is best described as distorted octahedral, while P(1) and P(2) are distorted tetrahedra. The geometry around N(1) is close to planar [sum of the bond angles = 357.9 (4)°] and is typical of aminophosphorus groups in which the nitrogen is relatively unconstrained (for example, not incorporated into small rings that may impose steric restrictions on geometry). The distance between P(1) and N(1) of 3.035 (3) Å indicates no significant interaction and far exceeds the corresponding distances in either the three-membered ring system such as **1** (ca. 1.9 Å)[1c] or transannulated **3** (2.36 Å). A significant trend is observed between the phosphorus chemical shift and the P-N distance: as the distance increases, the chemical shift moves further downfield, with the largest change occurring when going from a full P-N bond in **4** to a transannulated interaction in **3**.

The driving force for formation of **6** could be the elimination of lithium chloride; however, amide—metal bonds are known to insert a variety of organic molecules, particularly 1,2-dipoles.[2,8] Treatment of **4** with DMAD, an incipient 1,2-dipole, leads to a species **7** with a phosphorus chemical shift at δ 128, again indicative of P—N bond rupture. The IR and ^{13}C NMR spectra in the C≡O region are similar to **4**. Of the six additional resonances in the ^{13}C NMR spectrum, four show P—C coupling, which is readily explained by the insertion of DMAD into the Mo—N bond to give a metalated enamine. In fact, the additional carbon resonances for the alkene moiety are very close to those for another DMAD-inserted complex, $Cp_2Nb(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(CO_2Me)C{=}C(CO_2Me)H$.[9]

At this point, the mechanisms of the reactions involving the strained P-N-Mo ring are unknown. The traditional view of insertions into amide-metal bonds involves either the nitrogen initially forming a bond with the incoming electrophilic center in a stepwise reaction or a concerted path via a multicenter transition state.[8a] Either of these mechanisms may be operating in this system due to the unique geometry about the metalated nitrogen: previous structures on related systems have shown that the nitrogen is almost coplanar with the two methylene carbons and the metal to which it is bonded.[1] This should leave significant electron density above the plane, "trans" to the phosphorus, for amide-like behavior. However, alternative pathways are possible such as initial binding of the other axial nitrogen[10] to the incoming phosphine or alkyne, followed by rearrangement. (Our previous work[1,4,10] has shown that nitrogen reactivity occurs exclusively at the axial nitrogens of the cyclenP moiety.) If this latter pathway is operable, the observed products might be considered "formal" insertions.

Acknowledgment is made to the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates (4 pages). Ordering information is given on any current masthead page.

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Tetraaza Macrocyclic Derivatives of Arsenic: HcyclenAs, HcyclenAs·GaMe$_3$, and HcyclamAs

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Treatment of cyclen, a 12-atom tetraaza macrocycle, with tris(dimethylamino)arsine leads to HcyclenAs, the structure of which is best described as a distorted pseudo trigonal bipyramid (tbp) with two nitrogens and a lone pair of electrons at the equatorial positions and two nitrogens at the axial sites. One of the axial nitrogens is protonated and leads to a longer ("transannular") As···N distance [of 2.400 (7) Å]. A 1:1 complex, HcyclenAs·GaMe$_3$, is formed when HcyclenAs is treated with trimethylgallium where the site of complexation is the nonprotonated axial nitrogen. The geometry of the HcyclenAs moiety in the complex is essentially unchanged from the free ligand. Treatment of the larger 14-atom tetraaza macrocycle cyclam with tris(dimethylamino)arsine leads to the corresponding HcyclamAs species which has a structure similar to that of HcyclenAs except for a longer transannular interaction [2.722 (8) Å]. Thus, both macrocycles stabilize similar geometries about arsenic, and the three macrocyclic compounds can be envisioned as zwitterionic arsoranide (R_4As^-) species. Although cyclen also stabilizes a tbp geometry around phosphorus in cyclenPH, the latter contains a P-H rather than an N-H bond. The lack of an As-H bond is most likely due to the lower thermodynamic stability of this linkage. The X-ray data for HcyclenAs are as follows: $C_8H_{17}N_4As$, a = 21.532 (5) Å, b = 11.796 (2) Å, c = 17.396 (4) Å, β = 105.08 (2)°, monoclinic, $C2/c$, Z = 16. The X-ray data for HcyclenAs·GaMe$_3$ are as follows: $C_{11}H_{25}N_4GaAs$, a = 7.620 (2) Å, b = 13.073 (5) Å, c = 15.784 (5) Å, β = 90.0°, orthorhombic, $P2_12_12_1$, Z = 4. The X-ray data for HcyclamAs are as follows: $C_{10}H_{21}N_4As$, a = 15.866 (5) Å, b = 8.460 (3) Å, c = 9.333 (4) Å, β = 100.98 (3)°, monoclinic, $P2_1/c$, Z = 4.

The binding of macrocycles to transition metals has been extensively studied due to the novel properties of the resulting complexes such as high kinetic and thermodynamic stabilities, as well as the tendency of the macrocycle to

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Table I. Crystal Data for HcyclenAs, HcyclenAs•GaMe$_3$, and HcyclamAs

	HcyclenAs	HcyclenAs·GaMe$_3$	HcyclamAs
formula	$C_8H_{17}N_4As$	$C_{11}H_{25}N_4GaAs$	$C_{10}H_{21}N_4As$
fw	244.17	357.99	272.22
recryst solvent(s)	benzene/hexanes	benzene/hexanes	hot toluene
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P2_12_12_1$	$P2_1/c$
a, Å	21.532 (5)	7.620 (2)	15.866 (5)
b, Å	11.796 (2)	13.073 (5)	8.460 (3)
c, Å	17.396 (4)	15.784 (5)	9.333 (4)
β,°	105.08 (2)	90.0	100.98 (3)
V, Å^3	4266 (2)	1572.3 (9)	1229.8 (8)
Z	16	4	4
D_{calcd}, g cm^{-3}	1.520	1.512	1.470
μ, mm^{-1}	3.324	3.816	2.732
cryst dimens, mm	0.18 × 0.35 × 0.25	0.15 × 0.20 × 0.35	0.10 × 0.30 × 0.15
T, K	230	230	230
scan type	$\omega/2\theta$	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	3.5–45.0	3.5–50.0	3.5–42.0
scan speed (min, max), deg min^{-1}	5.0, 30.0	5.0, 25.0	5.0, 25.0
decay of data, %	0	0	0
data collcd	2874	1685	1535
unique data	2605	1606	1309
obsd reflcns, $I > 3.0\sigma(I)$	1691	1354	1015
params refined	235	154	136
trans coeff (min, max)	0.4523, 0.7487	0.6862, 0.8344	0.2021, 0.3444
GOF	1.34	1.64	2.79
residuals (max, min), e/Å^3	0.50, −0.45	0.39, −0.70	1.13, −0.56
R^a	0.043	0.036	0.056
$R_w{}^a$	0.052	0.051	0.080
g^a	0.0007	0.000 50	0.000 50

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, and $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$.

stabilize certain high oxidation states of the metal.[1] Work from our laboratory has focused on the binding of both nitrogen-[2] and oxygen-containing[3] macrocycles to main-group elements such as phosphorus. The macrocycles not only stabilize novel geometries around phosphorus, but these derivatives also display unique reactivities involving breaking and reforming bonds between the central phosphorus and the macrocycle. We are now expanding the scope of our studies to include other main-group atoms, particularly the heavier congeners, to compare and contrast the effects of macrocycle size, "central" atom size, and bond strengths on resulting geometries and reactivities. We herein report the synthesis, spectral properties, and X-ray crystal structures of HcyclenAs, HcyclenAs·GaMe$_3$, and HcyclamAs. A preliminary report on the synthesis and spectra of HcyclenAs appeared 10 years ago by Maroni et al.[4]

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P drybox or using standard Schlenk techniques, unless otherwise indicated. Solvents were dried (over calcium hydride or sodium hydride) and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents cyclen[2a,5] and tris(dimethylamino)arsine[6] were synthesized according to literature procedures; cyclam and trimethylgallium were obtained commercially. While cyclam was used without further purification, trimethylgallium was distilled under a nitrogen atmosphere prior to use. *Caution: trimethylgallium is pyrophoric!* All reactions were carried out at ambient temperature. NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.132 (^{1}H) and 50.327 (^{13}C) MHz. ^{1}H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. ^{13}C resonances were measured relative to solvent peaks and referenced to Me_4Si. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of HcyclenAs. A stirred solution of cyclen (500 mg, 2.90 mmol) in benzene (5 mL) was treated dropwise with tris(dimethylamino)arsine (600 μL, 3.24 mmol). After 24 h, the volatiles were pumped off. The residue was redissolved in toluene and filtered. Hexane was layered on top of the solution and allowed to slowly diffuse in. The resulting precipitate was collected by filtration and dried by slowly pumping the drybox atmosphere through the filter frit for about 15 m, yielding HcyclenAs as a white, air-sensitive, crystalline compound (450 mg, 64%). Mp: 110–112 °C. Exposure to light slowly turns the compound brown, so it was stored in an amber bottle in the drybox freezer (−40 °C). ^{1}H NMR (C_6D_6): δ 1.8 (br s, NH, 1 H), 2.3–3.1 (comp m, CH_2, 16 H). ^{13}C NMR (C_6D_6): δ 50.3, 51.4 (lit.[4] δ 45.1, 45.4 in $CDCl_3$). IR (Nujol, cm^{-1}): ν_{NH} 3131.

Synthesis of HcyclenAs·GaMe$_3$. A stirred solution of HcyclenAs (125 mg, 0.518 mmol) in benzene (2 mL) was treated dropwise with trimethylgallium (50 μL, 0.50 mmol). After 1 h, the volatiles were pumped off. The residue was redissolved in ether, and hexane was layered on top. The resulting precipitate was collected by filtration and pumped dry to yield HcyclenAs·GaMe$_3$ as a white, air-sensitive, crystalline compound (110 mg, 61%). Mp: 148–150 °C dec. Anal. Calcd for $C_{11}H_{26}N_4AsGa$: C, 36.80; H, 7.30; N, 15.61. Found: C, 36.61; H, 7.17; N, 15.58. ^{1}H NMR (C_6D_6): δ 0.03 (s, Me, 9 H), 1.1 (br, NH, 1 H), 1.7–3.3 (comp m, CH_2, 16 H). ^{13}C NMR (C_6D_6): δ −5.5, 46.0, 49.9, 51.7, 52.6. IR (Nujol, cm^{-1}): ν_{NH} 3182.

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Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for HcyclenAs

	x	*y*	*z*	*U*(eq)[a]
As(1)	7772 (1)	1893 (1)	2303 (1)	41 (1)
As(2)	9712 (1)	−1951 (1)	948 (1)	61 (1)
N(1)	7926 (3)	5 (6)	1873 (3)	51 (3)
N(2)	8679 (3)	1876 (6)	2497 (3)	51 (3)
N(3)	7798 (3)	3537 (6)	2309 (3)	54 (3)
N(4)	7482 (3)	2004 (6)	1194 (3)	53 (3)
N(11)	9594 (3)	−3385 (5)	1687 (4)	52 (3)
N(12)	9990 (3)	−3111 (6)	381 (4)	59 (3)
N(13)	9635 (3)	−1034 (6)	−138 (3)	53 (3)
N(14)	8806 (3)	−2003 (6)	606 (3)	48 (3)
C(1)	8617 (5)	−112 (9)	2131 (5)	75 (4)
C(2)	8942 (4)	1009 (9)	2090 (5)	72 (4)
C(3)	8914 (4)	3016 (8)	2403 (5)	69 (4)
C(4)	8466 (5)	3839 (8)	2674 (5)	68 (4)
C(5)	7594 (5)	3950 (8)	1470 (4)	70 (4)
C(6)	7130 (4)	3067 (8)	1001 (5)	65 (4)
C(7)	7152 (4)	988 (8)	815 (5)	66 (4)
C(8)	7649 (4)	19 (8)	1005 (4)	64 (4)
C(11)	9801 (5)	−4372 (8)	1338 (5)	74 (4)
C(12)	10307 (5)	−4016 (9)	913 (5)	78 (5)
C(13)	10327 (5)	−2653 (9)	−174 (5)	74 (5)
C(14)	9879 (4)	−1805 (9)	−664 (5)	72 (4)
C(15)	8958 (4)	−771 (8)	−414 (5)	69 (4)
C(16)	8549 (4)	−1705 (9)	−232 (5)	70 (4)
C(17)	8514 (5)	−2999 (8)	836 (7)	87 (5)
C(18)	8906 (5)	−3390 (8)	1641 (6)	91 (5)

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

Synthesis of HcyclamAs. A stirred solution of cyclam (507 mg, 2.53 mmol) in toluene (10 mL) was treated dropwise with tris(dimethylamino)arsine (510 μL, 2.75 mmol). After 18 h, the volatiles were pumped off. The residue was redissolved in toluene and filtered. Hexane was layered on top of the solution. The resulting precipitate was collected by filtration and pumped dry to yield HcyclamAs as a white, air-sensitive, crystalline compound (430 mg, 62%). Mp: 180–182 °C dec. Anal. Calcd for $C_{10}H_{21}N_4As$: C, 44.12; H, 7.78; N, 20.58. Found: C, 43.84; H, 7.55; N, 19.86. ^1H NMR ($CDCl_3$): δ 1.1 (s, NH, 1 H), 1.2–3.3 (comp m, CH_2, 20 H). ^{13}C NMR ($CDCl_3$): δ 26.5, 48.2, 49.2, 53.6, 57.7. IR (Nujol, cm⁻¹): ν_{NH} 3175.

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for HcyclenAs•GaMe₃

	x	*y*	*z*	*U*(eq)[a]
As	400 (1)	9036 (1)	236 (1)	30 (1)
Ga	51 (1)	10921 (1)	−1160 (1)	46 (1)
N(1)	−12 (9)	7521 (5)	1016 (4)	37 (2)
N(2)	−278 (10)	9528 (5)	1292 (4)	43 (2)
N(3)	1203 (9)	10460 (5)	−19 (4)	33 (2)
N(4)	2783 (8)	8681 (5)	398 (4)	35 (2)
C(1)	−752 (14)	7856 (7)	1827 (6)	56 (3)
C(2)	−1510 (14)	8909 (7)	1719 (6)	58 (3)
C(3)	−728 (15)	10592 (7)	1233 (6)	58 (4)
C(4)	727 (14)	11129 (7)	737 (6)	54 (3)
C(5)	3149 (11)	10396 (7)	−134 (6)	46 (3)
C(6)	3801 (11)	9619 (7)	485 (6)	44 (3)
C(7)	3046 (12)	7951 (7)	1110 (6)	44 (3)
C(8)	1776 (11)	7096 (7)	1059 (6)	44 (3)
C(9)	1150 (14)	12273 (7)	−1379 (6)	59 (4)
C(10)	799 (14)	9798 (7)	−1937 (5)	56 (3)
C(11)	−2519 (11)	10986 (9)	−880 (6)	58 (3)

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

Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for HcyclamAs

	x	*y*	*z*	*U*(eq)[a]
As	7198 (1)	94 (1)	566 (1)	33 (1)
N(1)	7752 (5)	3059 (10)	1400 (9)	39 (3)
N(2)	6713 (5)	1362 (9)	−1103 (8)	33 (3)
N(3)	7085 (5)	−1842 (9)	−471 (9)	34 (3)
N(4)	8355 (5)	21 (9)	440 (9)	37 (3)
C(1)	7439 (7)	3776 (13)	−11 (11)	44 (4)
C(2)	6605 (6)	3049 (11)	−727 (12)	41 (4)
C(3)	5869 (6)	734 (13)	−1795 (12)	45 (4)
C(4)	6216 (7)	−2131 (13)	−1326 (12)	51 (5)
C(5)	7770 (6)	−2002 (11)	−1279 (11)	40 (4)
C(6)	8565 (7)	−1474 (13)	−210 (12)	51 (5)
C(7)	9002 (7)	563 (13)	1618 (12)	46 (4)
C(8)	8623 (7)	3410 (13)	2055 (12)	47 (4)
C(9)	5901 (7)	−860 (13)	−2459 (12)	48 (4)
C(10)	9265 (7)	2300 (12)	1498 (14)	51 (5)

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

X-ray Structure Determination and Refinement. Crystals of the title compounds were mounted on a Siemans R3m/V diffractometer. Pertinent crystallographic data are summarized in Table I. Final unit cell parameters were obtained by a least-squares fit of the angles of 24 accurately centered reflections in the ranges 15° ≤ 2θ ≤ 26° (HcyclenAs), 19° ≤ 2θ ≤ 30° (HcyclenAs·$GaMe_3$), 17° ≤ 2θ ≤ 28° (HcyclamAs). Intensity data were collected using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Systematic absences were consistent with the space group assignments in Table I. Three standard reflections, monitored after every 150 reflections, did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied. The structures were solved by heavy-atom methods with the SHELXTL-Plus package.[7] Full-matrix least-squares refinement was performed. Scattering factors, with corrections for anomalous dispersion of As and Ga atoms, were taken from common sources.[8] Methylene hydrogen atoms were placed at idealized positions with fixed isotropic temperature factors (*U* = 0.08 Å²). The amine hydrogen atoms were located from the final difference Fourier maps for HcyclenAs·$GaMe_3$ and HcyclamAs. No meaningful features were found from the final difference Fourier maps to locate the amine hydrogen atom in HcyclenAs. For HcyclenAs, there are two molecules in an asymmetric unit. However, these two molecules are not equivalent, even though their internal geometries are essentially the same. Thermal parameters of As(2) are significantly larger than those of As(1). The thermal parameters and bond distances pertinent to the As(2) atom indicate that As(2) is disordered. As(2)–N(11) = 2.179 and As(2)–N(13) = 2.146 Å can be considered as the average values of bonding and "transannulated" (see below) distances between the As and axial N atoms [the average of As(1)–N(1) = 2.400 and As(1)–N(3) = 1.941 Å is 2.170 Å]. Intermolecular close contacts reveal that HcyclenAs exists as two infinite, approximately perpendicular, chains connected by hydrogen bonds.

Intermolecular Close Contacts. HcyclenAs: N(1)···N(3) (1.5 − *x*, −0.5 + *y*, 0.5 − *z*), 2.934 Å; N(11)···N(11) (2.0 − *x*, *y*, 0.5 − *z*), 2.913 Å; N(13)···N(13) (2.0 − *x*, −*y*, −*z*), 2.873 Å. HcyclenAs·$GaMe_3$: N(1)···N(4) (−0.5 + *x*, 1.5 − *y*, −*z*), 3.206 Å. HcyclamAs: N(1)···N(2) (*x*, 0.5 − *y*, 0.5 − *z*), 3.139 Å.

Atomic coordinates and isotropic thermal parameters for the compounds HcyclenAs, HcyclenAs·$GaMe_3$, and HcyclamAs are given in Tables II–IV, respectively. The atom labeling scheme was chosen for consistency among the structures.

Results and Discussion

Syntheses. Treatment of cyclen with tris(dimethylamino)arsine at room temperature leads to a single compound, HcyclenAs, which shows a complex pattern in the ^1H NMR spectrum. Previous analyses[4] of the low-temperature ^1H NMR spectra suggested the structure of the product to be either a tricoordinate aminoarsine (A) or a

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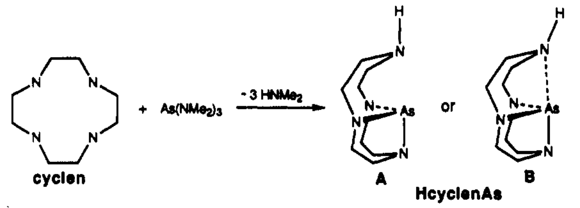
(7) Sheldrick, G. M. SHELXTL-Plus, Siemens Analytical X-Ray Instruments, Inc., 1990.

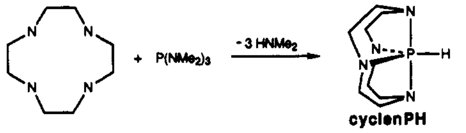
(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

"transannulated" species (**B**). These structures contrast



(1)

with the analogous phosphorus derivative cyclenPH which contains a pentacoordinate phosphorus with a P–H bond:



(2)

Additional support for the presence of the nitrogen-bound proton comes from the observation of a broad peak in the ^{1}H spectrum at δ 1.8 that integrates to one proton, as well as a band in the IR spectrum at 3131 cm^{-1}. No evidence for an As–H stretch (ca. 2100 cm^{-1}) is observed in the IR spectrum. The lack of an As–H bond is not surprising on thermodynamic grounds: the mean bond energy for an As–H bond is about 247 kJ/mol, somewhat 75 kJ/mol less than the P–H bond (and about 142 kJ/mol less than the N–H bond).[9]

Lone-pair electrons on the nitrogens and arsenic in HcyclenAs lead to several possibilities for Lewis acid/base derivatives; however, recent competition studies by Krannich and co-workers[10] using aminoarsines as Lewis bases suggest that nitrogen will be the primary site of adduct formation. Moreover, all of the accumulated evidence with cyclenPH and derivatives[2] indicate that only the axial nitrogens in the trigonal bipyramidal (tbp) structures exhibit substantial basicity. Thus, the most likely sites of complexation should be either the NH nitrogen or the nitrogen "trans" to it. Treatment of HcyclenAs with trimethylgallium leads to the 1:1 adduct HcyclenAs·GaMe$_3$. A band in the IR spectrum at 3182 cm^{-1} indicates that the N–H bond is still intact. This, combined with the integrated intensities in the ^{1}H spectrum, rules out the loss of methane which is a possibility in this reaction. However, the specific site of adduct formation was determined by the X-ray crystal structure (see below).

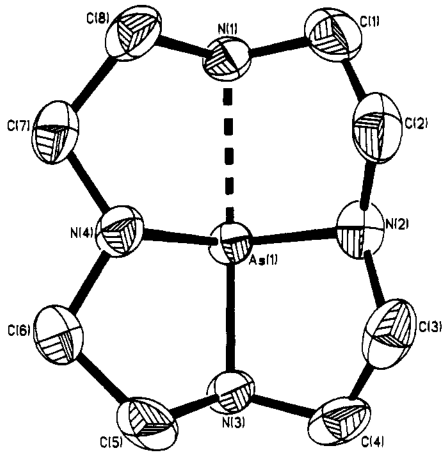


Figure 1. Computer-generated drawing of HcyclenAs with thermal ellipsoids at 50%. Methylene hydrogen atoms are omitted for clarity. The figure illustrates the nondisordered molecule.

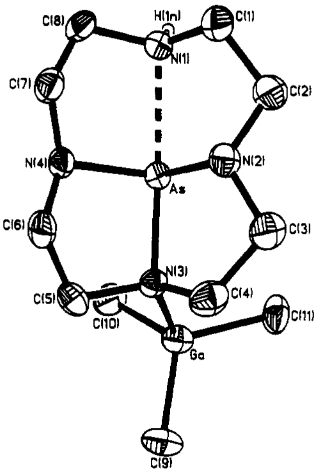


Figure 2. Computer-generated drawing of HcyclenAs·GaMe$_3$ with thermal ellipsoids at 50%. Methylene hydrogen atoms are omitted for clarity.

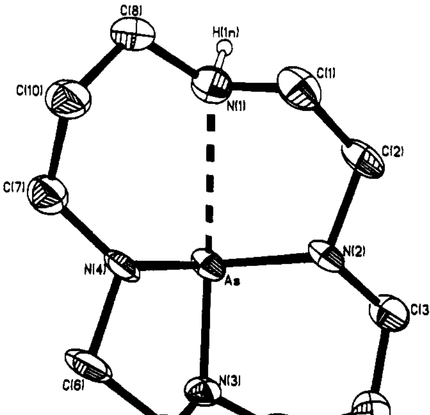


Figure 3. Computer-generated drawing of HcyclamAs with thermal ellipsoids at 50%. Methylene hydrogen atoms are omitted for clarity.

The effect of tetraazamacrocyclic size has been shown to have a dramatic effect on the resulting geometries[5] and subsequent reactivities[2,11,12] of phosphorus derivatives. While reaction of the 12-membered macrocycle cyclen with tris(dimethylamino)phosphine leads to the pentacoordinate (closed) structure for cyclenPH, the corresponding reaction with the 14-membered macrocycle cyclam leads to a mixture of closed and open forms, cyclamPH and HcyclamP, in an 82:18 ratio:

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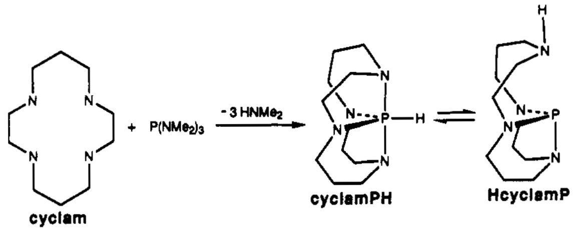
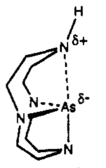


(3)

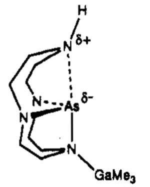
Treatment of cyclam with tris(dimethylamino)arsine leads to a single species, HcyclamAs, and as with the other arsenic compounds, an N–H stretch appears in the IR spectrum (at 3175 cm^{-1}).

Structural Descriptions. The X-ray crystal structures of the arsenic derivatives were obtained and are illustrated in Figures 1–3, respectively. Selected interatomic distances and angles are listed in Table V. The NH proton was located in two of the structures, HcyclenAs·GaMe$_3$ and HcyclamAs, but not in HcyclenAs. The position of the NH proton in the latter species is assumed by analogy to the others. Figure 1 illustrates the HcyclenAs molecule which is not disordered (see Experimental Section). In addition, Figure 2 reveals that the site of complexation of HcyclenAs to GaMe$_3$ is N(3).

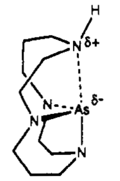
The first point to note is that all three derivatives exist as the transannulated structure (**B**). In fact, the structures are remarkably similar. The geometries about arsenic are best described as distorted pseudo tbp's, with N(2), N(4), and a lone pair occupying the equatorial positions, while N(1) and N(3) occupy the axial sites. The N(1)···As–N(3) angles vary from 157° to 160°, while the N(2)–As–N(4) range is 102–104°. The As···N(1) distance is longer than the other As–N distances. However, this interaction is substantial in the cyclen compounds where the As···N distance is only 0.4 Å longer than the sum of the As and N covalent radii and 1.1 Å shorter than the corresponding van der Waals sum. For HcyclamAs, these values are 0.7 and 0.8 Å, respectively. Thus, these macrocyclic compounds can be envisioned as zwitterionic arsoranide (R_4As^-) species:



HcyclenAs



HcyclenAs·GaMe$_3$



HcyclamAs

The site of nitrogen complexation in HcyclenAs·GaMe$_3$ is not surprising for transannulated HcyclenAs (see above). The Ga–N(3) bond distance of 2.092 (6) Å is very similar to the bond distance of 2.09 Å found in $Me_3N{\cdot}GaMe_3$.[13] Overall, there is little effect on the HcyclenAs geometry upon complexation of N(3); even the values of $\sum$ N(3) (where $\sum$N is defined as the sum of the two As–N–C and one C–N–C angle (Table V)) are within experimental error in the two species. The slight increase in the As–N(3) bond length upon coordination is accompanied by a small decrease in the As···N(1) distance.

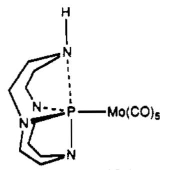
Table V. Selected Interatomic Distances (Å) and Angles (deg) (E = P, As)

	HcyclenAs[a]	HcyclenAs·GaMe$_3$	HcyclamAs	Hcyclen-PMo(CO)$_5$[b]
E–N(1)	2.400 (7)	2.353 (6)	2.722 (8)	2.356 (23)
E–N(2)	1.893 (6)	1.860 (7)	1.927 (7)	1.666 (20)
E–N(3)	1.941 (7)	2.001 (6)	1.893 (8)	1.809 (20)
E–N(4)	1.873 (6)	1.891 (6)	1.862 (9)	1.749 (20)
N(1)–C(1)	1.443 (12)	1.466 (11)	1.449 (13)	
N(1)–C(8)	1.472 (9)	1.473 (11)	1.432 (13)	
N(2)–C(2)	1.441 (13)	1.411 (12)	1.487 (12)	
N(2)–C(3)	1.461 (12)	1.436 (11)	1.471 (12)	
N(3)–C(4)	1.458 (11)	1.522 (11)	1.476 (13)	
N(3)–C(5)	1.493 (9)	1.497 (11)	1.442 (14)	
N(4)–C(6)	1.459 (11)	1.458 (11)	1.468 (14)	
N(4)–C(7)	1.460 (11)	1.489 (11)	1.429 (13)	
Ga–N(3)		2.092 (6)		
N(1)–E–N(2)	79.9 (3)	77.6 (3)	77.0 (3)	78.8 (13)
N(1)–E–N(3)	157.4 (3)	158.3 (2)	159.6 (3)	153.5 (13)
N(1)–E–N(4)	77.3 (3)	81.4 (3)	77.3 (3)	82.0 (12)
N(2)–E–N(3)	89.0 (3)	86.7 (3)	94.8 (3)	90.7 (9)
N(2)–E–N(4)	103.6 (3)	103.3 (3)	102.4 (4)	120.8 (12)
N(3)–E–N(4)	86.4 (3)	87.8 (3)	86.4 (3)	82.8 (11)
E–N(1)–C(1)	101.9 (5)	104.9 (5)	95.2 (6)	
E–N(1)–C(8)	104.9 (5)	102.6 (5)	123.1 (6)	
C(1)–N(1)–C(8)	115.5 (7)	115.4 (7)	115.9 (9)	
E–N(2)–C(2)	116.1 (5)	114.5 (6)	113.0 (6)	
E–N(2)–C(3)	110.0 (5)	110.1 (5)	110.1 (6)	
C(2)–N(2)–C(3)	114.0 (7)	115.3 (8)	108.3 (7)	
E–N(3)–C(4)	105.7 (5)	107.7 (5)	114.0 (6)	
E–N(3)–C(5)	108.7 (5)	105.9 (5)	110.0 (6)	
C(4)–N(3)–C(5)	110.6 (7)	111.3 (7)	114.9 (8)	
E–N(4)–C(6)	108.1 (5)	108.5 (5)	111.0 (6)	
E–N(4)–C(7)	113.6 (5)	112.9 (5)	120.9 (7)	
C(6)–N(4)–C(7)	116.1 (6)	113.4 (6)	114.1 (8)	
$\sum$N(1)[c]	322.3 (10)	322.9 (10)	334.2 (12)	318.2 (37)
$\sum$N(2)	340.1 (10)	339.9 (11)	331.4 (11)	360.0 (34)
$\sum$N(3)	325.0 (10)	324.9 (10)	338.9 (12)	329.8 (35)
$\sum$N(4)	337.8 (9)	334.8 (9)	346.0 (12)	352.8 (34)

[a] Data for the nondisordered molecule. [b] Data from ref 2a. [c] $\sum$N is defined as the sum of the two E–N–C and one C–N–C angles.

Incorporation of arsenic into the larger macrocycle cyclam leads to somewhat larger changes in the overall geometry, most significant of which is the lengthening of the As···N(1) distance, accompanied by a shortening of the As–N(3) bond. Significantly, in HcyclenAs and HcyclenAs·GaMe$_3$ the axial As–N(3) bonds are longer than the equatorial As–N bonds. This is not the case in HcyclamAs and, most likely, reflects the "residual hypervalency" in the three-center/four-electron bond in the former species with the shorter As···N(1) distances.

Turning now to the effect of the central main-group atom, the tetraaza macrocyclic phosphorus species that most closely resembles the arsenic derivatives is HcyclenPMo(CO)$_5$:[2h,n]



HcyclenPMo(CO)$_5$

Selected interatomic parameters for this compound are included in Table V for comparison (using a similar numbering scheme for the nitrogens). The primary difference between HcyclenAs and HcyclenPMo(CO)$_5$, besides the central atom, is the presence of a lone pair on arsenic and a Mo(CO)$_5$ moiety on phosphorus, the latter in a staggered conformation relative to the PN$_4$ skeleton. As expected, the As–N bonds in HcyclenAs are ca. 0.1–0.2 Å longer than the P–N bonds.[14] However, the E···N(1) (E = P, As) transannular interaction is identical within experimental error for both congeners. Most of the N–E–N angles in the two derivatives are quite similar except for N(2)–E–N(4); this angle is ca. 17° less in HcyclenAs. A substantial

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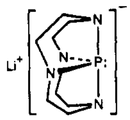
component of this diminution must be due to the lone pair on arsenic. Previous structural data on lithium cyclenphosphoranide,[2f] Li[cyclenP]



Li[cyclenP]

has shown that the N-P-N equatorial angle is 15-20° smaller than other cyclenPR derivatives. However, the axial N-P-N angle is also decreased, but to a lesser degree, being on the order of 5-10°. There appears to be no such effect on the "axial" angles in HcyclenAs or any of the arsenic species. The arsenic lone pair repulsive effects must be severely diminished with the transannular interaction.

In contrasting HcyclenAs and $HcyclenPMo(CO)_5$, another significant difference is found in the sums of the angles around the nitrogens. The values for $\sum N(1)$ and $\sum N(3)$ are similar for the two; however, the values for $\sum N(2)$ and $\sum N(4)$ are 15-20° smaller for arsenic. Previous structural work by Rømming and Songstad[15] has shown very similar structures for trimorpholinophosphine and -arsine [morpholino = $N(CH_2CH_2)_2O$], where the values for $\sum N$ in the arsine are only an average of about 3° lower than in the phosphine. While the smaller bond angles in the arsenic species may be due to the contracted N-As-N equatorial angles, and there is evidence in the data for Li[cyclenP] to support this, it is by no means a general trend.[1f] At this point, the origin of this difference is not clear.

In summary, while there are small differences due to macrocycle ring size and complexation, cyclen and cyclam stabilize pseudo tbp geometries around arsenic, and all three derivatives can be described as zwitterionic arsoranide species. The fact that no As-H bonded derivatives are formed contrasts with the corresponding phosphorus compounds. Since cyclen stabilizes similar geometries around both arsenic and phosphorus, the lack of an As-H bond must be due to its lower thermodynamic stability. In addition, the fact that cyclam stabilizes a pseudo tbp geometry around As in HcyclamAs via a transannular interaction suggests that a similar geometry may exist for the phosphorus open form HcyclamP.

Acknowledgment is made to the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates and a packing diagram for HcyclenAs showing the chainlike structure (7 pages). Ordering information is given on any current masthead page.

OM920246F

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[15] Rømming, C.; Songstad, J. *Acta Chem. Scand.* 1980, *A34*, 365.

Unprecedented Trimetallic Cluster with an In-Plane μ_3-Hydride Ligand. X-ray Crystal Structure of $[Mo_2(CO)_8(\mu\text{-dppm})(\mu_3\text{-H})(\mu\text{-AuPPh}_3)]$

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The salt $(NEt_4)[Mo_2(CO)_8(\mu\text{-dppm})(\mu\text{-H})]$ [dppm = bis(diphenylphosphino)methane] reacts with $XMPPh_3$ (M = Au, Cu, Ag; X = Cl, I) in tetrahydrofuran to yield $[Mo_2(CO)_8(\mu\text{-dppm})(\mu_3\text{-H})(\mu\text{-MPPh}_3)]$ (M = Au, **1a**; M = Ag, **1b**; M = Cu, **1c**). The structure of **1a** has been determined by X-ray diffraction methods. Crystals are orthorhombic, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions $a = 12.361$ (5), $b = 15.179$ (6), and $c = 25.800$ (8) Å. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares on the basis of 2309 observed reflections to R and R_w values of 0.0504 and 0.0668, respectively. The structure of **1a** is without precedent in that the metal core, consisting of an almost symmetric Mo_2Au triangular framework, is held by a hydride ligand located in the same plane defined by the metal atoms. Although an accurate location of this hydride was not possible, there are several lines of evidence in agreement with this position. The Mo-Mo separation is 3.771 (3) Å, and the Mo-Au bond lengths are 2.900 (3) and 2.914 (2) Å. Reaction of $(NEt_4)[Mo_2(CO)_8(\mu\text{-dppm})(\mu\text{-H})]$ with $(ClAu)_2(\mu\text{-PP})$ (PP = dppm, dppe [1,2-bis(diphenylphosphino)ethane], and dppp [1,3-bis(diphenylphosphino)propane]) leads to the hexametallic complexes $[\{Mo_2(CO)_8(\mu\text{-dppm})(\mu_3\text{-H})(\mu\text{-Au})\}_2(PP)]$ (PP = dppm, **2a**; PP = dppe, **2b**; PP = dppp, **2c**), which contain two metal cluster fragments linked by a bridging diphosphine. The bonding within the Mo_2HAu skeleton and the structural differences between **1a** and the parent anion $[Mo_2(CO)_8(\mu\text{-dppm})(\mu\text{-H})]^-$ are explained on the basis of molecular orbital calculations.

Introduction

The synthesis, structural characterization, and reactivity study of gold hydride species is a rapidly expanding area because of their potential use in the field of homogeneous and heterogeneous bimetallic catalysis.[1] Although mononometallic gold hydride compounds have not been directly observed, several heterobimetallic complexes are known in which a hydride ligand bridges a transition metal and

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[1] Braunstein, P.; Rosé, J. *Gold. Bull.* 1985, *18*, 17.