonance to the As 3 methyl. The distribution of the resonances as five singlets indicates an unsymmetrical arrangement of methyl groups about the arsenic chain, *e.g.* a pair of *cis* methyl groups at As 3 and 4 rather than 2 and 4. The formation of an unsymmetrical rather than a symmetrical isomer may relate to the initial point of fission of an As–As bond, *e.g.* primary coordination followed by cleavage of the As–As bond between As 1 and 5 or 1 and 2 of pentamethylcyclopentaarsine(V)[14].

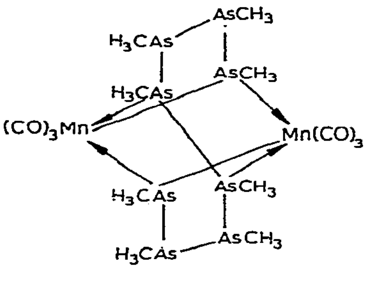


(IV)



(V)

The reaction of pentamethylcyclopentaarsine with decacarbonyl dimanganese in benzene at 150° yields an orange complex with molecular formula $Mn_2(CO)_6$-$(AsCH_3)_8$. A parent ion is observed in the mass spectrum together with peaks representing ions formed by a stepwise loss of CO to provide $Mn_2(AsCH_3)_8^+$ which undergoes fragmentation via binuclear or mononuclear ions of general formulae Mn_2As_x-$(CH_3)_y$ and $MnAs_x(CH_3)_y$, respectively.



(VI)

Structure (VI) is proposed, in which an eight-membered arsenic chain has been formed and is attached by its two terminal arsenic atoms to each Mn atom. In addition, a further coordination link from each of these As atoms to a neighbouring Mn atom must be postulated to keep the EAN rule. The proton NMR spectrum is complex, presumably indicating the presence of conformational isomers.

EXPERIMENTAL

Cyclic arsines were prepared and purified as previously described[7]. The metal complexes were air-sensitive in solution and all operations were carried out in a dry nitrogen atmosphere using glove bags.

Spectroscopic measurements were made with the following instruments: infrared, Perkin–Elmer 521; ^1H NMR, Varian HA100 and A60; mass, Hitachi Perkin–Elmer RMU-6E. Mass spectra were generally recorded at an ionizing beam energy of 70 eV and masses determined by calibration with perfluorokerosene and tris(perfluoroheptyl)-*s*-triazine.

Cyclic arsines and pentacarbonyliron

In general, 1/2 mixtures of the arsine (5 mmoles) and pentacarbonyl iron (10 mmoles) were heated with benzene (5 ml) in evacuated tubes at temperatures between 120 and 160°. After the reaction, the contents of the tubes were filtered, and the filtrate reduced in volume before being chromatographed on silica gel with benzene as eluent. The products generally crystallised from acetone or benzene.

Pentamethylcyclopentaarsine (125°, 20 h): orange needles (benzene), m.p. 256–257° (decompn.). Sublimation at 180° (0.1 mm) was possible but some decomposition of the compound occurred. (Found: C, 18.8; H, 2.4; As, 47.0. $C_{10}H_{12}As_4Fe_2O_6$ calcd.: C, 18.8; H, 1.9; As, 47.0%) Mass spectrum: most intense ion *m/e* 472 $Fe_2(AsCH_3)_4 = 100\%$: parent ion *m/e* 640 $Fe_2(CO)_6(AsCH_3)_4$, 42%; also $Fe_2(CO)_m(AsCH_3)_4$, $m=5$ to 1, 30 to 8%; $Fe_2As_4(CH_3)_m$, $n=4$ to 1, 100 to 2%; Fe_2As_m, $m=4$ to 1, 99 to 30%; Fe_2 99%; $Fe_2As_m(CH_3)_n$, $m=3$ to 1, $n=2$ to 1, 19 to 5%; Fe_2AsCH, 30%; Fe_2AsC, 55%; Fe_2AsH, 30%; Fe_2CH_2, 46%; Fe_2H, 18%; $FeAs_m(CH_3)_n$, $m=4$ to 0, $n=4$ to 0, 40 to 4%; $FeAsCH$, 44%; $Fe(CH_3)$, 99%; $FeCH$, 35%. Fragments which do not contain iron include As_4, 5%; $As_2(CH_3)_m$, $m=4$ to 0, 30 to 5%; As_2CH, 16%; AsC_2H_4, 60%; $AsCH_3$, 34%; $AsCH_2$, 40%.

Pentaethylcyclopentaarsine (140°, 24 h): orange needles (acetone), m.p. 135–136°. (Found: C, 24.9; H, 3.1. $C_{14}H_{20}As_4Fe_2O_6$ calcd.: C, 24.2; H, 2.9%.) Mass spectrum: most intense ion *m/e* 412 $Fe_2As_4 = 100\%$; parent ion *m/e* 696 $Fe_2(CO)_6(AsC_2H_5)_4$, 20% $Fe_2(CO)_m(AsC_2H_5)_4$, $m=5$ to 1, 20 to 10%; $Fe_2As_4(C_2H_5)_n$, $n=4$ to 2, 20 to 10% and other ions comparable to those obtained from the methyl analogue.

Hexaphenylcyclohexaarsine (150°, 24 h): suitable recrystallisation solvents could not be found for the red-black solid residue (m.p. 180–190° after partially melting at 112°) which was obtained after chromatography. A mass spectrum of this residue showed a peak at *m/e* 738 corresponding to $Fe_2(CO)_6As_2(C_6H_5)_4^+$ and a complete fragmentation pattern comparable to that reported for $Fe_2(CO)_6P_2(C_6H_5)_4$[11]. Other weak peaks (< 1% of the most intense peak at *m/e* 416 $(Fe_2As_2(C_6H_5)_2^+)$ were observed at *m/e* 888 $[Fe_2(CO)_6(AsC_6H_5)_4^+]$ and in the *m/e* range 832 to 748 corresponding to the ions $Fe_2(CO)_x(AsC_6H_5)_4$, $x=5$ to 0. Several attempts at chromatographic separation on silica gel or alumina (acid-washed) using hexane, hexane/benzene (1/1) and methylene chloride as eluents failed; moreover, the mixture appeared to be decomposing with continued handling. An infrared spectrum of the mixture in chloroform showed carbonyl stretching frequencies at 2040 s, 2005 s, 1980 s, 1965 s cm^{-1}.

Pentamethylcyclopentaarsine and decacarbonyl dimanganese

(*a*). A mixture of the arsine (0.8 g, 2 mmoles), decacarbonyl dimanganese (0.6 g, 2 mmoles) and benzene (10 ml) in an evacuated Pyrex tube was exposed to sunlight in the laboratory. After carbon monoxide had been evolved and the decacarbonyl dissolved, the tube was cooled in ice whereupon a yellow crystalline precipitate appeared. This was filtered and washed with benzene but the solid rapidly turned red in colour. Unreacted manganese carbonyl was sublimed from the product at 50° (0.01 mm) and the bright red residue recrystallised from benzene at room temperature (decompn. above 300°). The same product was also produced when a ratio of 2 arsine to 1 carbonyl was used. (Found: C, 19.9; H, 1.8; As, 47.0. $C_{13}H_{15}As_5Mn_2O_8$ calcd.: C, 19.9; H, 1.9; As, 47.8%.) A similar mixture of reagents did not evolve CO when stored in darkness at room temperature but at 80° reaction occurred to give the same compound described above. Mass spectrum: most intense ion *m/e* 70 $MnCH_3$ set as 100%; parent ion *m/e* 784 $Mn_2(CO)_8(AsCH_3)_5$, 7%; also $Mn_2(CO)_m(AsCH_3)_5$, $m=7$ to 1, 20 to 3%; $Mn_2(AsCH_3)_5$, 43%; $Mn_2As_m(CH_3)_n$, $m=4$ to 1, $n=3$ to 1, 30 to 4%; Mn_2As_m, $m=5$ to 1, 18 to 4%; $MnAs_m(CH_3)_n$, $m=5$ to 1, $n=4$ to 2, 37 to 2%. The $(AsCH_3)_5$ pattern[7] below *m/e* 300 (As_4^+) was obtained.

(*b*). An equimolar mixture of the arsine and decacarbonyl dimanganese in benzene was heated in an evacuated tube at 150° for 24 h. The red oil obtained after evaporation of the solvent was chromatographed on silica gel using benzene as eluent. Evaporation of the eluate and dilution with pentane provided an orange powder which was purified by precipitation from benzene/pentane, m.p. >300°. (Found: C, 16.8; H, 2.6; As, 59.7; $C_7H_{12}As_4MnO_3$ calcd.: C, 16.9; H, 2.4; As, 60.1%.) Mass spectrum: most intense ion *m/e* 70 $MnCH_3$ 100%; parent ion *m/e* 998, $Mn_2(CO)_6(AsCH_3)_8$, 4%; also $Mn_2(CO)_5(AsCH_3)_8$, 4%; $Mn_2(CO)_3(AsCH_3)_8$, 12%; $Mn_2(AsCH_3)_8$, 6%; $Mn_2As_m(CH_3)_n$, $m=8$ to 3, $n=6$ to 1, 6 to 2%; Mn_2As_m, $m=8$ to 3, 7 to 2%; $MnAs_m(CH_3)_n$, $m=7$ to 3, $n=$ 4 to 0, 17 to 2%. The $(AsCH_3)_5$ pattern[15] below *m/e* 300 (As_4^+) was obtained. ^1H *NMR spectrum*: The major methyl signals occurred at δ 1.48 (6H), 1.65 (6H), 2.28 (6H), 2.53 (6H) with minor signals, presumably due to isomers, at δ 1.16, 2.03, 2.16, 2.58, 2.61 (total integration 6H).

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