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Arsenic–Sulfur Polydentate Ligands. II. Palladium(II) Complexes of Bis[phenyl(*o*-thiomethylphenyl)arsino]butane

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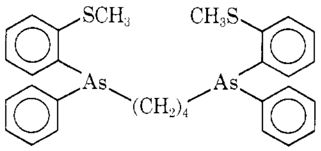
Received March 6, 1970

Synthesis of a potentially quadridentate arsenic–sulfur ligand, bis[phenyl(*o*-thiomethylphenyl)arsino]butane, C_4, is described. The palladium(II) complexes of the ligand that were isolated are of two types: (1) The $Pd_2(C_4)X_4$ complexes ($X = Cl, I$) have a bridging C_4 ligand and each planar palladium ion is coordinated to two halides, one thiomethyl group, and one arsenic atom. (Both the sulfur and arsenic donors are attached to the same benzene ring.) (2) The $[Pd_2(C_4)_2X_2][B(C_6H_5)_4]_2$ complexes are dimeric, bi-univalent electrolytes in polar solvents and have two arsenic atoms and one exchanging thiomethyl group coordinated to each palladium(II), along with a halide ion. A complex of the didemethylated ligand Pd(demethylated C_4) has also been isolated and is discussed in terms of a dimeric structure.

In part I[2] of this series, we reported a study of palladium(II) complexes of bis(phenyl-*o*-thiomethylphenylarsino)ethane (C_2) and bis(phenyl-*o*-thiomethylphenylarsino)propane (C_3). That study revealed that a variety of factors are involved in deciding which of several possible structures takes precedence under a given set of conditions. The dominating factors are the competition between halide ions and thiomethyl groups for coordination sites, the polarity of the solvent, and the flexibility of the polydentate ligand. In no case did the C_2 and C_3 ligands chelate in a quadridentate manner with a single metal ion. We now report the synthesis of a related potentially quadridentate ligand, bis(phenyl-*o*-thiomethylphenylarsino)butane (abbreviated C_4, structure I), in which the same two sets of *o*-thiomethylphenylarsino groups are linked by a flexible, aliphatic four-carbon chain. A study of its coordination properties toward palladium(II) was undertaken for the purpose of comparing its ligating behavior with those of the C_2 and C_3 ligands.



I

Phenyldichloroarsine was allowed to react with 1,4-dibromobutane in aqueous alkali medium and, after careful acidification, butanebis(phenylarsonic acid) was obtained.[2,3] The arsonic acid was reduced by sulfur dioxide in aqueous hydrochloric acid medium (~ 4 *M*) to butanebis(phenylchloroarsine).[2,3] Finally the reaction between the chloroarsine and *o*-lithiothioanisole[2] produced the C_4 ligand, which was recovered as white crystals from an acetone–ethanol medium. The infrared spectrum showed no absorption around 900 cm^{-1}, thus indicating the absence of the As═O group in the final product.

The four-carbon backbone of the ligand adds greater flexibility to the ligand and this leads to some new features and limitations in the syntheses of palladium(II) complexes, as compared to those of the C_2 and C_3 ligands. Whereas, in the cases of the latter two ligands, the addition of the chloropalladate solution (in butanol) to that of the ligands (in acetone–ethanol) in 1:1 molar proportion always provided the complexes $Pd(C_2)Cl_2$ and $Pd(C_3)Cl_2$ in pure crystalline form,[2] similar reaction conditions in the present case immediately lead to the separation of $Pd_2(C_4)Cl_4$. The filtrate from this preparation is quite colored (orange-yellow) and the addition of sodium tetraphenylborate facilitates the isolation of $[Pd(C_4)Cl][B(C_6H_5)_4]$. In the absence of the tetraphenylborate ion, the filtrate could be concentrated to collect more of the first mentioned product, $Pd_2(C_4)Cl_4$. When the filtrate (after separation of $Pd_2(C_4)Cl_4$) is treated with lithium bromide before addition of sodium tetraphenylborate, one obtains the complex $[Pd(C_4)Br][B(C_6H_5)_4]$. Similar addition of lithium iodide and sodium tetraphenylborate does not provide pure $[Pd(C_4)I][B(C_6H_5)_4]$. Treatment of $[Pd_2(C_4)Cl_4]$ with lithium iodide in dichloromethane leads to $[Pd_2(C_4)I_4]$. Several attempts to obtain complexes of the type $[Pd(C_4)X_2]$ (X = halide ion) failed to yield the desired products. The preparative methods are depicted in Figure 1.

The complexes reported in this paper can be classified as follows: A, $Pd_2(C_4)X_4$ ($X = Cl, I$); B, $[Pd(C_4)X][B(C_6H_5)_4]$ ($X = Cl, Br$); C, Pd(demethylated C_4).

$Pd_2(C_4)X_4$.—An alternative formulation as electrolytes $[Pd(C_4)][PdX_4]$ is inconsistent with the low conductance values of the compounds in dimethylformamide ($Pd_2(C_4)I_4$, ~ 10 mhos cm^2 mol^{-1}; Table I). Moreover the electronic spectra (Table II) do not show the long-wavelength bands that are characteristic of tetrahalopalladate(II) ions.[4] Thus $Pd_2(C_4)Cl_4$ has an absorption band around 365 mμ and $Pd_2(C_4)I_4$ around 455–460 mμ. The electronic spectra of $Pd_2(C_4)X_4$ ($X = Cl, I$) are very similar to those of $Pd_2(C_2)X_4$ and $Pd_2(C_3)X_4$ ($X = Cl, I$), and, as discussed earlier,[2] we adduce structure II where each *o*-thio-

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[1] On leave from the University of Burdwan, Burdwan, West Bengal, India.

[2] R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970).

[3] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 610 (1939).

[4] C. K. Jørgensen, "Halogen Chemistry," Vol. I, V. Gutman, Ed., Academic Press, New York, N. Y., 1967, p 344.

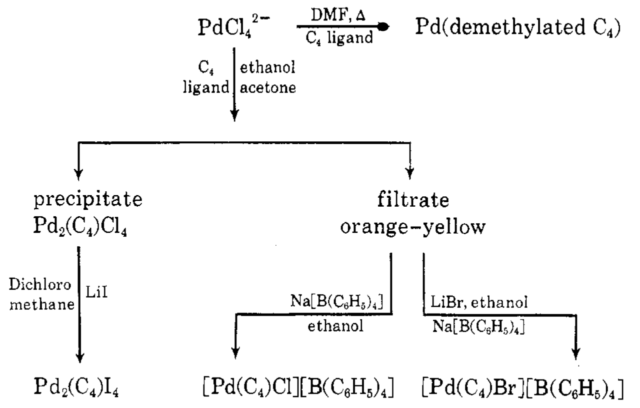


Figure 1.—Methods of preparation of the palladium(II) complexes of 1,4-bis[phenyl(*o*-thiomethylphenyl)arsino]butane (C_4).

TABLE I

CONDUCTANCE VALUES OF THE COMPLEXES $[Pd(C_4)X][B(C_6H_5)_4]$ AND $Pd_2(C_4)X_4$

Complex	Molar conductance, Λ_M, ohm^{-1} cm^2 mol^{-1} Nitromethane[a]			
	Nitromethane[a]	Acetonitrile[a]	Dimethylformamide[a]	Slope *A*, in acetonitrile[b]
$[Pd(C_4)Cl][B(C_6H_5)_4]$	57	101	. . .	930
$[Pd(C_4)Br][B(C_6H_5)_4]$	56	97	. . .	960
$Pd_2(C_4)I_4$	. . .	. . .	10	. . .

[a] Values reported for 1:1 and 2:1 electrolytes in nitromethane, acetonitrile, and dimethylformamide are 80–95, 160–190; 135–155, 250–310; and 70–80, 140–150, respectively: T. D. DuBois and D. W. Meek, *Inorg. Chem.* **8**, 146 (1969); M. Ciampolini and P. Paoletti, *ibid.*, **6**, 1261 (1967). For tetraphenylborate salts the molar conductivities are generally considerably lower than the ranges given: G. A. Pneumaticakis, *Chem. Ind.* (London), 770 (1968). [b] Slope of the plot ($\Lambda_0 - \Lambda_e$) *vs.* $\sqrt{c}$, where the symbols have their usual significance.

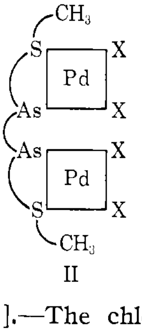
TABLE II

ELECTRONIC SPECTRA OF THE COMPLEXES $[Pd(C_4)X][B(C_6H_5)_4]$ AND $Pd_2(C_4)X_4$

(λ_{max} IN mμ; EXTINCTION COEFFICIENTS IN PARENTHESES)

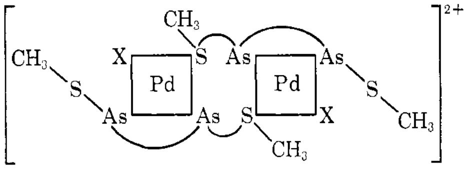
Complex	Halocarbon oil (mull)	Dichloromethane	Chloroform	DMF
$[Pd(C_4)Cl][B(C_6H_5)_4]$	350	342 (5700)	345 (5400)	. . .
$[Pd(C_4)Br][B(C_6H_5)_4]$	380	360 (4400)	355 (4600)	350 (4800)
$Pd_2(C_4)Cl_4$	. . .	. . .	. . .	365 (4700)
$Pd_2(C_4)I_4$	455	460 (8400)	460 (7900)	455 (7900)
Pd(demethylated C_4)	480–490	. . .	. . .	. . .

methylphenylarsino group is chelated to a different PdX_2 unit.



II

$[Pd(C_4)X][B(C_6H_5)_4]$.—The chloro and the bromo complexes of this series have been isolated. These complexes exhibit the expected apparent uni-univalent electrolyte conductances in nitromethane (~57 mhos cm^2 mol^{-1}; Table I) and in acetonitrile (~97–101 mhos cm^2 mol^{-1}; Table I). However, dilution conductance studies in acetonitrile show Onsager slopes[5,6] (930, 960) corresponding to 2:1 electrolytes (Table I). This supports a dimeric formulation, $Pd_2(C_4)_2X_2^{2+}$ (*e.g.*, structure III), which is analogous to a structure proposed[2] for the palladium(II) complexes of the C_3 ligand. The proton magnetic resonance spectrum of the chloro complex $[Pd(C_4)Cl][B(C_6H_5)_4]$ in deuteriochloroform shows two thiomethyl resonances of approximately equal intensity around τ 7.40 and 7.65 (reference TMS) and is comparable to the previously reported[2] spectrum of $[Pd(C_3)I][B(C_6H_5)_4]$. The S–CH_3 resonance of the free ligand in the same solvent appears at τ 7.65. It, therefore, is reasonable to conclude that there are two kinds of thiomethyl groups in these complexes, one coordinated and the other uncoordinated. It follows that the complexes are ultimately to be regarded as four-coordinate in structure. The molecular weights (Table III) found for $[Pd(C_4)X][B(C_6H_5)_4]$ (X = Cl, Br) in chloroform show a concentration dependence and are higher than those expected on the basis of a dimeric formulation. These higher values are not inconsistent with the expected ion association in nonpolar solvents.[2,7] The molecular weights are comparable in relative magnitude to those of $[Pd(C_n)X][B(C_6H_5)_4]$ (n = 2, 3; X = Cl, Br, I).[2]



III

TABLE III

MOLECULAR WEIGHTS OF $[Pd(C_4)X][B(C_6H_5)_4]$ COMPLEXES (CHLOROFORM SOLVENT)

Complex	Concn, g/l.	Mol wt found	Empirical formula wt
$[Pd(C_4)Cl][B(C_6H_5)_4]$	5.35	960	1067
	7.80	1026	
$[Pd(C_4)Br][B(C_6H_5)_4]$	4.55	1034	1112
	6.885	1147	

Pd(demethylated C_4).—In the absence of complexes of the type $Pd(C_4)X_2$, a mixture of $PdCl_4^{2-}$ and the C_4 ligand was refluxed in 1:1 molar proportion in dimethylformamide to give Pd(demethylated C_4).[2,8] Unfortunately, this demethylated complex is insoluble in common solvents so that its molecular complexity could not be established. However, its electronic mull spectrum is quite comparable to those of Pd(demethylated C_2) and Pd(demethylated C_3);[2] by analogy with the dimeric nature[2] of these latter complexes,

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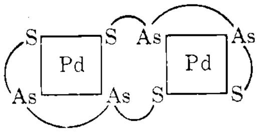
(5) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 931 (1967).

(6) M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *ibid.*, **7**, 2426 (1968).

(7) T. Tarantelli and C. Furlani, *J. Chem. Soc. A*, 1717 (1968).

(8) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).

we assign dimeric structure IV to the C_4 complex as well. The complex undergoes S-alkylation[2,8,9] with methyl iodide but the isolated product did not provide satisfactory and reproducible analyses for the expected product, $Pd(C_4)I_2$. This observation is not surprising in view of the strong tendency toward formation of the species $Pd_2(C_4)I_4$.



IV

Experimental Section

Synthesis of 1,4-Bis(phenyl-*o*-thiomethylphenylarsino)butane.—1,4-Butanebis(phenylarsonic acid) was prepared from phenyldichloroarsine (64 g) and 1,4-dibromobutane (32 g) following a procedure[2,3] analogous to those used for propanebis-(phenylarsonic acid) and ethanebis(phenylarsonic acid). The crude material was recrystallized from hot 1:1 ethanol–water; yield, 30–34 g; mp 194–196°. *Anal.* Calcd for $C_{16}H_{20}As_2O_4$: C, 45.09; H, 4.73; As, 35.16; O, 15.02. Found: C, 45.28; H, 4.75; As, 35.30; O (by difference), 14.67.

1,4-Butanebis(phenylchloroarsine) was prepared from butanebis(phenylarsonic acid) by reduction in cold aqueous hydrochloric acid (~4 *M*) with sulfur dioxide gas for 2 hr. The yellow oily material was allowed to stand with the mother liquor for 2 days. The viscous material was then separated, washed with cold 4 *M* HCl, and dried over KOH and Drierite; yield, 28–30 g.

The final product, 1,4-bis(phenyl-*o*-thiomethylphenylarsino)butane was obtained as follows. *o*-Bromothioanisole (14 g) was allowed to react with *n*-butyllithium (1.6 *N*, 45 ml) in ether and then with butanebis(phenylchloroarsine) (15 g in 20 ml of dry tetrahydrofuran).[2] After hydrolysis with dilute HCl the white precipitate was collected and dried. The product was recrystallized from a 1:3 acetone–ethanol mixture; yield, 9–10 g, mp 73–75°. *Anal.* Calcd for $C_{30}H_{32}As_2S_2$: C, 59.40; H, 5.32; As, 24.70; S, 10.57. Found: C, 59.41; H, 5.28; As, 24.80; S, 10.67.

Preparation of Complexes.—A stock solution of $PdCl_4^{2-}$ was prepared as described earlier.[2] In order to prepare $Pd_2(C_4)Cl_4$ the C_4 ligand (0.3 g, 0.0005 mol) was dissolved in hot 1:3 acetone–ethanol and treated with the chloropalladate solution (2.5 ml, 0.0005 mol). The soft, fluffy precipitate was filtered, washed with acetone, and dried. *Anal.* Calcd for $C_{30}H_{32}As_2Cl_4Pd_2S_2$: C, 37.49; H, 3.36; Cl, 14.75. Found: C, 38.05; H, 3.58; Cl, 14.66.

$[Pd(C_4)Cl][B(C_6H_5)_4]$ was obtained from the filtrate from the above preparation by treating it with an ethanol solution of sodium tetraphenylborate. The resulting precipitate was collected, washed with ethanol, and dried. *Anal.* Calcd for $C_{54}H_{52}As_2BPdClS_2$: C, 60.75; H, 4.91; Cl, 3.32. Found: C, 60.53; H, 4.98; Cl, 3.42.

$[Pd(C_4)Br][B(C_6H_5)_4]$ was isolated from the filtrate from the preparation of $Pd_2(C_4)Cl_4$ by first treating with lithium bromide and then adding an ethanol solution of sodium tetraphenylborate. The precipitate was washed with ethanol and dried. *Anal.* Calcd for $C_{54}H_{52}As_2BBrPdS_2$: C, 58.32; H, 4.71; Br, 7.19. Found: C, 58.58; H, 4.64; Br, 7.35.

To produce $Pd_2(C_4)I_4$, freshly prepared $Pd_2(C_4)Cl_4$ was suspended in dichloromethane and stirred with an ethanol solution of lithium iodide. The resulting dark red solution was filtered and allowed to crystallize. *Anal.* Calcd for $C_{30}H_{32}As_2I_4Pd_2S_2$: C, 27.15; H, 2.43; I, 38.25. Found: C, 27.11; H, 2.37; I, 38.20.

Pd(demethylated C_4) was formed when a solution made up of C_4 ligand (0.6 g, 0.001 mol) in dimethylformamide (30 ml) and chloropalladate stock solution (5 ml, 0.001 mol) was heated under reflux for 6 hr. The crystals which separated were collected, washed with ethanol, and dried. *Anal.* Calcd for $C_{25}H_{26}As_2PdS_2$: C, 49.25; H, 3.84; S, 9.39. Found: C, 49.12; H, 3.88; S, 9.67.

Acknowledgment.—We are grateful for the support of the U. S. Public Health Service (Grant GM 10040-08, National Institute of General Medical Sciences).

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[9] N. J. Rose, C. A. Root, and D. H. Busch, *Inorg. Chem.*, **6**, 1431 (1967).

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Crystal Structure of Potassium Pentafluorotellurate($KTeF_5$)[1]

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Received November 5, 1969

The crystal structure of potassium pentafluorotellurate, $KTeF_5$, has been determined by a three-dimensional single-crystal X-ray diffractometer study. A full-matrix least-squares refinement using 646 observed reflections resulted in a final weighted *R* factor of 2.18%. The structure was refined in the orthorhombic space group Pbcm. The cell constants are a = 4.735 (1) Å, b = 9.209 (2) Å, and c = 11.227 (2) Å. With four molecules per unit cell, the calculated density is 3.547 g/cm^3; the observed density is 3.55 g/cm^3. The structure contains isolated TeF_5^- ions which approximate a square pyramid but which in fact have only the C_s symmetry required by the space group. The apical Te–F distance is 1.862 (4) Å; the basal Te–F distances are 1.953 (3) and 1.952 (3) Å, respectively.

Introduction

Shortly after we had collected diffractometer data for a crystal of potassium pentafluorotellurate, the crystal structure was reported by Edwards and Mouty,[3] who used film methods and photometric techniques to collect their intensity data. However, since five-coordi-

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] Los Alamos Scientific Laboratory, University of California, postdoctoral appointee.

[3] A. J. Edwards and M. A. Mouty, *J. Chem. Soc. A*, 703 (1969).