Synthesis and crystal structure of a molybdenum carbonyl complex, $Mo(CO)_4[cyclo(Ph_6P_3As_3)]$, with scrambled phosphorus/arsenic identities obtained from a perfectly alternating phosphorus–arsenic heterocycle, 1,3,5-tris(phenylphospha)-2,4,6-tris(phenylarsa)-cyclohexane, $[cyclo(Ph_6P_3As_3)]$

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Abstract

1,3,5-Tris(phenylphospha)-2,4,6-tris(phenylarsa)cyclohexane, *cyclo*$(Ph_6As_3P_3)$, whose perfectly alternating pnictogen structure was determined by the absence of direct P–P coupling in NMR spectra, reacts with $Mo(CO)_6$ at 80 °C to form a complex, $Mo(CO)_4[c\text{-}(Ph_6As_3P_3)]$, containing completely scrambled phenylpnictidene units. The structure of the complex has been crystallographically determined: monoclinic, $P2_1/n$, $a = 11.756(3)$, $b = 22.691(9)$, $c = 14.777$ Å, $\beta = 99.89(2)°$, $V = 3883.5(22)$ Å^3, $Z = 4$, $R_F = 5.66\%$. The original chair conformation of the heterocycle is converted to a twist-boat form in the product, but the presence of concentrated phosphorus character in the 1 and 4 positions coordinated to Mo indicates that ring-opening and ring-scrambling equilibria preceded complex formation.

Introduction

cyclo-Polyarsines, $c(RAs)_n$, are isolobally related to cycloalkanes and are versatile synthons in the formation of an extremely broad range of transition-metal/main-group hybrid clusters and complexes [1]. The products may contain monoarsenic units or be composed of rings or chains of up to ten arsenic units, either naked or clothed with the original organic substituent. In almost all cases the number of arsenic units in the products differs from the number in the cyclic precursor. The transition-metal reactant has often been a metal carbonyl or cyclopentadienyl (or both) complex.

We have earlier reported that hexaphenylcyclohexaarsine, *cyclo*$(PhAs)_6$, reacted with $Mo(CO)_6$ at 130 °C to produce the complex, *cis*-$Mo(CO)_4[c(PhAs)]$ (**1**), containing an intact six-membered PhAs ring system in a twist-boat conformation with 1,4-bidentate (bow and stern) coordination to Mo [2]. In comparison, the free cyclohexaarsine crystallizes in the expected chair conformation. We wish now to present evidence that the occurrence of six-membered rings, differing only in conformation, in both the starting material and product is only coincidental, and that ring and chain oligomerization equilibria completely scramble the reactant rings during product formation.

Results

Several options were considered as methods to determine the extent to which ring-opening equilibria led to scrambling prior to formation of complex **1**. The first strategy considered was to prepare a mixture of two closely similar polyarsines (e.g. $c(C_6H_5As)_6$ and $c(C_6D_5As)_6$, or $c(C_6H_5As)_6$ and $c(p\text{-}CH_3C_6H_4As)_6$), allow them to react with $Mo(CO)_6$, and to analyze the distribution of products by mass spectrometry. While it was obvious from a qualitative inspection of the mass spectral data that extensive scrambling occurred, as shown by the presence of fragments obtainable only by mixed aryl-substitution products, several factors made it difficult to extract quantitative data: (i) molecular ions were seldom observed even when FAB and other specialized ionization techniques were used, (ii) the complex Mo isotope pattern made a quantitative H versus D discrimination difficult, (iii) *p*-tolyl-substituted polyarsine is unusual in that both cyclopentameric and hexameric forms are stable and difficult to separate adding the unwanted new dimension of differences in reactivity between the two cyclooligomers, and (iv) given

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the proclivity of RAs groups to lose organic substituents even under extremely mild conditions [1], scrambling of organic groups could occur without breaking As–As bonds.

To overcome these deficiencies, the strategy of placing the differentiating species in the ring, instead of on the substituent, was explored. For this purpose we sought mixed-pnictogen rings. Previous work [3, 4] indicated that the condensation of phenylphosphine, $PhPH_2$ and phenyldichloroarsine, $PhAsCl_2$, led to the formation of *cyclo*($Ph_6As_3P_3$) (**2**), according to the equation

$$PhPH_2 + PhAsCl_2 \longrightarrow c(Ph_6As_3P_3)$$
2

Our ^{31}P and ^{1}H NMR analysis of this product showed no evidence for directly bonded P–P couplings in the freshly prepared ligand, in agreement with earlier results [4]. This indicates a perfect alternation of P and As atoms in the heterocycle. Additionally, **2** is of high thermal stability indicated by its ability to melt without decomposition at 190 °C. Also, from unit-cell parameters, we have determined that the crystal structure of **2** is isomorphous with the cyclohexaarsine analogue [5] and is easily obtained in high purity by recrystallization from pyridine. Furthermore, given the 120% difference in *Z* for P and As, P versus As occupancy refinement can be used to produce accurate and reliable quantitative data from a single-crystal structure.

Under conditions identical to those used to form **1**, we were able to prepare a complex of **2**, $Mo(CO)_4[c(Ph_6P_3As_6)]$ (**3**), that is isostructural with **1** [2]

$$2 + Mo(CO)_6 \longrightarrow Mo(CO)_4[c(Ph_6As_3P_3)] + 2CO$$
3

The crystallographic structure of **3** is shown in Fig. 1 and selected bond distances and angles are given in Table 1. All of the atoms forming the hexapnictogen ring are composites of P and As character. Those labelled PAs(x) are predominantly phosphorus: PAs(1) = 75.3(3)% P, and PAs(4) = 78.6(3)% P; those labelled AsP(x) are predominantly arsenic: AsP(2) = 60.4(3)% As, AsP(3) = 61.4(3)% As, AsP(5) = 60.5(3)% As, and AsP(6) = 60.5(3)% As. These occupancies result in a measured P/As ratio of 2.9/3.1; this close similarity to the expected 1/1 ratio confirms that the use of refined occupancies (without imposed constraints on total occupancy) is capable of producing reliable quantitative data.

The E–E bond distances also reflect the composite nature of the ring system. The bonds to the two PAs atoms, at the bow and stern of the boat where coordination to Mo occurs, have an average PAs–AsP distance of 2.33 Å, whereas the two AsP–AsP bonds average 2.40 Å. A typical As–As single bond distance, that found in $c(PhAs)_6$ is 2.454(1) Å [5], and a typical P–P bond distance in the phosphorus analogue is 2.233(9) Å [6].

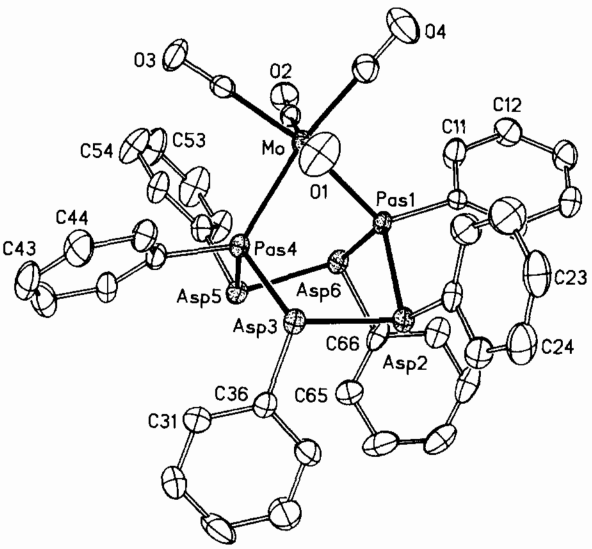

Fig. 1. Molecular structure of **3** drawn with 40% probability thermal ellipsoids. The atoms labelled PAs are predominantly P character, whereas those labelled AsP are predominantly As character.

TABLE 1. Selected bond distances and angles for $Mo(CO)_4[c(Ph_6As_3P_3)]$

Bond distances (Å)			
Mo–PAs(1)	2.517(2)	Mo–C(1)	2.034(10)
Mo–PAs(4)	2.503(2)	Mo–C(2)	2.016(8)
PAs(1)–AsP(2)	2.314(2)	Mo–C(3)	1.982(9)
AsP(2)–AsP(3)	2.409(2)	Mo–C(4)	1.992(11)
AsP(3)–PAs(4)	2.345(2)	O(1)–C(1)	1.131(12)
PAs(4)–AsP(5)	2.310(2)	O(2)–C(2)	1.153(11)
AsP(5)–AsP(6)	2.390(2)	O(3)–C(3)	1.146(11)
AsP(6)–PAs(1)	2.355(2)	O(4)–C(4)	1.138(13)
Bond angles (°)			
PAs(1)–Mo–PAs(4)	76.0(1)	C(2)–Mo–C(4)	89.7(4)
PAs(1)–Mo–C(1)	98.7(3)	C(3)–Mo–C(4)	94.4(4)
PAs(4)–Mo–C(1)	89.2(3)	PAs(1)–AsP(2)–AsP(3)	91.7(1)
PAs(1)–Mo–C(2)	88.7(2)	AsP(2)–AsP(3)–PAs(4)	102.9(1)
PAs(4)–Mo–C(2)	98.6(2)	AsP(3)–PAs(4)–AsP(5)	104.8(1)
C(1)–Mo–C(2)	170.4(4)	PAs(4)–AsP(5)–AsP(6)	93.5(1)
PAs(1)–Mo–C(3)	167.2(3)	AsP(5)–AsP(6)–PAs(1)	103.0(1)
PAs(4)–Mo–C(3)	94.2(2)	AsP(6)–PAs(1)–AsP(2)	98.9(1)
C(1)–Mo–C(3)	89.3(4)	Mo–C(1)–O(1)	173.8(9)
C(2)–Mo–C(3)	84.5(3)	Mo–C(2)–O(2)	173.6(7)
PAs(1)–Mo–C(4)	96.5(3)	Mo–C(3)–O(3)	177.3(8)
PAs(4)–Mo–C(4)	168.6(3)	Mo–C(4)–O(4)	177.9(9)
C(1)–Mo–C(4)	83.4(4)		

Discussion

While it was attractive in its simplicity to propose that **1** forms by a direct dicarbonyl substitution involving only a ring-conformation change, several related facts suggested that the true course of events was more complex. For instance, other complexes of the same composition as **1** of general formula $M(CO)_4[c\text{-}(RE)_6]$ can be prepared from cyclopentamer precursors under identical conditions and must require a ring-expansion step [1]. Other reactions of cyclopolyarsines are known in which ring size can increase up to nine and ten members in reactions with metal carbonyl precursors. These observations lead to the conclusion that, in the presence of metal carbonyls, cyclopolyarsines can undergo rapid ring-opening, ring-closing reactions with concomitant changes in ring size under conditions where the cyclopolyarsines themselves are completely stable*.

The most striking demonstration that scrambling does occur in the present system is the very high degree of phosphorus character concentrated in the 1 and 4 ring positions which are coordinated to the $Mo(CO)_4$ group. Only through scrambling of the original, perfectly-alternating ring could the 1 and 4 positions both become predominantly P. This result is clearly thermodynamically driven and is based on the stronger Mo–E bond formed to phosphorus. The Mo–PAs distances (av. 2.510 Å) are considerably shorter than the comparable bonds in **1** (av. 2.617 Å) and more nearly similar to those found in typical Mo–phosphine structures (*c.* 2.47–2.50 Å). This supports the presence of high P character in the Mo bonded pnictogen atoms.

Given the lower homoatomic bond energy for an As–As bond, compared to a P–P bond, it may be assumed that a P–As bond will be stronger than an As–As bond. Thus, it is reasonable to conclude that if a mixed P–As ring system is completely scrambled, that the homoarsenic system is also. This conclusion neglects any contribution to reactivity due to the slightly polar nature of a P–As bond, but this effect is likely to be insignificant given the radical nature of these reactions. Therefore, it may be concluded that the occurrence of a six-membered ring in both the reactants and products of the reactions that form **1** and **3** is only coincidental, and that these products are determined by the steric and electronic requirements of the *cis*-$Mo(CO)_4$ group. Clearly, the ring-conformation change is required only in that it places two pnictogen atoms in the correct positions for *cis*-coordination. The non-bonded 1...4 distance in **3** is 3.091(2) Å, compared to 3.196(1) Å in **1**. These distances are considerably shorter than any transannular distances found in the chair-conformation homocycles.

*The study of scrambling in cyclopolyphosphines and arsines is made difficult by the profound effects of trace-level impurities on the temperature of onset of redistribution and the oligomeric products formed. When samples from different synthetic procedures are compared, very different results are possible [7]. Only work in this field following recognition of the effects of impurities is reliable; the most comprehensive studies have been by Baudler and co-workers [8].

Experimental

General procedures

All solvents were dried over Na/K alloy under an N_2 atmosphere, unless otherwise noted. $Mo(CO)_6$ (Alfa) was used as supplied. $PhPH_2$ [9] and $PhAsCl_2$ [10] were prepared by published methods. IR data were obtained with a Nicolet 5DXB FTIR. ^{31}P NMR were taken with a Bruker WM-250 spectrometer at 101.27 MHz and are referenced to 85% external H_3PO_4. Mass spectra for **3** were recorded with the Extrel FTMS-2000 at a probe temperature of 150 °C. Preparation of **2** from $PhPH_2$ and $PhAsCl_2$ used a literature procedure [4].

Preparation of $Mo(CO)_4(cis\text{-}cyclo\text{-}Ph_6P_3As_3)$ (3)

cyclo($Ph_6As_3P_3$) (0.36 g, 0.46 mmol) and $Mo(CO)_6$ (0.12 g, 0.46 mmol) were placed in a three-neck flask fitted with a condenser, thermometer and stir bar. The system was evacuated and flushed with dry dinitrogen three times, after which 50 ml of dry, deoxygenated toluene was introduced via a cannula. The solution was stirred, and slowly heated to 80 °C, where the solution became dark orange. After heating for 12 h at 80 °C, the solution was rotary evaporated to dryness, redissolved in a small quantity of ethyl acetate and chromatographed on a neutral alumina column. A yellow band was eluted with an 85/15 petroleum ether/ethyl acetate solvent mixture. The band was concentrated, yielding yellowish green crystals suitable for X-ray diffraction. Yield 85.9 mg (8.69×10^{-2} mmol, 18.9% yield based on $Mo(CO)_6$). The compound is air stable in the solid phase over a period of days, decomposes rapidly in air at 50 °C, and rapidly degrades in solution. It is very soluble in most polar solvents, and sparingly soluble in alkanes, cycloalkanes and ethers. Differential scanning calorimetry under anaerobic conditions yields a broad melt at 187–194 °C, 41.36 J/g (1.78 mg sample), followed by an ignition at approximately 425 °C. IR ($CHCl_3$): 2071 (w,s), 2021 (m,s), 1933, 1948, both very strong and broad, cm^{-1}. For comparison: IR of **1** in CH_2Cl_2: 2021, 1920, 1891 cm^{-1} (3). FTMS: (EI) 30 eV, *m/z*(rel. intensity): 110(8.7) $PhPH_2+$, 111(15.3) $PhPH_3+$, 125(21.5) 126(7.8) 127(10.1) $Mo(CO)+$, 152(88.4) $PhAs+$, 227(100) $PhAs_2+$, 229(33) Ph_2As+, 262(22.8) Ph_3P+, 306(100) Ph_2As_2+, 412(7.4) Ph_3PAs_2+, 456(50.0) Ph_3As_3+, 703(7.5) $Ph_5P_3As_3+$. ^{31}P NMR (in C_6D_6) δ(ppm) 32.2(25.3) $P_{1,4}$–Mo; 14.9(9.1) $P_{2,3}$.

X-ray crystallography

Crystallographic data for **3** are collected in Table 2. A yellow specimen was affixed to a fine glass fiber by epoxy cement and was found photographically to possess $2/m$ Laue symmetry. Systematic absences in the diffraction data uniquely determined the space group. Data were corrected for absorption by empirical (ψ-scan) methods. The structure was solved by automated heavy-atom methods which located the Mo and As-dominated atomic positions. The pnictogen-identity disorder for the six-membered ring, was handled in the following way. All six sites were initially refined as half-occupancy, co-located P and As atoms with a common isotropic thermal parameter. The results of thermal parameter refinement clearly showed that the six sites could be divided into two groups. Two sites (1 and 4) had high thermal parameters and were subsequently treated as being predominantly phosphorus (identified as PAs sites), while four sites (2, 3, 5 and 6) had low thermal parameters and were subsequently treated as predominantly arsenic sites (identified as AsP sites).

TABLE 2. Crystallographic data for $(Ph_6P_3As_3)Mo(CO)_6$

Crystal parameters	
Formula	$C_{42}H_{30}As_3MoO_6P_3$
Formula weight	1044.32
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.756(3)
b (Å)	22.691(9)
c (Å)	14.777(4)
β (°)	99.89(2)
V (Å^3)	3883.5(22)
Z	4
Crystal dimensions (mm)	0.24×0.28×0.33
Crystal color	yellow
D_{calc} (g cm^3)	1.786
μ(Mo Kα) (cm^{-1})	30.2
Temperature (K)	297
T_{max}/T_{min}	1.15
Data collection	
Diffractometer	Nicolet R3m
Monochromator	graphite
Radiation	Mo Kα (λ=0.71073 Å)
2θ scan range (°)	4–50
Data collected (h,k,l)	±14, +27, +18
Reflections collected	7327
Independent reflections	7111
Independent observed reflections $F_o \geq 5\sigma(F_o)$	3976
Variation in standards	<1
Refinement	
R_F (%)	5.66
R_{wF} (%)	5.50
Δ/σ_{max}	0.11
$\Delta(\rho)$ (e Å^{-3})	0.962
N_o/N_v	10.1
GOF	1.273

TABLE 3. Atomic coordinates (×10^4) and isotropic thermal parameters (Å^2×10^3) for $(Ph_6P_3As_3)Mo(CO)_4$

	x	y	z	U[a]
Mo	3296.3(6)	416.1(3)	2909.8(5)	33.6(2)
PAs(1)	1534(2)	1065(1)	2712(1)	33(1)
AsP(2)	1329(1)	1804(1)	3752(1)	40(1)
AsP(3)	3390(1)	1892(1)	4202(1)	38(1)
PAs(4)	4097(2)	1440(1)	2983(1)	34(1)
AsP(5)	3533(1)	2055(1)	1741(1)	43(1)
AsP(6)	1627(1)	1653(1)	1415(1)	41(1)
O(1)	3832(7)	310(4)	5074(4)	88(4)
O(2)	2918(6)	188(3)	766(4)	67(3)
O(3)	5682(5)	−173(3)	2832(5)	66(3)
O(4)	2005(7)	−767(3)	3132(6)	92(4)
C(1)	3630(8)	382(4)	4306(7)	49(4)
C(2)	3040(7)	306(4)	1536(6)	38(3)
C(3)	4808(7)	36(4)	2882(6)	43(3)
C(4)	2476(8)	−340(5)	3034(7)	54(4)
C(11)	−91(5)	413(3)	1562(4)	61(4)
C(12)	−1167	154	1268	67(4)
C(13)	−2074	260	1743	66(4)
C(14)	−1905	627	2513	71(5)
C(15)	−829	886	2807	58(4)
C(16)	78	779	2332	38(3)
C(21)	1160(6)	767(3)	4930(4)	67(5)
C(22)	958	515	5748	85(6)
C(23)	704	873	6455	85(5)
C(24)	652	1483	6343	78(5)
C(25)	853	1735	5524	57(4)
C(26)	1108	1377	4818	46(3)
C(31)	4707(5)	2917(3)	4099(5)	65(4)
C(32)	4920	3522	4104	70(5)
C(33)	4006	3919	4047	90(6)
C(34)	2878	3712	3984	114(7)
C(35)	2664	3107	3979	71(5)
C(36)	3579	2710	4036	40(3)
C(41)	6254(5)	2001(3)	2977(4)	54(4)
C(42)	7388	2134	3375	75(5)
C(43)	7892	1859	4190	78(5)
C(44)	7261	1451	4608	70(4)
C(45)	6126	1318	4211	56(4)
C(46)	5623	1593	3396	45(3)
C(51)	3431(5)	1663(3)	−80(4)	65(4)
C(52)	3786	1371	−814	94(6)
C(53)	4764	1012	−661	88(6)
C(54)	5387	946	225	84(5)
C(55)	5032	1239	959	58(4)
C(56)	4054	1597	806	48(4)
C(61)	−487(6)	2217(3)	1452(4)	58(4)
C(62)	−1245	2684	1504	76(5)
C(63)	−814	3252	1695	77(5)
C(64)	374	3352	1834	87(6)
C(65)	1131	2885	1782	64(4)
C(66)	701	2317	1591	48(4)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Thereafter, the PAs sites were assigned P scattering factors and the AsP sites As scattering factors, and refinement of occupancy was used to determine the elemental composition of each site using the equation

$$\frac{x(Z_1)+(1-x)(Z_2)}{Z_1}=\text{occupancy}$$

where x is the fractional content of the element of atomic number Z_1. The results of this refinement are given in the text.

All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as fixed, updated, idealized, isotropic contributions. The phenyl rings were refined as rigid, planar hexagons. All computations used the SHELXTL software library which also served as the source of scattering factors [11]. Atomic coordinates are given in Table 3, and selected bond distances and angles in Table 1.

Supplementary material

Tables of anisotropic thermal parameters and structure factors are available from the authors on request.

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