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Palladium(II) Complexes with Polydentate Phosphorus–Sulfur Ligands[1,2]

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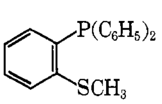
Various types of palladium(II) complexes have been characterized with four polydentate ligands: diphenyl(*o*-methylthiophenyl)phosphine (SP), bis(*o*-methylthiophenyl)phenylphosphine (DSP), tris(*o*-methylthiophenyl)phosphine (TSP), and tris(*o*-methylthiophenyl)arsine (TSA). The planar complexes [Pd(SP)Cl_2] and [$Pd(SP)_2$]$(ClO_4)_2$ are obtained with the ligand SP. Bis(*o*-methylthiophenyl)phenylphosphine functions as a bidentate ligand in [Pd(DSP)Cl_2], but as a tridentate in [Pd(DSP)Cl]ClO_4. The potentially tetradentate ligands TSP and TSA function only as bidentates in [Pd(TSA)Cl_2] and [Pd(TSP)Cl_2], but they function as tetradentates in the [Pd_2(TSP)Cl_4] and [Pd_2(TSA)Cl_4] complexes by coordinating to two different palladium ions. Both ligands form deeply colored bis complexes, [$Pd(TSA)_2$]$(ClO_4)_2$ and [$Pd(TSP)_2$]$(ClO_4)_2$, which exhibit electronic absorption spectra quite different from that of the colorless [$Pd(SP)_2$]$(ClO_4)_2$ complex. The behavior of palladium(II) toward these ligands is contrasted with that of nickel(II), which forms five-coordinate complexes with all three phosphorus–sulfur ligands.[4-6] Also the failure of the sulfur-containing tetradentates TSP and TSA to form trigonal-bipyramidal complexes with palladium(II) is contrasted with the ready formation of such complexes by similar tetraarsine and tetraphosphine ligands.[7]

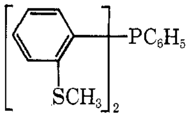
Introduction

Recent investigations have shown that polydentate ligands containing donor atoms of groups V and VI give a variety of palladium(II) complexes.[7-11] Palladium(II) normally forms planar, four-coordinate complexes; however, five-coordinate complexes have also been isolated with certain ligands. For example, Venanzi and co-workers[7] have shown that palladium(II) forms trigonal-bipyramidal complexes with the sterically rigid tetradentate ligands As[*o*-$C_6H_4As(C_6H_5)_2$]$_3$ (QAS) and P[*o*-$C_6H_4P(C_6H_5)_2$]$_3$ (QP). The monodentate ligand 2-phenylisophosphindoline forms a distorted square-pyramidal, five-coordinate Pd(II) complex.[12] All of the above types of ligands, which give five-coordinate palladium(II) complexes, also form five-coordinate nickel(II) complexes.

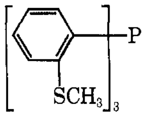
Following the discovery that nickel(II) forms a series of five-coordinate complexes with each of the phosphorus–sulfur polydentate ligands—diphenyl(*o*-methylthiophenyl)phosphine (I, SP, bidentate),[4] bis(*o*-methylthiophenyl)phenylphosphine (II, DSP, tridentate),[5] and tris(*o*-methylthiophenyl)phosphine (III, TSP, tetradentate)[6]—we became interested in investigating whether the corresponding metal ion in the second transition series, *i.e.*, palladium(II), would form similar complexes with these chelating agents. The results of the present investigation permit two comparisons: (a) the differential behavior between the d^8 metal ions, palladium(II) and nickel(II), with regard to the types of complexes they form with these polydentate phosphorus–sulfur ligands; and (b) the different coordinating properties of the sulfur, phosphorus, and arsenic donor atoms in structurally similar polydentate ligands.



I, SP



II, DSP

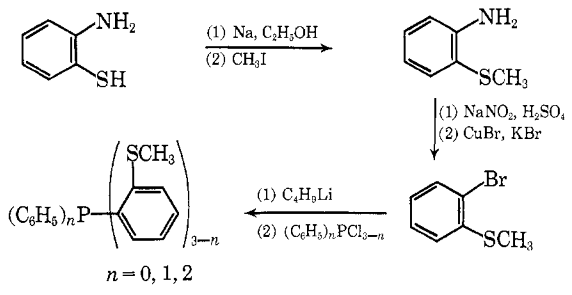


III, TSP

Experimental Section

Syntheses of the Ligands.—The three phosphorus–sulfur ligands were prepared by the reaction sequence[4,6] in Scheme I. The tetradentate arsenic–sulfur ligand (TSA, As(*o*-$C_6H_4SCH_3$)$_3$), analogous to TSP, was prepared by the above sequence of reactions using arsenic trichloride in the final step.[6]

SCHEME I



n	Compd	Designation
0	P(*o*-$C_6H_4SCH_3$)$_3$	TSP
1	C_6H_5P(*o*-$C_6H_4SCH_3$)$_2$	DSP
2	$(C_6H_5)_2P$(*o*-$C_6H_4SCH_3$)	SP

Preparation of the Complexes. [Pd(SP)Cl_2].—A solution of Li_2PdCl_4[13] (2 mmoles) in 1-butanol (10 ml) was added with stirring

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[3] NDEA Predoctoral Fellow, 1962–1965.

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[13] A stable 1-butanol solution of Li_2PdCl_4 was prepared conveniently by dissolving $PdCl_2$ (1.77 g, 0.01 mole) and lithium chloride (0.95 g, 0.02 mole) in 50 ml of hot 1-butanol and then filtering the solution. No observable decomposition to palladium metal occurred when the solution was boiled or when it was kept at room temperature for several months.

TABLE I

CHARACTERIZATION DATA FOR THE PALLADIUM(II) COMPLEXES

Complex	Color	Yield, %	Conductance,[a] ΛM, cm²/ohm mole	Analyses,[b] %							
				C		H		Cl		As or P	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Pd(SP)_2](ClO_4)_2$[c]	White	82	179	49.50	50.16	3.72	3.70	7.69	8.05	6.72	6.72 (P)
$[Pd(SP)Cl_2]$[c]	Yellow	72	3.8	46.99	46.76	3.53	3.49			6.38	6.45 (P)
$[Pd(DSP)Cl_2]$[d]	Yellow	70	19[a]	45.17	45.36	3.60	3.77	13.33	13.16	5.82	5.59 (P)
$[Pd(DSP)Cl]ClO_4$[d]	Light yellow	85	164[a]	40.32	40.59	3.21	3.23	11.90	11.84	5.20	5.14 (P)
$[Pd(DSP)I_2]$[g]	Red	50	<2[a]	33.65	34.15	2.68	2.82	35.60	34.98 (I)		
$[Pd(TSA)Cl_2]$[e]	Orange	30	<2	40.56	40.60	3.40	3.44			12.05	12.18 (As)
$[Pd(TSP)Cl_2]\cdot DMF$[f]	Yellow	60	43	44.30	44.49	4.34	4.45			4.76	4.92 (P)
$[Pd_2(TSA)Cl_4]$[e]	Yellow-brown	82	Insol	31.56	31.99	2.65	3.31			9.37	9.46 (As)
$[Pd_2(TSP)Cl_4]$[f]	Yellow-brown	85	Insol	33.40	33.05	2.80	2.48	18.78	18.31	4.10	4.34 (P)
$[Pd(TSA)_2](ClO_4)_2$[e]	Orange-brown	88	165	42.20	42.90	3.54	3.77	5.94	5.99	12.51	12.10 (As)
$[Pd(TSP)_2](ClO_4)_2$[f]	Brown	85	184	45.50	45.60	3.83	3.82	6.42	6.58	5.60	5.64 (P)

[a] Molar conductance values on approximately 10^{-3} *M* solutions in nitromethane; the three DSP complexes were done on 10^{-3} *M* solutions in acetonitrile. [b] Microanalyses for C, H, and halogen were determined by Galbraith Laboratories, Knoxville, Tenn.; P or As analyses were determined colorimetrically in this laboratory. [c] SP, $(C_6H_5)_2P(o\text{-}C_6H_4SCH_3)$. [d] DSP, $C_6H_5P(o\text{-}C_6H_4SCH_3)_2$. [e] TSA, $As(o\text{-}C_6H_4SCH_3)_3$. [f] TSP, $P(o\text{-}C_6H_4SCH_3)_3$. [g] Mol wt: Calcd, 714; found, 756 in dimethylformamide.

to a hot solution of SP (0.62 g, 2 mmoles) in 1-butanol (30 ml). A yellow compound crystallized as the resulting orange-yellow solution cooled; it was collected on a sintered-glass funnel, washed with chlorobenzene and acetone, and then dried with a stream of dry air.

$[Pd(SP)_2](ClO_4)_2$.—A 1-butanol solution (5 ml) of Li_2PdCl_4 (1 mmole) was added to SP (2 mmoles) in hot 1-butanol (30 ml), and the resulting solution was treated with excess lithium perchlorate (0.5 g) dissolved in hot 1-butanol (10 ml). After stirring for 1 min, the solution deposited colorless needles, which were collected and washed successively with 1-butanol, chlorobenzene, and acetone.

$[Pd(DSP)Cl_2]$.—Sodium tetrachloropalladate(II) (0.6 g, 2 mmoles) was dissolved in 20 ml of warm 1-butanol and mixed with 0.70 g (2 mmoles) of DSP dissolved in 10 ml of warm 1-butanol. The solution was stirred for 1 hr and cooled to 0°. The resulting crystals were collected on a sintered-glass funnel and dried in a stream of dry air and finally *in vacuo*.

$[Pd(DSP)Cl]ClO_4$.—The $[Pd(DSP)Cl_2]$ complex (0.5 g, 1 mmole) was dissolved in warm 1-butanol and mixed with a large excess of sodium perchlorate in 10 ml of butanol. The product crystallized from the solution and it was collected on a funnel, dried in a stream of dry air, and recrystallized from dichloromethane.

$[Pd(TSA)Cl_2]$.—A filtered solution of sodium tetrachloropalladate(II) (5 mmoles) in ethanol (100 ml) was added dropwise to a refluxing suspension of $As(o\text{-}C_6H_4SCH_3)_3$, TSA, (2.22 g, 5 mmoles) in ethanol (250 ml). The very insoluble $[Pd_2(TSA)Cl_4]$ began to precipitate during the latter part of the addition. When the reaction mixture had cooled to room temperature, the yellow-brown $[Pd_2(TSA)Cl_4]$ (1.40 g) was separated by filtration, and the orange-red filtrate was allowed to stand 48 hr. Red crystals (0.93 g, 1.5 mmoles, 30% yield) were then collected, and the resulting filtrate was almost colorless. The orange product was washed several times with boiling 1-butanol.

$[Pd_2(TSA)Cl_4]$.—TSA (0.89 g, 2 mmoles) dissolved in 30 ml of dichloromethane was added to sodium tetrachloropalladate(II) (1.6 g, 5.4 mmoles) in absolute ethanol (200 ml). The resulting extremely insoluble complex was collected on a filter, washed several times with ethanol, and then dried *in vacuo*.

$[Pd(TSA)_2](ClO_4)_2$.—Sodium tetrachloropalladate(II), $Na_2PdCl_4\cdot 4H_2O$ (0.61 g, 1.67 mmoles), dissolved in 30 ml of ethanol was filtered and added dropwise to a suspension of TSA ligand (2.22 g, 5 mmoles) in refluxing ethanol (50 ml) containing 1 g of anhydrous lithium perchlorate. After refluxing for 1 hr, a mixture of red crystals and excess ligand (2.0 g) was collected. The excess ligand was removed by boiling the mixture with 1-butanol (three successive 100-ml portions), in which the red palladium complex was practically insoluble.

$[Pd(TSP)_2](ClO_4)_2$.—This compound was prepared in the same manner as the analogous TSA compound and recrystallized from dichloromethane and 1-butanol.

Characterization Measurements.—The spectral, magnetic, and conductance measurements were obtained as described previously.[6]

Discussion

The characterization data of the palladium(II) complexes are given in Table I. In each case the product which is isolated from palladium chloride solutions exhibits very low conductivity and contains two coordinated chloride ions. The electronic absorption spectra confirm the bidentate nature of the ligands. For example, the spectral shapes and intensities of the nonelectrolyte complexes of SP, DSP, and TSA with palladium(II) chloride (Figure 1) are essentially the same, although the absorption maximum of $[Pd(TSA)Cl_2]$ is shifted to lower energy, as expected from ligand field considerations whenever a phosphorus donor is replaced by a similar arsenic donor.

Attempts to demonstrate by nmr the presence of uncoordinated thiomethyl groups in the $[Pd(DSP)Cl_2]$ and $[Pd(TSA)Cl_2]$ complexes were unsuccessful owing to the low solubility of the compounds in appropriate solvents. However, the slight conductivity of $[Pd(DSP)Cl_2]$ in acetonitrile (Table I) suggested that the free thiomethyl group had a tendency to displace one of the coordinated chloride ions. In fact, when an ethanol solution of $[Pd(DSP)Cl_2]$ was treated with lithium perchlorate, the lighter yellow, uni-univalent electrolyte $[Pd(DSP)Cl]ClO_4$ was isolated (Table I). Thus, the reactions in Scheme II can be used to isolate different planar complexes in which DSP functions both as a bidentate and as a tridentate in the respective complexes.

SCHEME II

$$\begin{tikzcd}
{[PdCl_4]^{2-} + DSP} \arrow[r] & {[Pd(DSP)Cl_2] + 2Cl^-} \arrow[d, "LiClO_4"] \\
 & {[Pd(DSP)Cl]ClO_4 + Cl^-}
\end{tikzcd}$$

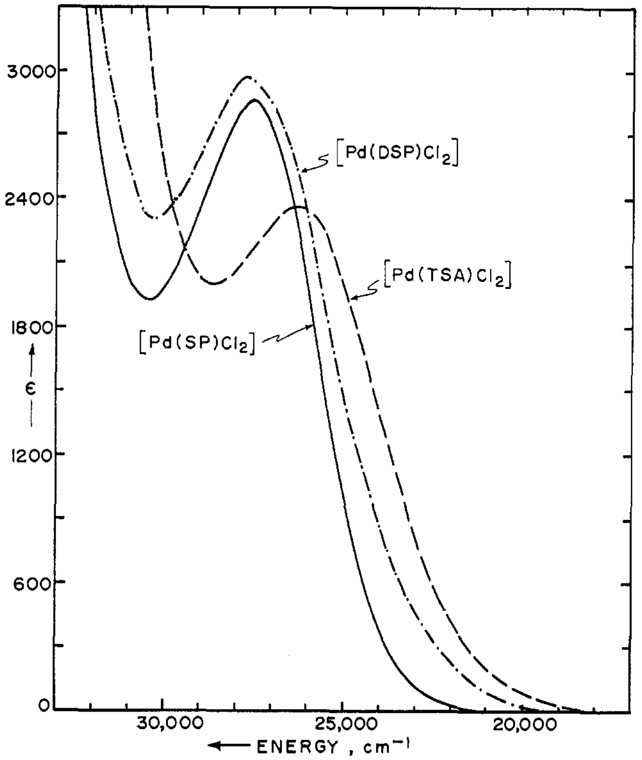

Figure 1.—Electronic absorption spectra of (———) [Pd(SP)Cl_2], (— · —) [Pd(DSP)Cl_2], and (— —) [Pd(TSA)Cl_2] in dichloromethane solutions.

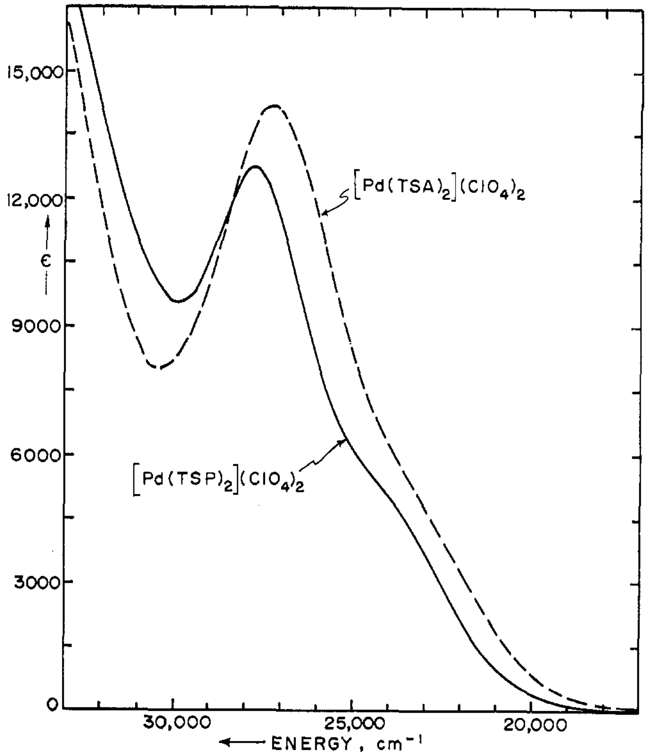

Figure 2.—Electronic absorption spectra of (———) [Pd$(TSP)_2$]$(ClO_4)_2$ and (— —) [Pd$(TSA)_2$]$(ClO_4)_2$ in dichloromethane solutions.

The electronic spectrum of [Pd(DSP)Cl]ClO_4 shows that replacement of a chloride ion in [Pd(DSP)Cl_2] by a thiomethyl donor has increased the energy of the first transition slightly ($E_{\max}$ 29,000 cm^{-1}, compared with 27,600 cm^{-1} in [Pd(DSP)Cl_2]), but the intensity of the band has doubled (ϵ increased from 3000 to 6000).[5] The increased intensity may result from the greater π-bonding character of sulfur than of chloride, and from the nonplanarity of the donor atoms around palladium. Because of the rigidity of the aryl framework and the normal bonding angles of phosphorus and sulfur, both sulfur atoms cannot lie in a plane with the P–Pd bond.

With the exception of DSP, the di-univalent [Pd(ligand)$_2$]$(ClO_4)_2$ complexes are obtained when [PdCl_4]$^{2-}$ is treated with an excess of these polydentate ligands in the presence of perchlorate ion. The four-coordinate [Pd$(SP)_2$]$(ClO_4)_2$ complex is nearly white because the first electronic transition occurs in the ultraviolet region and is obscured by the intense charge-transfer band at 31,850 cm^{-1} (ϵ 18,000), whereas solid [Pd$(TSA)_2$]$(ClO_4)_2$ is orange and solid [Pd$(TSP)_2$]$(ClO_4)_2$ is intensely reddish brown. The color of the latter compound changes rapidly from brown to yellow by grinding it to a powder or by dissolving it in several solvents, even in noncoordinating ones such as CH_2Cl_2. The electronic spectra of both compounds in dichloromethane solution are given in Figure 2.

Since the TSP and TSA ligands are not functioning as simple bidentates in the intensely colored [Pd(ligand)$_2$]$(ClO_4)_2$ compounds, it is instructive to consider how the spectra would be affected if five-coordinate palladium(II) complexes were formed. The extinction coefficients are higher and the energies of the first electronic transitions are lower in five-coordinate complexes than in square-planar complexes with the same ligands.[6,7,14] Both of these effects are observed in the [Pd$(TSP)_2$]$(ClO_4)_2$ and [Pd$(TSA)_2$]$(ClO_4)_2$ complexes. Therefore, since the spectra (Figure 2) differ so markedly from that of the planar [Pd$(SP)_2$]$(ClO_4)_2$ and fit the qualitative trends of five-coordinate complexes, it has been concluded that one of the potential tetradentates must be involved with bonding more than two of its donor atoms. An X-ray structural determination would be required to tell the exact number of bonded donor atoms and the correct stereochemistry.

It has been concluded from the change in the electronic spectrum of [Pd$(SP)_2$]$(ClO_4)_2$ upon the addition of iodide, shown in Figure 3, that the iodide ion adds to the coordination sphere to form a five-coordinate species in solution. In fact, when the solution was concentrated, the five-coordinate [Pd$(SP)_2$I]ClO_4 compound was obtained as deep orange crystals. The spectrum of the latter compound was identical with the solution spectrum shown in Figure 3. Bromide causes a much smaller shift to lower energy, whereas chloride has essentially no effect. This decreasing tendency of association may reflect the decreasing polarizability and covalent bonding trend of the halides as the ionic radius decreases. The [Pd(DSP)Cl]ClO_4 complex also adds iodide to form a five-coordinate species in solution. In fact, deep red crystals of [Pd(DSP)I_2] were obtained from the solution (Table I).

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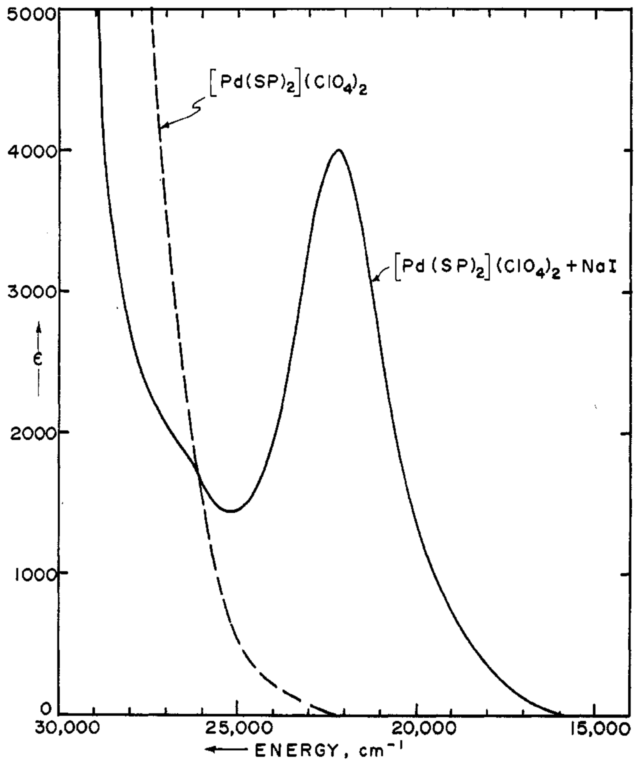

Figure 3.—Edge of the intense charge-transfer band (E_{max} 31,850 cm^{-1}, ε 18,110) of (— —) [Pd(SP)$_2$](ClO$_4$)$_2$ in DMF and (———) the electronic spectrum of [Pd(SP)$_2$](ClO$_4$)$_2$ in the presence of excess sodium iodide in DMF.

Numerous attempts to isolate pure [Pd(TSP)Cl]ClO$_4$ and [Pd(TSA)Cl]ClO$_4$ complexes, in which the ligands would function as tridentates, where unsuccessful owing to the insolubility of the [Pd(ligand)$_2$](ClO$_4$)$_2$ and the dinuclear Pd$_2$Cl$_4$·(ligand) compounds. Also, attempts to prepare [Pd(DSP)$_2$](ClO$_4$)$_2$ resulted only in the insoluble [Pd(DSP)Cl$_2$] and [Pd(DSP)Cl]ClO$_4$ complexes being isolated, even though the color of the solution was similar to those from which [Pd(TSP)$_2$](ClO$_4$)$_2$ and [Pd(TSA)$_2$](ClO$_4$)$_2$ were isolated. Solubility relationships seem to preclude isolation of pure samples of some of the species in solution. A similar solubility situation has been noted with a triarsine ligand.[15]

Conclusions

The polydentate phosphorus–sulfur and arsenic–sulfur ligands investigated in this study exhibit a much smaller tendency to form five-coordinate palladium(II) complexes than nickel(II) complexes, where all three phosphorus–sulfur ligands readily formed the five-coordinate complexes [Ni(SP)$_2$X]ClO$_4$,[4] [Ni(DSP)X$_2$],[5] and [Ni(TSP)X]ClO$_4$.[6] These results reflect the observation[16] that for a given oxidation state and electronic configuration (*e.g.*, M(II), d^8), the tendency to form five-coordinate complexes decreases with increasing atomic number.

When compared with structurally similar polyarsine and polyphosphine ligands, these phosphorus–sulfur ligands appear to exhibit less tendency to form five-coordinate palladium(II) complexes. This trend results primarily from an electronic effect; *i.e.*, thioethers are less easily polarized and form less covalent bonds with Pd(II) than tertiary arsines and phosphines. Steric factors may also aid formation of five-coordinate palladium(II) complexes with rigid tetradentates such as P(o-C$_6$H$_4$P(C$_6$H$_5$)$_2$)$_3$ and As(o-C$_6$H$_4$As(C$_6$H$_5$)$_2$)$_3$.[7]

Acknowledgment.—The authors thank the Ohio State University Computer Center for a grant which aided this study.

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