The situation is more complicated in the reactions with O_2 and NH_3. At the pressures used O_2 absorbs light at 1849 A, but not as strongly as borazine. In the borazine–ammonia reaction both molecules absorb strongly at 1849 A. For the borazine–water reaction we can visualize the initial photochemical step

$$B_3N_3H_6 + h\nu \longrightarrow B_3N_3H_5 + H$$

followed by

$$B_3N_3H_5 + H_2O \longrightarrow B_3N_3H_5OH + H$$

and further reactions of the hydroxy derivative to form diborazinyl ether. For the borazine–ammonia reaction we can write for the reaction following the initial photochemical step

$$B_3N_3H_5 + NH_3 \longrightarrow B_3N_3H_5NH_2 + H$$

or assuming the initial photochemical step[11]

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

we can write

$$B_3N_3H_6 + NH_2 \longrightarrow B_3N_3H_5NH_2 + H$$

Further discussion of the mechanism must be deferred until quantitative measurements of quantum yields are available.

[11] H. S. Taylor, *J. Phys. Chem.*, **42**, 783 (1938).

Contribution from the School of Chemistry,
University of New South Wales, Kensington, N.S.W., Australia

S-Dealkylation and S-Alkylation Reactions of Metal Chelates of Sulfur Ligands

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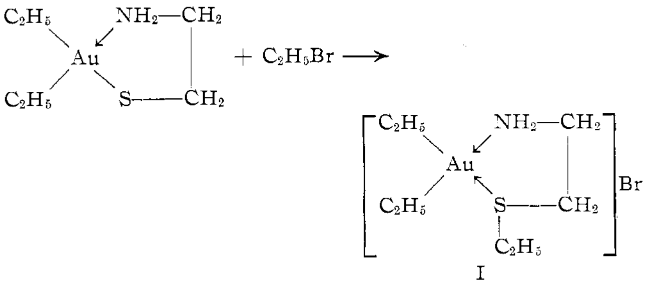
S-Demethylation of the ligand has been observed to occur when palladium(II) and platinum(II) chelates of dimethyl-*o*-methylthiophenylarsine and 8-methylthioquinoline are heated in dimethylformamide to yield complexes of the corresponding thiols, *viz.*, dimethyl-*o*-mercaptophenylarsine and 8-quinolinethiol. S-Debenzylation of dichloro(dimethyl-*o*-benzylthiophenylarsine)palladium(II) was effected in a similar manner. Some of the S-dealkylated metal chelates can be S-alkylated to give metal chelates of the original or another thioether.

Introduction

S-Alkylation is known to occur *in situ* when certain metal complexes of thiols are treated with alkyl halides. One of the earliest reported examples of this type of reaction was the alkylation of $Pt(SC_2H_5)_2$ by reaction with ethyl iodide or methyl iodide in sealed tubes at 70–80° to form the thioether complexes $Pt(SR_2)_2I_2$ (R = methyl, ethyl).[1,2]

Similar alkylation of mercapto complexes of mercury(II) was reported by Ray.[3,4] The first reaction of this type involving a metal chelate was reported by Ewens and Gibson,[5] who showed that the gold(III) complex of 2-mercaptoethylamine reacts with ethyl bromide to yield the S-alkylated complex I.



I

Busch, *et al.*,[6,7] allowed the nickel(II) complex of β-mercaptoethylamine to react with alkyl halides in dimethylformamide solution and obtained S-alkylated derivatives. A typical reaction is[7]

$$\underset{\text{square diamagnetic}}{Ni(SCH_2CH_2NH_2)_2} + 2CH_3I \longrightarrow \underset{\text{octahedral paramagnetic}}{Ni(CH_3SCH_2CH_2NH_2)_2I_2}$$

S-Alkylation has been used for the preparation of macrocyclic nickel chelates;[8] in these reactions the original nickel complex serves as a template.[9] These and other similar S-alkylation reactions have been discussed in recent reviews.[10–13]

Attempts to prepare a gold(III) complex of 8-methylthioquinoline (II) (N–SCH_3) by the reaction of sodium tetrachloroaurate(III) with II led to S-demethylation of the ligand and the isolation of a gold(III) complex of 8-quinolinethiol, *viz.*, $Au(N\text{–}S)Cl_2$.[14] This led us to

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[1] K. A. Hofman and W. O. Rabe, *Z. Anorg. Chem.*, **14**, 293 (1897).

[2] S. Smiles, *J. Chem. Soc.*, **77**, 106 (1900).

[3] P. C. Ray, *ibid.*, **109**, 131, 603 (1916); **111**, 101 (1917).

[4] P. C. Ray and P. C. Guha, *ibid.*, **115**, 261, 541, 548, 1148 (1919).

[5] R. V. G. Ewens and C. S. Gibson, *ibid.*, 431 (1949).

[6] D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 125.

[7] D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

[8] M. C. Thompson and D. H. Busch, *ibid.*, **86**, 3651 (1964).

[9] D. F. Martin in "Preparative Inorganic Reactions," Vol. I, W. M. Jolly, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter III, p 69.

[10] R. S. Nyholm, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, 25 (1965).

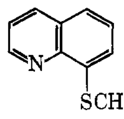
[11] Q. Fernando, *Advan. Inorg. Chem. Radiochem.*, **7**, 185 (1965).

[12] S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

[13] D. St. C. Black and E. Markham, *Rev. Pure Appl. Chem.*, **15**, 109 (1965).

[14] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Australian J. Chem.*, **19**, 1391 (1966).

investigate further S-dealkylation, and in a preliminary publication[15] we reported S-demethylation reactions of some metal chelates of thioethers.



II

Blomstrand[16] in 1883 reported S-demethylation of dimethyl sulfide in the presence of platinum(II) as in

$$PtCl_2 + 2(CH_3)_2S \longrightarrow Pt(SCH_3)_2 + 2CH_3Cl \qquad (1)$$

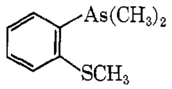
He also reported that, whereas the dialkyl sulfides R_2S (R = ethyl, *n*-propyl, and *n*-butyl) reacted as in (2), when R = amyl, reaction 1 occurred. However, in a later paper[17] Blomstrand showed that the observed reaction of diamyl sulfide was due to the presence of amyl mercaptan as an impurity. When pure amyl mercaptan was used, no $Pt(SC_5H_{11})_2$ was obtained and the reaction proceeded as in (2).

$$PtCl_2 + 2R_2S \longrightarrow Pt(R_2S)_2Cl_2 \qquad (2)$$

To our knowledge no other examples of S-dealkylation in metal complexes of thioethers have been reported.

Results and Discussion

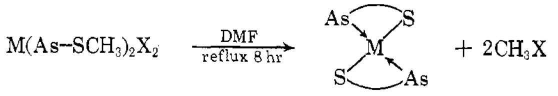
Mono and bis chelated complexes of dimethyl-*o*-methylthiophenylarsine (III) ($As-SCH_3$) of the types



III

$Pd(As-SCH_3)X_2$, $M(As-SCH_3)_2X_2$ (M = Pd, Pt; X = Cl, Br, I), $Pt(As-SCH_3)I_2$, and $[Pt(As-SCH_3)_2][PtX_4]$ (X = Cl, Br) have been reported.[18,19] S-Demethylation of the ligand occurs when these compounds are heated under reflux in dimethylformamide (DMF), as shown in Schemes I–III.

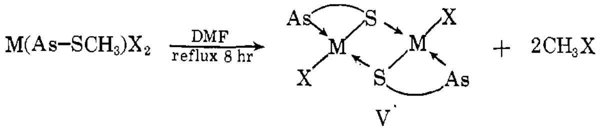
SCHEME I



IV

M = Pd; X = Cl, Br and M = Pt; X = Cl, I

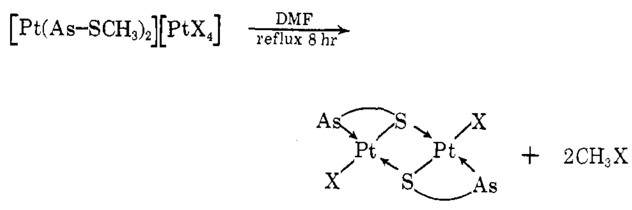
SCHEME II



V

M = Pd; X = Cl, Br, I and M = Pt; X = I

SCHEME III



VI

X = Cl, Br

The crystalline demethylated complexes, which are listed in Table I, were obtained in good yield (40–90%). The low solubilities of the complexes of empirical formula M(As–S)X did not permit determination of their molecular weights, but these compounds are assumed to be dimeric with the configurations V and VI, since similar dimeric μ-thiolo complexes of palladium and platinum have been reported.[20,21] The mass spectra of the compounds $Pd_2(As-S)_2X_2$ (X = Cl, Br) and $Pt_2(As-S)_2Cl_2$ were obtained. The spectra display a strong peak corresponding to the dimeric molecular ion in each case but, in addition, they show a peak corresponding to the trimeric molecular ion. The relative intensity of the trimeric peak compared to that of the dimeric peak varies from ~2% for $Pd_2(As-S)_2Br_2$ to ~20% for $Pt_2(As-S)_2Cl_2$. In the absence of confirmatory X-ray structural data, it is assumed that the compounds exist in the solid state essentially as dimers but in the vapor state at least a small amount exists in a cyclic trimeric form.

TABLE I

COMPLEXES OF DIMETHYL-*o*-MERCAPTOPHENYLARSINE

Complex	Color	Λ_{2000} in CH_3NO_2 at 25°, mhos
$Pd(As-S)_2$	Yellowish orange	1.1
$Pd_2(As-S)_2Cl_2$	Orange	0.3
$Pd_2(As-S)_2Br_2$	Orange	0.7
$Pd_2(As-S)_2I_2$	Reddish orange	Insoluble
$Pt(As-S)_2$	Pale yellow	0.1
$Pt_2(As-S)_2Cl_2$	Yellow	0.8
$Pt_2(As-S)_2Br_2$	Yellow	1.8
$Pt_2(As-S)_2I_2$	Yellow	Insoluble

Dimethylformamide is known to react with alkyl halides.[22,23] This may be a factor in the facile demethylation of these thioether complexes; however, demethylation of $Pd(As-SCH_3)Br_2$ was effected in boiling cyclohexanone. It is noteworthy that an attempt to achieve S-demethylation of this compound in acetone was unsuccessful: after 80 hr at the reflux temperature, the original compound was recovered.

The S-demethylation reaction is comparable to the Zeisel cleavage of an ether by hydrogen halide. The initial reaction in the latter case involves protonation of the ether to form an oxonium ion; cleavage then occurs by nucleophilic attack by the halide ion on the protonated ether (3). This can proceed by either an SN1 or SN2 mechanism, depending on the conditions

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(15) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature*, **211**, 519 (1966).

(16) C. W. Blomstrand, *J. Prakt. Chem.*, **27**, 161 (1883).

(17) C. W. Blomstrand, *ibid.*, **38**, 523 (1888).

(18) S. E. Livingstone, *J. Chem. Soc.*, 4222 (1958).

(19) B. Chiswell and S. E. Livingstone, *ibid.*, 1071 (1960).

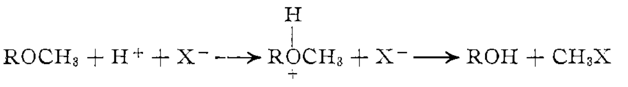
(20) S. E. Livingstone, *ibid.*, 1989, 1994 (1956).

(21) J. W Wrathall and D. H. Busch, *Inorg. Chem.*, **2**, 1182 (1963).

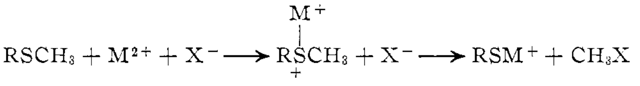
(22) G. M. Coppinger, *J. Am. Chem. Soc.*, **76**, 1372 (1954).

(23) N. Kornblum and R. K. Blackwood, *ibid.*, **78**, 4037 (1956).

and the structure of the ether. A similar type of nucleophilic attack mechanism can be postulated for the S-demethylation reaction as in (4).

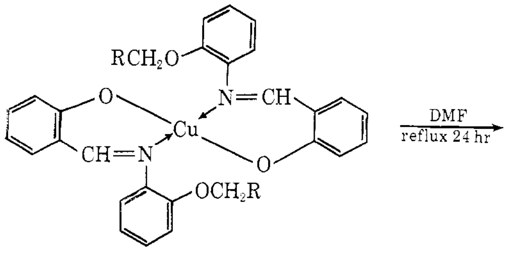


$$ROCH_3 + H^+ + X^- \longrightarrow R\overset{H}{\underset{+}{O}}CH_3 + X^- \longrightarrow ROH + CH_3X \quad (3)$$

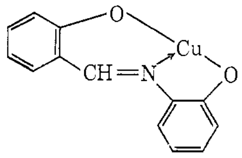


$$RSCH_3 + M^{2+} + X^- \longrightarrow R\overset{M^+}{\underset{+}{S}}CH_3 + X^- \longrightarrow RSM^+ + CH_3X \quad (4)$$

O-Dealkylation has been reported to occur when the compounds bis[N-(2-methoxyphenyl)salicylideneaminato]copper(II) (VII, R = H) and bis[N-2-benzoylphenyl)salicylideneaminato]copper(II) (VII, R = C_6H_5) are heated for 24 hr in dimethylformamide to give the chelate VIII[24] which is most likely dimeric with bridging oxygen atoms.



VII



VIII

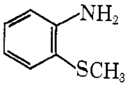
S-Demethylation of the palladium and platinum chelates of 8-methylthioquinoline (II) (N–SCH_3) was effected by heating the complexes $M(N–SCH_3)X_2$ (M = Pd, Pt; X = Cl, Br) in dimethylformamide for 2 hr. The demethylated compounds, which are listed in Table II, no doubt possess thiolo-bridged structures which may be dimeric but their insolubility in all common solvents suggests that they may be higher oligomers. However, in the Experimental Section, for the sake of consistency, we have named these compounds as dimers. The compound $[Pd(N–S)Br]_n$ was obtained as a solvate containing one-third of a molecule of DMF (per monomeric unit) which is retained at 100°. The presence of DMF was confirmed by the appearance of a band at 1660 cm^{-1} in the infrared spectrum. Other clathrate complexes containing DMF display a C=O stretching frequency in the range 1665–1690 cm^{-1}.[25]

Table II

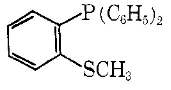
Complexes of Quinoline-8-thiol

Complex	Color
$[Pd(N–S)Cl]_n$	Red
$[Pd(N–S)Br]_n$	Red
$[Pt(N–S)Cl]_n$	Orange
$[Pt(N–S)Br]_n$	Orange

We have also observed that S-demethylation of the ligand occurs with some metal chelates of *o*-methylthioaniline (IX)[26] and diphenyl-*o*-methylthiophenylphosphine (X).[27]



IX



X

Busch, *et al.*,[6] have reported that the metal chelate XI, upon treatment with alkyl halides in chloroform, yields the S-alkylated derivatives XII, as in

$$\underset{XI}{Pd(SCH_2CH_2NH_2)_2} + 2RX \xrightarrow{CHCl_3} \underset{XII}{Pd(RSCH_2CH_2NH_2)X_2} + RSCH_2CH_2NH_2 \quad (5)$$

Using a similar method, we have S-alkylated the complexes $M(As–S)_2$ (M = Pd, Pt) which had been prepared by demethylation of the thioether complexes $M(As–SCH_3)_2X_2$, as shown in

$$M(As–S)_2 + 2RX \xrightarrow{CHCl_3} M(As–SR)X_2 + As–SR \quad (6)$$

where M = Pd; RX = CH_3I, *n*-C_3H_7Br, $C_6H_5CH_2Cl$, *p*-$NO_2C_6H_4CH_2Br$ or M = Pt; RX = CH_3I.

We were unable to effect S-alkylation of the thiolo-bridged complexes $M_2(As–S)_2X_2$; this parallels the observations of Busch, *et al.*,[6] who failed to achieve alkylation of bridging sulfur atoms.

S-Debenzylation of $Pd(As–SCH_2C_6H_5)Cl_2$, as outlined in Scheme II, gave $Pd_2(As–S)_2Cl_2$, indicating that the phenomenon is not restricted to S-demethylation. The complexes $M(As–S)_2$ (M = Pd, Pt) can be converted into the thiolo-bridged complexes $M_2(As–S)_2X_2$ by reaction with K_2MX_4 (X = Cl, Br) in aqueous acetone.

The types of reactions discussed in this paper are summarized in Scheme IV. They provide a means of preparing metal chelates of thiols which may be difficult to prepare otherwise: for example, previous attempts to synthesize dimethyl-*o*-mercaptophenylarsine, $(CH_3)_2AsC_6H_4SH$(As–SH), were unsuccessful.[28] They also offer methods of effecting alkyl exchange of thioethers.

Experimental Section

The dimethylformamide (DMF) (British Drug Houses) used for the demethylation reactions was reagent grade and was dried over molecular sieves.

Microanalyses for carbon, hydrogen, and nitrogen were determined by Dr. E. Challen of the Microanalytical Laboratory of this university. Sulfur was determined by the Australian Microanalytical Service, Melbourne.

Mass Spectra.—The mass spectra were recorded on an MS9 mass spectrometer.

Dealkylation Reactions.—All compounds were washed with alcohol and dried at 100°.

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[24] R. P. Houghton and D. J. Pointer, *J. Chem. Soc.*, 4214 (1965).

[25] L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, and N. C. Stephenson, *Australian J. Chem.*, **19**, 1165 (1966).

[26] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *ibid.*, in press.

[27] S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Letters*, in press.

[28] B. Chiswell, R. K. Y. Ho, and S. E. Livingstone, unpublished results.

SCHEME IV

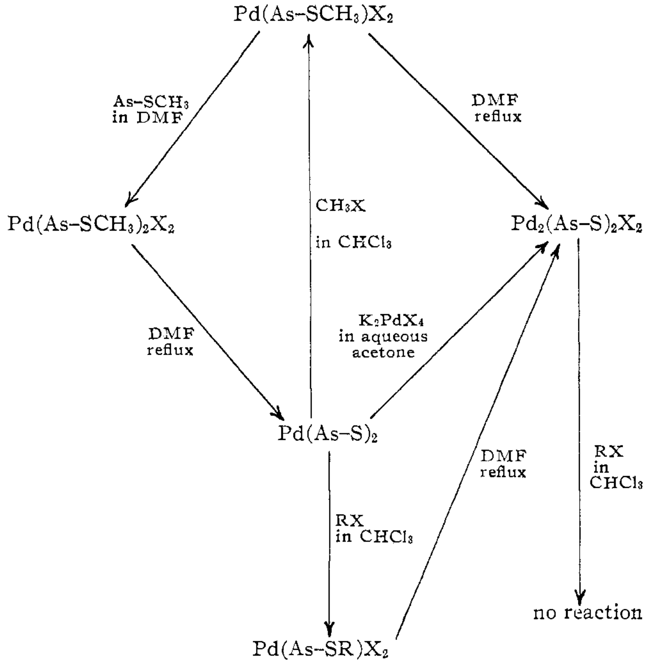

TABLE III

ANALYSES OF Pd(II) AND Pt(II) COMPLEXES OF DIMETHYL-*o*-METHYLTHIOPHENYLARSINE (As–SCH$_3$) AND 8-METHYLTHIOQUINOLINE (N–CH$_3$) PREPARED BY PUBLISHED METHODS[14,18,19]

Compound	Carbon, %	Hydrogen, %
Pd(As–SCH$_3$)Cl$_2$	26.5 (26.7)[a]	3.3 (3.2)
Pd(As–SCH$_3$)Br$_2$	22.5 (21.9)	2.8 (2.65)
Pd(As–SCH$_3$)I$_2$	18.3 (18.4)	2.5 (2.2)
Pd(As–SCH$_3$)$_2$I$_2$	25.9 (26.5)	3.3 (3.2)
[Pt(As–SCH$_3$)$_2$][PtCl$_4$]	22.3 (21.9)	3.0 (2.7)
[Pt(As–SCH$_3$)$_2$][PtBr$_4$]	19.0 (18.5)	2.4 (2.25)
Pt(As–SCH$_3$)I$_2$	16.0 (16.0)	2.2 (1.9)
[Pt(As–SCH$_3$)$_2$I][I·2H$_2$O	22.2 (23.0)	3.5 (3.2)
Pd(N–SCH$_3$)Cl$_2$	34.3 (34.1)	2.2 (2.6)
Pd(N–SCH$_3$)Br$_2$	26.8 (27.2)	2.2 (2.1)
Pt(N–SCH$_3$)Cl$_2$	27.2 (27.2)	2.2 (2.1)
Pt(N–SCH$_3$)Br$_2$	21.9 (22.7)	1.9 (1.7)

[a] Calculated values in parentheses.

Dichlorobis(dimethyl-*o*-μ-thiolo-phenylarsine)dipalladium(II).—Dichloro(dimethyl-*o*-methylthiophenylarsine)palladium(II) (2.0 g) in DMF (100 ml) was heated at reflux for 8 hr, during which time the initial yellow solution darkened to reddish brown. The solution was then concentrated to 30 ml, filtered, diluted with hot alcohol (250 ml), and allowed to stand. The *complex* deposited as orange flakes; yield, 1.55 g (90%). *Anal.* Calcd for $Pd_2(C_8H_{10}AsS)_2Cl_2$: Pd, 29.9; C, 27.1; H, 2.8; S, 9.0; Cl, 10.0. Found: Pd, 29.9; C, 27.3; H, 3.2; S, 8.6; Cl, 9.5.

Dibromobis(dimethyl-*o*-μ-thiolo-phenylarsine)dipalladium(II).—Dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (1.2 g) in DMF (30 ml) was heated at reflux for 8 hr, during which time the solution darkened to reddish brown. The solution was then filtered, concentrated to 5 ml, diluted with hot alcohol (250 ml), and allowed to stand. The *complex* crystallized as orange flakes; yield, 0.6 g (60%). *Anal.* Calcd for $Pd_2(C_8H_{10}AsS)_2Br_2$: Pd, 26.6; C, 24.05; H, 2.5; S, 8.0; Br, 20.0. Found: Pd, 26.3; C, 24.0; H, 2.6; S, 7.4; Br, 20.3.

By a similar procedure dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (0.6 g) in cyclohexanone (20 ml) gave the same product; yield, 0.6 g (60%). *Anal.* Found: C, 24.6; H, 2.7.

Diiodobis(dimethyl-*o*-μ-thiolo-phenylarsine)dipalladium(II).—Diiodo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (0.5 g) in DMF (20 ml) was heated at reflux for 8 hr during which time the solution darkened to deep red. The solution was then filtered, concentrated to 10 ml, diluted with hot alcohol (150 ml), and allowed to stand. The *complex* deposited as reddish orange crystals; yield, 0.3 g (80%). *Anal.* Calcd for $Pd_2(C_8H_{10}AsS)_2I_2$: C, 21.5; H, 2.3; S, 7.2. Found: C, 22.1; H, 2.5; S, 6.8.

Bis(dimethyl-*o*-thiolophenylarsine)palladium(II).—A solution of dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (6.7 g) in DMF (75 ml) was treated with dimethyl-*o*-methylthiophenylarsine (4.0 g) and then heated at reflux for 8 hr, concentrated to 30 ml, filtered, diluted with hot alcohol (150 ml), and allowed to stand, whereupon the *compound* separated as yellowish orange flakes; yield, 6.2 g (85%). *Anal.* Calcd for $PdC_{16}H_{20}As_2S_2$: Pd, 20.0; C, 36.1; H, 3.8; S, 12.0; Br, 0. Found: Pd, 19.9; C, 36.2; H, 4.1; S, 12.0; Br, 0.

Similar treatment in DMF of dichloro(dimethyl-*o*-methylthiophenylarsine)palladium(II) with dimethyl-*o*-methylthiophenylarsine also yielded bis(dimethyl-*o*-thiolophenylarsine)palladium(II). *Anal.* Found: C, 35.6; H, 3.9.

Heating of diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II) in DMF led, however, to the formation of a mixture of the mono and bis ligand demethylated products (found for mixture: Pd, 21.1). A pure sample of each of these products was obtained from the mixture by several fractional recrystallizations using alcohol and chloroform as recrystallizing solvents. *Anal.* Found for $Pd(C_{16}H_{20}As_2S_2)$: C, 35.8; H, 3.7. Found for $Pd_2(C_8H_{10}AsS)_2I_2$: C, 21.7; H, 2.6.

Dichlorobis(dimethyl-*o*-μ-thiolo-phenylarsine)dipalladium(II).—(From dichloro(dimethyl-*o*-benzylthiophenylarsine)palladium(II).) Dichloro(dimethyl-*o*-benzylthiophenylarsine)palladium(II) (*vide infra*) (0.3 g) in DMF (15 ml) was heated at reflux for 8 hr during which time the initial yellow solution turned orange. It was concentrated to 7 ml, filtered, diluted with hot alcohol (250 ml), and allowed to stand. The demethylated product formed as orange crystals; yield, 0.1 g. *Anal.* Calcd for $Pd_2(C_8H_{10}AsS)_2Cl_2$: C, 27.1; H, 2.8. Found: C, 27.1; H, 2.9.

This compound was also obtained by heating bis(dimethyl-*o*-methylthiophenylarsine)palladium(II) (0.26 g) and potassium chloropalladate(II) (0.16 g) in 90% aqueous acetone (400 ml) for 40 min. Concentration of the solution to 50 ml yielded crystals of the complex; yield, 0.2 g. *Anal.* Found: C, 27.1; H, 3.0.

Dichlorobis(dimethyl-*o*-μ-thiolo-phenylarsine)diplatinum(II).—Bis(dimethyl-*o*-methylthiophenylarsine)platinum(II) chloroplatinate(II) (0.8 g) in DMF (20 ml) was heated at reflux for 8 hr. The yellow solution which had darkened to orange during this time was concentrated to 6 ml, filtered, diluted with hot alcohol (100 ml), and allowed to stand. The *demethylated complex* was deposited as yellow crystals; yield, 0.3 g (40%). *Anal.* Calcd for $Pt_2(C_8H_{10}AsS)_2Cl_2$: Pt, 44.0; C, 21.7; H, 2.3. Found: Pt, 43.9; C, 21.55; H, 2.3.

This compound was also obtained by heating bis(dimethyl-*o*-methylthiophenylarsine)platinum(II) (0.31 g) and potassium chloroplatinate(II) (0.21 g) in 80% aqueous acetone (400 ml) for 40 min. Concentration of the solution to 50 ml yielded crystals of the complex; yield, 0.15 g. *Anal.* Found: C, 21.4; H, 2.6.

Dibromobis(dimethyl-*o*-μ-thiolo-phenylarsine)diplatinum(II).—Bis(dimethyl-*o*-methylthiophenylarsine)platinum(II) bromoplatinate(II) (1.0 g) in DMF (20 ml) was heated at reflux for 8 hr. The solution was concentrated to 6 ml, filtered, diluted with alcohol (30 ml), and allowed to stand. The *complex* was deposited as yellow crystals; yield, 0.5 g (60%). *Anal.* Calcd for $Pt_2(C_8H_{10}AsS)_2Br_2$: C, 19.7; H, 2.1. Found: C, 20.0; H, 2.3.

Diiodobis(dimethyl-*o*-μ-thiolo-phenylarsine)diplatinum(II).—Diiodo(dimethyl-*o*-methylthiophenylarsine)platinum(II) (1.1 g) in DMF (25 ml) was heated at reflux for 8 hr. The solution, which had darkened from yellow to red, was concentrated to 15 ml, filtered, diluted with hot 80% alcohol (400 ml), and allowed to stand. The product formed as yellow crystals which were recrystallized from acetone; yield, 0.6 g (70%). *Anal.* Calcd for $Pt_2(C_8H_{10}AsS)_2I_2$: Pt, 36.5; C, 18.0; H, 1.9. Found: Pt, 36.5; C, 18.1; H, 2.0.

Bis(dimethyl-*o*-thiolophenylarsine)platinum(II).—A solution of bis(dimethyl-*o*-methylthiophenylarsine)platinum(II) chloroplatinate(II) (3.9 g) in DMF (60 ml) was treated with dimethyl-*o*-methylthiophenylarsine (1.9 g) and refluxed for 8 hr, then concentrated to 25 ml, filtered, diluted with hot alcohol (30 ml), and allowed to stand, whereupon the *complex* was deposited as yellow crystals; yield, 3.9 g. (80%). *Anal.* Calcd for $PtC_{16}H_{20}As_2S_2$: C, 30.9; H, 3.2; Cl, 0. Found: C, 31.0; H, 3.1; Cl, 0.

This compound was also prepared directly from iodobis(dimethyl-*o*-methylthiophenylarsine)platinum(II) iodide dihydrate. The product was purified by recrystallization from alcohol. *Anal.* Found: C, 30.3; H, 3.3.

Dichlorodi(8-μ-thiolo-quinoline)dipalladium(II).—Dichloro(8-methylthioquinoline)palladium(II) (0.4 g) in DMF (50 ml) was heated at reflux for 2 hr. The orange solution darkened to deep brownish red, and at the end of this time, red crystals of the *complex* had been deposited. The solution was cooled and the product was filtered off; yield, 0.3 g (85%). *Anal.* Calcd for $Pd_2(C_{18}H_{12}N_2S_2)Cl_2$: Pd, 35.2; C, 35.8; H, 2.0. Found: Pd, 35.0; C, 34.9; H, 2.1.

Dibromodi(8-μ-thiolo-quinoline)dipalladium(II).—By an identical procedure dibromo(8-methylthioquinoline)palladium(II) (0.5 g) was demethylated to yield red crystals of the solvated *bromo complex;* yield, 0.3 g (95%). *Anal.* Calcd for $Pd_2(C_{18}H_{12}N_2S_2)Br_2\cdot{}^2/_3DMF$: Pd, 28.7; C, 32.4; H, 2.3; N, 5.0. Found: Pd, 28.6, 29.0; C, 32.0, 32.3; H, 2.3, 2.1; N, 4.5.

Dichlorodi(8-μ-thiolo-quinolinoline)diplatinum(II).—By an identical procedure dichloro(8-methylthioquinoline)platinum(II) (0.4 g) was demethylated to yield orange crystals of the *iodo complex;* yield, 0.2 g (55%). *Anal.* Calcd for $Pt_2(C_{18}H_{12}N_2S_2)Cl_2$: Pt, 49.9; C, 27.7; H, 1.55. Found: Pt, 49.8; C, 27.6; H, 1.75.

Dibromodi(8-μ-thiolo-quinoline)diplatinum(II).—By an identical procedure dibromo(8-methylthioquinoline)platinum(II) (0.5 g) was demethylated to yield orange crystals of the *bromo-bridged platinum complex;* yield, 0.4 g (95%). *Anal.* Calcd for $Pt_2(C_{18}H_{12}N_2S_2)Br_2$: Pt, 44.8; C, 24.8; H, 1.4. Found: Pt, 44.1; C, 25.1; H, 1.5.

Attempted Demethylation of Dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) in Acetone.—Dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (0.5 g) in acetone (100 ml) was heated at reflux for 80 hr. The solution was then concentrated and allowed to stand, whereupon yellow crystals of the unchanged starting material were deposited. *Anal.* Calcd for $Pd(C_9H_{13}AsS)Br_2$: Pd, 21.6. Found: Pd, 21.6.

Alkylation Reactions.—Unless indicated otherwise, all products were washed with alcohol and dried *in vacuo* over phosphoric oxide.

Diiodo(dimethyl-*o*-methylthiophenylarsine)palladium(II).—Bis(dimethyl-*o*-thiolophenylarsine)palladium(II) (0.5 g) was dissolved in chloroform (50 ml) containing methyl iodide (8 ml). The orange solution was placed in a sealed flask at room temperature and after 5 min the solution had changed from orange to red. The solution was allowed to stand a further 2 hr and then was concentrated to 15 ml. Red crystals of product formed on standing overnight; yield, 0.4 g (75%). *Anal.* Calcd for $Pd(C_9H_{13}AsS)I_2$: C, 18.4; H, 2.2; S, 5.45. Found: C, 18.0; H, 2.2; S, 5.0.

Diiodo[dimethyl-*o*-(*n*-propylthio)phenylarsine]palladium(II).—Bis(dimethyl-*o*-thiolophenylarsine)palladium(II) (0.4 g) in chloroform (40 ml) was treated with *n*-propyl iodide (4 ml). This orange solution was allowed to stand at room temperature for 4 hr and then was concentrated to 10 ml and allowed to evaporate to 3 ml over 2 days during which time large red rhombs of the *alkylated complex* formed. These contained chloroform; yield, 0.35 g (70%). *Anal.* Calcd for $Pd(C_{11}H_{17}AsS)I_2\cdot{}^1/_2CHCl_3$: C, 20.4; H, 2.6; S, 4.7. Found: C, 20.5; H, 2.8; S, 4.7.

The above product was heated to 135° and decrepitation occurred; the chloroform was expelled from the crystals to yield the unsolvated complex. Λ_{2000} in nitrobenzene at 25°, 0.2 mho. *Anal.* Calcd for $Pd(C_{11}H_{17}AsS)I_2$: Pd, 17.3; C, 21.4; H, 2.8. Found: Pd, 17.0; C, 21.5; H, 2.9.

Dichloro(dimethyl-*o*-benzylthiophenylarsine)palladium(II).—Bis(dimethyl-*o*-thiolophenylarsine)palladium(II) (0.45 g) and benzyl chloride (3.5 ml) were dissolved in chloroform (35 ml) and the solution was allowed to stand overnight, then concentrated to 5 ml. On cooling, the solution deposited yellow crystals of the *complex;* yield, 0.25 g (60%). Λ_{1000} in nitrobenzene, 0.8 mho. *Anal.* Calcd for $Pd(C_{15}H_{17}AsS)Cl_2$: C, 37.4; H, 3.6; S, 6.7; Cl, 14.7. Found: C, 37.6; H, 3.9; S, 6.7; Cl, 14.6.

Dibromo[dimethyl-*o*-(*p*-nitrobenzylthio)phenylarsine]palladium(II).—A solution of bis(dimethyl-*o*-thiolophenylarsine)palladium(II) (0.8 g) and *p*-nitrobenzyl bromide (3.0 g) in chloroform (80 ml) was warmed for 10 min, then allowed to stand and evaporate over 3 days. Large yellow crystals of the *complex* formed; these contained chloroform; yield, 0.95 g (95%). Λ_{1000} in nitrobenzene, 0.1 mho. *Anal.* Calcd for $PdC_{15}H_{16}AsNO_2SBr_2\cdot{}^1/_3CHCl_3$: Pd, 16.2; C, 28.1; H, 2.5; N, 2.1; S, 4.9; Br, 24.4; Cl, 5.4; loss of $^1/_3$ $CHCl_3$, 6.1. Found: Pd, 15.9; C, 28.1; H, 2.5; N, 2.1; S, 4.7; Br, 26.7; Cl, 4.9; loss on heating, 7.6 (determined thermogravimetrically).

Diiodo(dimethyl-*o*-methylthiophenylarsine)platinum(II).—A solution of bis(dimethyl-*o*-thiolophenylarsine)platinum(II) (0.4 g) and methyl iodide (5 ml) in warm chloroform (15 ml) was allowed to stand at room temperature for 1 hr, then concentrated to 4 ml. It was allowed to stand overnight, whereupon yellow crystals of the complex were deposited. The product was washed with alcohol and dried at 110°; yield, 0.3 g (70%). *Anal.* Calcd for $PtC_9H_{13}AsSI_2$: C, 16.0; H, 1.9. Found: C, 16.4; H, 2.2.

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