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A surprise landing on the *terra incognita* of macrocyclic dibridgehead diorganoarsines: syntheses, structures, and reactivities†

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Reactions of *trans*-[Fe(CO)$_2$(NO)(As((CH$_2$)$_n$)$_3$As)]$^+$ BF$_4^-$ (*n* = 10, 12, 14) and Bu$_4$N$^+$ Cl$^-$ afford the title compounds As((CH$_2$)$_n$)$_3$As, which upon reaction (*n* = 14) with MCl$_2$ (M = Pt, Ni), Rh(CO)(Cl), and Fe(CO)$_3$ sources reconstitute cage like complexes *trans*-ML$_n$(As((CH$_2$)$_{14}$)$_3$As). Reactions with H$_2$O$_2$ and BH$_3$ give the corresponding arsine oxides and boranes. Crystal structures of metal-free species reveal *out*,*out* isomers, but cage complex formation is proposed to entail homeomorphic isomerization to *in*,*in* isomers with *endo* directed lone pairs.

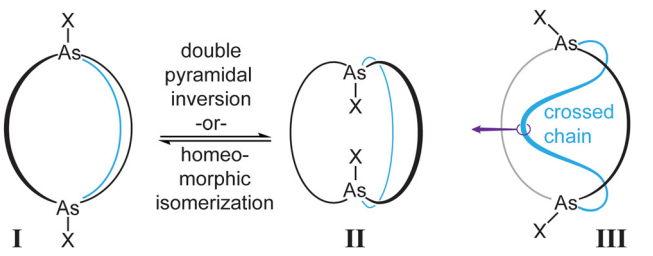
Triorganoarsines[1] and their broad variety of functional applications[2] continue to attract much interest and attention. Recent studies highlight biological probes,[3] designer ligands for metal catalysts,[4] reagents in organic synthesis,[5] and framework units in porous materials.[6] Unusual systems with arsenic–heteroatom–carbon linkages have also received attention.[7]

However, potentially useful types of trialkylarsines have remained inaccessible or unknown. For example, dibridgehead diamines such as DABCO (N((CH$_2$)$_2$)$_3$N) have played major roles in synthetic organic chemistry,[8] and macrocyclic analogs have provided cornerstones for classical mechanistic investigations[9] and disembarkment points for cryptand architectures. The dibridgehead diphosphine literature is not as extensive, with species of the formula P((CH$_2$)$_n$)$_3$P limited to n = 3–4[10] until our recent work extending n to 14 and 18.[11,12] In contrast, analogous dibridgehead diarsines As((CH$_2$)$_n$)$_3$As (**1**) have remained unknown for all values of n, although systems with one or more short As(CR=CR)As or AsOAs bridges have been reported.[13]

Our routes to the dibridgehead diphosphines P((CH$_2$)$_{14}$)$_3$P and P((CH$_2$)$_{18}$)$_3$P are stoichiometric in platinum[11] or rhodium,[12] and other ring sizes are challenging to access due to low yield steps. In this communication, we report the serendipitous finding that the dibridgehead diarsines **1** are available by routes that involve an earth abundant metal, iron, and avoid low yield steps. These diarsines can, per their parentage, serve as cage like *trans* spanning ligands for a variety of metal fragments, and readily undergo other types of derivatization. Some of these processes implicate unusual dynamic phenomena involving *out*,*out* and *in*,*in* isomers (see **I**, **II** in Scheme 1), and crystallographic reference points for both stereochemical limits are described.

As sketched in Scheme 2, the cationic iron dicarbonyl nitrosyl complexes *trans*-[Fe(CO)$_2$(NO)(As((CH$_2$)$_n$)$_3$As)]$^+$ BF$_4^-$ (3; n = **a**, 10; **b**, 12; **c**, 14) were prepared in three steps from (BDA)Fe(CO)$_3$ and the readily available arsines As((CH$_2$)$_m$CH=CH$_2$)$_3$ (m = 4, 5, 6) as previously reported.[14] The key step involves a threefold intramolecular (and interligand) olefin metathesis, which despite several obvious potential side reactions proceeds in reasonable yields, aided by conformational factors detailed earlier.[15,16] The dibridgehead diarsine ligands feature thirteen- to seventeen-membered macrocycles, and there is no intrinsic upper limit on the ring size, as long as it is odd.

The salts **3a-c** were treated with Bu$_4$N$^+$ Cl$^-$ in CH$_2$Cl$_2$. The analogous diphosphine complexes undergo carbonyl ligand



Scheme 1 *out*,*out* (I) and *in*,*in* (II) isomers of macrocyclic dibridgehead diarsines or Lewis acid adducts thereof. Structure III illustrates the homeomorphic isomerization of II (pull the distal blue chain through the ring defined by the other two) to I.

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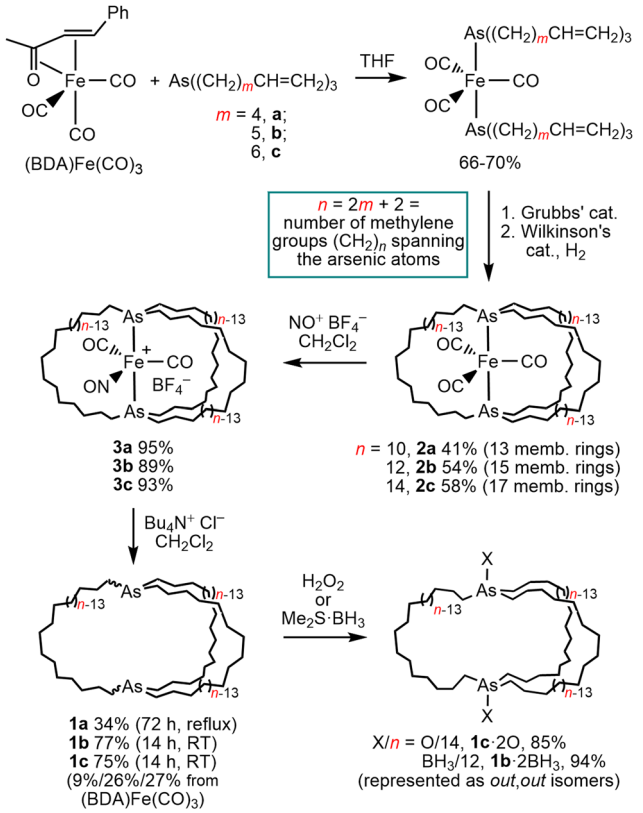


Scheme 2 Syntheses of macrocyclic dibridgehead diarsines and Lewis acid adducts.

substitutions to give neutral Fe(CO)(NO)(Cl) adducts.[17] Surprisingly, workups gave the free dibridgehead diarsines **1a-c** in 77–34% yields as air stable white solids. The salt with the smallest cage, **3a**, required longer times and heating. Conditions and nucleophiles were varied in attempts to secure any type of Fe(CO)(NO)(X) species, as these would be valuable candidates for molecular gyroscopes.[16] However, the weaker metal-arsenic *versus* metal-phosphorus bonds[18] apparently lead to orthogonal reactivity channels. Dark green reaction solutions always formed, but IR spectra did not reveal any ν_{CO} or ν_{NO} bands and the iron byproduct remains unidentified.

The diarsines **1a-c** were characterized by NMR (^{1}H, ^{13}C) and microanalyses. Consideration was first given to the disposition of the lone pairs. Pyramidal inversion at arsenic normally requires temperatures of ~200 °C,[19] and the lone pairs in the precursors **3a-c** are directed *in* towards the central iron atom. Thus, one might expect that **1a-c** would be generated as *in*,*in* isomers (**II**, Scheme 1). However, suitable macrobicyclic compounds can turn themselves "inside out", a topological process termed homeomorphic isomerization.[9] This would convert **II** to an *out*,*out* isomer **I**, for the same net effect as a two-fold pyramidal inversion. A key stage in the homeomorphic isomerization is illustrated in **III**.

Compounds **1a-c** lack NMR "handles" that facilitate the investigation of such processes, which are very rapid with the phosphorus analog of **1c**.[11a,b] Thus, the accessibility of *out*,*out* isomers was probed in several ways. First, crystals of **1b** were

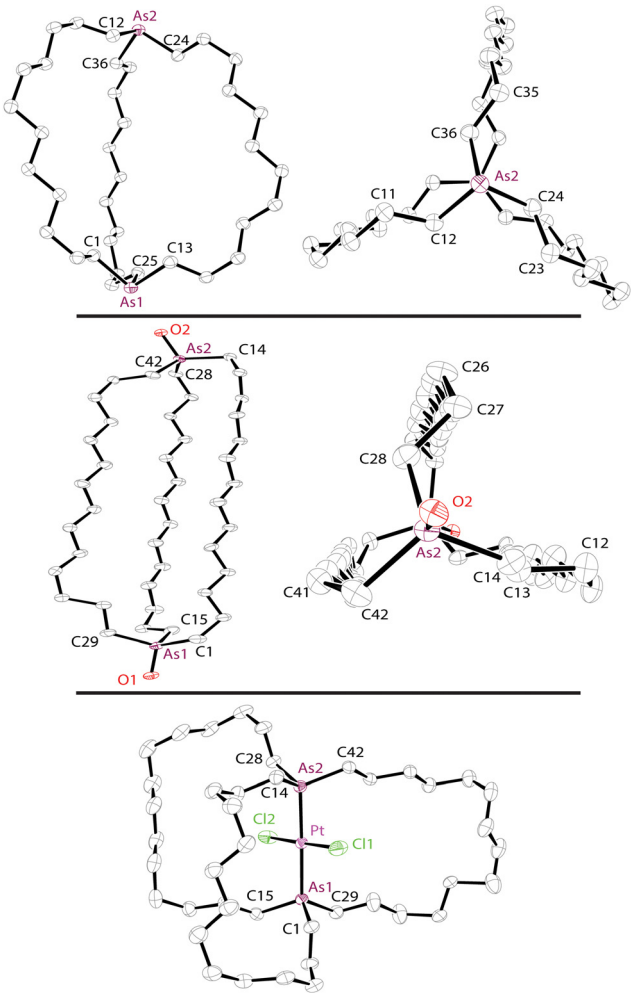
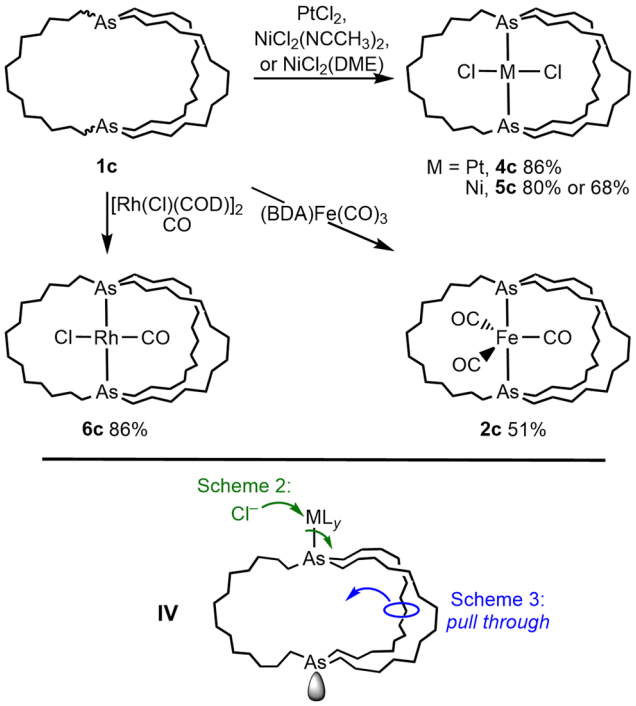


Fig. 1 Thermal ellipsoid diagrams (50% probability) of **1b** (top), **1c**·2O·$(H_2O)_4$ (middle), and **4c** (bottom; solvent molecules omitted).

obtained, and the X-ray structure (Fig. 1, top) showed an *out*,*out* conformation. Second, **1c** was treated with H_2O_2 as depicted in Scheme 2. Workup gave the expected dibridgehead diarsine dioxide **1c**·2O as a hygroscopic white solid that exhibited a characteristic IR $\nu_{As=O}$ band at 881 cm^{-1}.[20] As shown in Fig. 1 (middle), the crystal structure also featured an *out*,*out* conformation. However, these data by no means require that *out*,*out* isomers dominate in solution.

Reactions of **1b**,**c** and various types of Lewis acids were studied. The addition of **1b** and $Me_2S{\cdot}BH_3$ afforded the oily bis(borane) adduct **1b**·2BH_3 in 94% yield (Scheme 2).[1,21] As shown in Scheme 3, the reaction of **1c** and $PtCl_2$ afforded the gyroscope like complex *trans*-Pt(Cl)$_2$(As((CH$_2$)$_{14}$)$_3$As) (**4c**, 86%), which is formally an adduct of *in*,*in*-**1c**. Combining **1c** and common $NiCl_2$ sources gave the nickel analog **5c** (80–68%). Diphosphine analogs of **4c** and **5c** have been previously reported.[11b,22]

Reactions of **1c** with [Rh(Cl)(COD)]$_2$/CO and Fe(CO)$_3$(BDA) were also investigated. As shown in Scheme 3, the former afforded *trans*-Rh(CO)(Cl)(As((CH$_2$)$_{14}$)$_3$As) (**6c**; 86%). The latter



Scheme 3 Reintroduction of metal fragments into dibridgehead diarsine **1c**.

gave **2c** (51%), which serves as a precursor to **1c** in Scheme 2. Thus, such diarsines can be viewed as "container molecules" from which metal fragments can be reversibly incorporated and extruded. A speculation that ties these phenomena together is presented as IV in Scheme 3. Perhaps the mechanism by which the arsines are extruded from **3a–c** involves the cleavage of *one* iron–arsenic bond, homeomorphic isomerization to IV, and displacement of the second arsenic atom by a chloride nucleophile. For the reactions in Scheme 3, the appropriate metal fragment would bind to one arsenic atom of *out*,*out*-**1c**, and then homeomorphic isomerizations coupled with metal–arsenic bond formation would yield the cage like products.

The crystal structure of the platinum complex **4c** could also be determined (Fig. 1, bottom), and sets up a number of comparisons. The arsenic–arsenic distance expands from 4.76 Å in *trans*-chelated **4c** to 16.77 Å in **1c**·2O, both of which feature $(CH_2)_{14}$ bridges. The distance in $(CH_2)_{12}$-bridged **1b** is intermediate (11.15 Å). The degree of bridgehead pyramidalization, as reflected by the sums of the three CH_2–As–CH_2 bond angles, increases in the order **1c**·2O (331.4–328.1°) < **4c** (318.3–314.7°) < **1b** (288.3–287.9°). The average angle in **1b** (96.0°) reflects the high degree of *p* character in the orbitals used for bonding in trivalent organoarsines,[23] whereas that in **1c**·2O (109.9°) indicates a nearly tetrahedral geometry. None of the compounds exhibit any crystallographic symmetry, but there is an approximate C_3 axis that passes through both arsenic atoms in **1b**. The As–As–X angles in **1b** and **1c**·2O (X = lone pair, O), which would be 180° in idealized *out*,*out* isomers, contract to 172.4°/172.8° and 150.9°/167.1°, respectively. Arsine oxides are known to be good hydrogen bond acceptors,[24] and the hydrogen atoms of some of the water

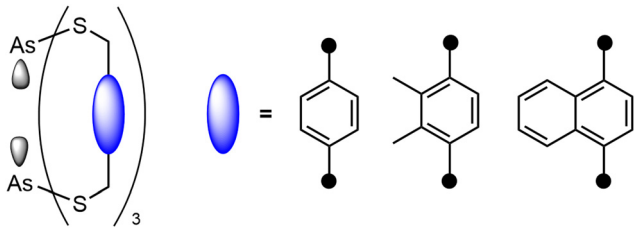


Fig. 2 Additional types of dibridgehead diarsenic compounds, which are notable for their *in*,*in* stereochemistry.

molecules associated with **1c**·2O clearly interact with the As═O moiety.

As noted above, there is little precedent for the chemistry in Schemes 2 and 3. However, Johnson has prepared novel diarsines that feature sulfur substituted AsS_3 bridgeheads,[7] a few of which are exemplified in Fig. 2. These have only been accessed as *in*,*in* isomers that feature rigid arylene bridge components such that homeomorphic isomerization would be challenging. No coordination chemistry has yet been reported, although interesting possibilities exist.

In summary, this study has established the ready availability of a series of structurally flexible macrocyclic dibridgehead diorganoarsines that hint at fascinating dynamic properties and represent launching pads for a variety of unprecedented molecular architectures. These themes will be developed in subsequent reports.

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Conflicts of interest

There are no conflicts to declare.

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