Tertiary-arsinomacrocycles and their Molybdenum Carbonyl Complexes

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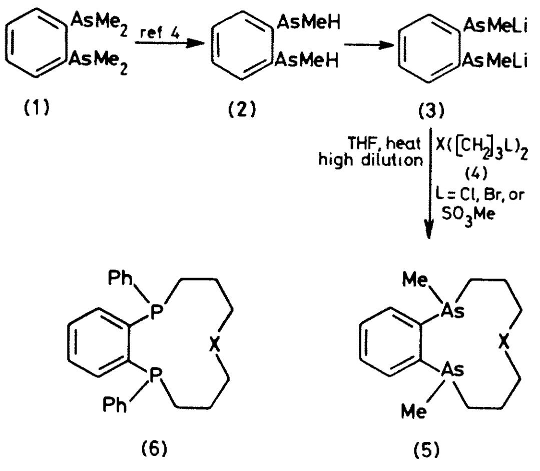
Summary Three new tertiary-arsine-containing macrocycles have been synthesized and their stereochemistries deduced on the basis of molybdenum carbonyl complexations.

RECENT efforts have resulted in the synthesis and characterization of a number of multidentate macrocycles containing tertiary-phosphino ligating sites,[1,2] but to our knowledge there have been no reports of tertiary-arsino-containing macrocycles. We now report the synthesis and formation of transition metal complexes of three such arsine-containing macro-rings.

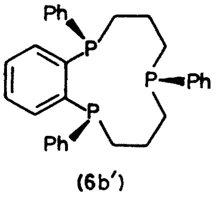
The Scheme outlines the synthesis of the arsino-macrocycles (**5a**—**c**). Although 1,2-bis(dimethylarsino)benzene (**1**) is commercially available, owing to its high cost, it was synthesized from dimethylarsine and 1,2-dichlorobenzene as reported.[3] The three-step transformation from (**1**) to (**2**) proceeds in 40% yield, as described by Wild.[4] Treatment of (**2**) in tetrahydrofuran (THF) with 2 equiv. of n-butyllithium in hexane generates the bis-nucleophile (**3**), which reacts with the bis-electrophile (**4**) in boiling THF under high-dilution conditions to give (**5a**—**c**) in 30—60% isolated yields.† Species (**5a**—**c**) are viscous oils at room temperature, and all appear to be less susceptible to air oxidation than the corresponding phosphorus macrocycles.



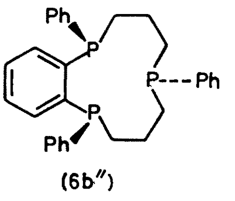
SCHEME

a, X = AsPh **d**, X = O
b, X = PPh **e**, X = NMe
c, X = S **f**, X = NPh

Since the inversion barrier for an aryldialkylarsine is *ca.* 43 kcal/mol[5] (1 cal = 4·184 J) and that for the corresponding phosphine is *ca.* 33 kcal/mol,[5,6] the macrocycles (**5a**,**b**) may exist in three isomeric forms [two *meso* and one (±) pair] and (**5c**) in two [one *meso*, one (±) pair]. We have established that when the 1,2-bis(phenylphosphino)-benzene unit is incorporated in 11-, 13-, and 14-membered rings, the phenyl groups are always *cis* across the benzo fusion, and thermal equilibration does not generate the *trans*-Ph$_2$ isomer to any significant extent.[2] In the present work, we have found the crude reaction mixtures of (**5c**) as well as the purified (silica gel chromatography, anaerobic) materials contain only one isomer on the basis of ^{1}H [δ (AsMe) 1·20] and ^{13}C [δ (AsMe) 9·69 p.p.m.] n.m.r. spectroscopy. Although we do not as yet have single crystal *X*-ray structural data on any of the macrocycles (**5**), examination of Dreiding and Corey–Pauling–Koltun space-filling models indicates that the isomers with the *cis*-dimethyl configuration across the 1,2-diarsinobenzene fusion should be more stable than those with a *trans*-configuration, and we present evidence below which supports these observations. With (**5c**), the chromatographed material was distilled (temp. > 230 °C) to give a 4:1 mixture of isomers with the major isomer having the same spectroscopic properties [minor isomer: δ (AsMe) ^{1}H, 1·16; ^{13}C 8·58 p.p.m.] as the material prior to distillation (*vide infra*). Examination of the crude products of macrocyclization of (**5a**) and (**5b**) showed the presence of two isomers in both cases [*ca.* 5:4 for (**5a**) and 5:1 for (**5b**)].‡ We have been unable as yet to separate the isomers of (**5b**), but have separated the two isomers of (**5a**) by careful anaerobic chromatography on silica gel, and describe our evidence for structural assignment of these isomers.



(**6b′**)



(**6b″**)

We have established previously that (**6b**,**c**, and **e**) form the corresponding *fac*-tricarbonylmetal derivatives when heated with group 6 metal hexacarbonyls in aromatic solvents, whereas (**6d**) and (**6f**) form only the tetracarbonyl species.[7] We have also found that the two isomers of (**6b**), (**6b′**) and (**6b″**), behave differently upon heating with Mo(CO)$_6$ in xylene (135 °C); the configuration of (**6b″**) has been determined by *X*-ray diffraction.[2] Thus (**6b′**) gives the molybdenum tricarbonyl derivative in *ca.* 20 min, whereas (**6b″**) gives only the tetracarbonyl derivative in the same time. The latter species is converted rather inefficiently into the same tricarbonyl derivative as obtained from (**6b′**) when heated at 135 °C for 24 h. We now find that heating the less abundant isomer of (**5a**), (**5a′**), with Mo(CO)$_6$ in toluene (110 °C) gives the *fac*-tricarbonyl derivative rapidly, whereas the more abundant isomer (**5a″**) gives only the tetracarbonyl species.[8] We thus assign (**5a′**) as the *meso-cis*-isomer, analogous to (**6b′**), and (**5a″**) as the *meso-trans*-species, analogous to (**6b″**). Similar complexation of the undistilled (**5c**) with Mo(CO)$_6$ in boiling toluene gave the corresponding *fac*-tricarbonyl derivative. Inspection of Dreiding models of (**5c**) with a *trans*-Me$_2$ configuration shows that it is impossible to obtain the *fac*-tricarbonyl species with this configuration. Since the reaction temperature is far below that expected to effect inversion at a tertiary arsine site[5] we conclude that the macrocyclization leading to (**5c**) gives only the *cis*-Me$_2$ configuration.

We are most grateful to the National Science Foundation, the Air Force Office of Scientific Research, and the Robert A. Welch Foundation for generous support of this work.

(*Received*, 30*th January* 1980; *Com.* 102.)

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† All new compounds gave satisfactory combustion and spectroscopic analyses.

‡ (**5a**): ^{1}H n.m.r. δ (AsMe) 1·17 and 1·13 (5:4 area ratio); ^{13}C δ (AsMe) 9·24 (major) and 8·96 p.p.m. (minor); (**5b**): ^{1}H n.m.r. δ (AsMe) 1·18 and 1·22 (5:1 ratio); ^{13}C δ (AsMe) 9·43 (major) and 8·52 (minor) p.p.m.; ^{31}P δ −27·0 (major) and −21·2 (minor) p.p.m. (upfield from external 85% H_3PO_4).

[1] For another paper in the series, Phosphino-macrocycles, see R. E. Davis, E. P. Kyba, A. M. John, and J. M. Yep, *Inorg. Chem.*, accepted for publication.

[2] E. P. Kyba, A. M. John, S. B. Brown, C. W. Hudson, M. J. McPhaul, A. Harding, K. Larsen, S. Niedzwiecki, and R. E. Davis, *J. Am. Chem. Soc.*, 1980, **102**, 139, and references contained therein.

[3] R. D. Feltham and W. Silverthorn, *Inorg. Synth.*, 1967, **10**, 159.

[4] K. Henrick and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, 1975, 1506.

[5] R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, 1972, **94**, 2859; L. Horner and W. Hofer, *Tetrahedron Lett.*, 1965, 4091.

[6] R. Baechler and K. Mislow, *J. Am. Chem. Soc.*, 1970, **92**, 3090.

[7] Macrocycles (**6e**) and (**6f**), E. P. Kyba and S. B. Brown, *Inorg. Chem.*, accepted for publication.

[8] The *fac*-(macrocycle) Mo(CO)$_3$ and *cis*-(macrocycle) Mo(CO)$_4$ are easily distinguishable by i.r. spectroscopy: P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, New York, 1975.