most of the solvent and excess olefin. Upon addition of petroleum ether, with vigorous stirring, extensive precipitation took place. The product was separated by filtration and washed with petroleum ether, yielding a light yellow-orange powder which melted with partial decomposition at 144–145°.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF IONIC COMPLEXES, $H(UnPtCl_3)$

Solvent, HCl in ethanol, 0.01 mole/l.

Un	Long wave length max.		Short wave length, max.	
	mμ	log ε	mμ	log ε
cis-2-Pentene	342	2.23	248	3.70
4-Methyl-*cis*-2-pentene	341	2.25	248	3.70
4-Methyl-*trans*-2-pentene	340	2.24		

TABLE II

INFRARED ABSORPTION[a] SPECTRA OF COVALENT COMPLEXES, $(UnPtCl_2)_2$; Nujol mull

Un = *cis*-2-pentene μ	4-Methyl-*cis*-2-pentene μ	4-Methyl-*trans*-2-pentene μ
7.70m	7.76m	7.74m
8.65w	8.61m	7.88shoulder
9.30m	9.05m	8.03shoulder
9.57m	9.50shoulder	8.50m
9.80w	9.56m	8.64shoulder
10.04m	9.84m	9.04m
10.84m	9.97m	9.56m
11.23w	10.45shoulder	9.81m
11.80m	10.65vs	10.49vs
12.98m	10.80m	10.90s
	11.00m	11.25m
	11.40m	11.99m
	12.25m	

[a] w = weak intensity, m = medium intensity, s = strong intensity, vs = very strong intensity.

1,3-Bis-(4-methyl-*cis*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum was prepared in the same manner as the *cis*-2-pentene complex. The product was a pale yellow powder which melted with partial decomposition at 157–158°.

Anal.[4] Calcd.: C, 20.6; H, 3.45. Found: C, 20.6 H, 3.53.

1,3-Bis-(4-methyl-*trans*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum also was prepared in the same manner as the *cis*-2-pentene complex. The product was a light yellow powder melting with partial decomposition at 139–140°.

Anal. Calcd.: C, 20.6; H, 3.45. Found: C, 20.3; H, 3.50.

Equilibrium Constants by Ultraviolet Spectroscopy.—The same method as employed previously[2] was used for the determination of equilibrium constants.

All ultraviolet spectra of the ionic complexes were obtained by dissolving the corresponding covalent complexes in 0.01 molar alcoholic hydrochloric acid and taking readings at intervals of 2 mμ or less, on a Beckman DU quartz spectrophotometer. The spectra are summarized in Table I.

Infrared Spectra.—All infrared spectra of complexes were obtained in Nujol mull, using a Baird Atomic Infrared Spectrophotometer with a sodium chloride prism. The spectra are summarized in Table II. The spectra of the isomeric olefin complexes are obviously different. The same conclusion had been reached previously in the case of the isomeric 2-butene complexes.[1]

Results and Discussion

The results of the equilibrium study are shown in Table III. It is apparent from the table that in the competition between styrene and the aliphatic olefin for coördination with the platinum-(II), the simple olefin is the preferred ligand. If stoichiometric quantities of styrene and the aliphatic olefin complex are permitted to react, at equilibrium the ratio of 4-methyl-*cis*-2-pentene complex to styrene complex is 3.2. The similar ratio with 4-methyl-*trans*-2-pentene is 1.7. On this basis one can conclude that the *cis* complex is almost twice as stable as the corresponding *trans* isomer. Table III also shows that the unsubstituted *cis*-2-pentene gives a complex that is slightly less stable than the methyl substituted *cis*-2-pentene. Apparently substitution at the α-position to the double bond makes the pi electrons more available for complexing, and the steric factors, if any, are outweighed by this inductive effect. It is also of interest to note that the 1-dodecene complex[2] is approximately twice as stable as the most stable 2-pentene complex, probably because of steric factors.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE REACTION OF PENTENE COMPLEXES WITH STYRENE

$$PhCH = CH_2 + (UnPtCl_3)^- \rightleftharpoons Un + (PhCH = CH_2PtCl_3)^-$$

Temp. = 25.0 ± 0.2°

Un	Concn. of HCl, mole/l.	Anal. wave length, mμ	K
cis-2-Pentene	0.0090	308	0.14 ± 0.002
4-Methyl-*cis*-2-pentene	.0092	308	.095 ± .001
4-Methyl-*trans*-2-pentene	.0099	310	.34 ± .004

Acknowledgment.—This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

CINCINNATI, OHIO

---

(3) All olefins were obtained from the Phillips Petroleum Company, Bartlesville, Oklahoma. The *cis*-2-pentene and 4-methyl-*cis*-2-pentene were 95 mole %. The 4-methyl-*trans*-2-pentene was 99.5 mole %. We are grateful to Dr. Fred E. Frey for his generous help in securing some of these materials.

(4) Analyses were performed by Geller Laboratories, Bardonia, New York.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY]

Bidentate Chelate Compounds. II

BY HAROLD A. GOODWIN[1] AND FRANCIS LIONS

RECEIVED JULY 22, 1958

α-Picolyldimethylarsine has been prepared and studies made of its ability to coördinate with the salts of certain metals Some features of its coördination chemistry are unusual.

Organic compounds are common whose molecules are capable of offering simultaneously to the same metal atom two donor nitrogen atoms. Less

---

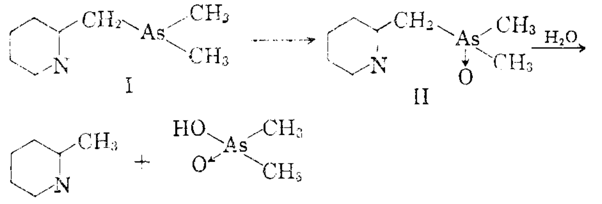
(1) Commonwealth Research Student, University of Sydney.

usual, but much reported on recently, are those ditertiary arsines whose molecules can simultaneously present two donor arsenic atoms to the same metal atom. The most important of these, originally prepared and studied by Mann and Chatt,[2] would appear to be tetramethyl-*o*-phenylene-bis-arsine. Studies of the coördination compounds it forms with the salts of different metals have been made by Nyholm and his colleagues.[3]

It occurred to us that it would be of some value to prepare an organic compound whose molecule could simultaneously present a nitrogen atom and a tertiary arsine arsenic atom to the same metal atom as donors, coördinating to form a type of heterocyclic ring compound with nitrogen, arsenic and metal atoms as ring members.[4]

The marked stability of many complex salts derived from 2,2′-bipyridine and of 1,10-phenanthroline on the one hand[5] and from tetramethyl-*o*-phenylene-bis-arsine on the other suggested that a useful molecular design would be one incorporating a pyridine ring with an attached tertiary arsine group, the nitrogen and arsenic atoms being separated by two carbon atoms.

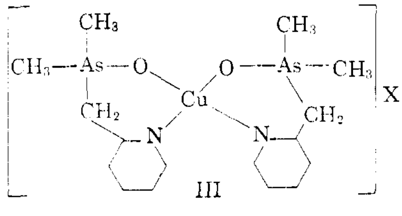
In consequence, we have synthesized α-picolyldimethylarsine (I) in approximately 33% yield by



treating lithium α-picolyl[6] in dry ether in a nitrogen atmosphere with dimethyliodo-arsine. It is a pungent smelling colorless mobile oil which can be distilled *in vacuo* but which rapidly oxidizes when exposed to air and which is also sensitive to light. Study of this aerial oxidation showed that the presumed first product of oxidation—the arsine oxide(II)—is, apparently, rapidly hydrolyzed to α-picoline and cacodylic acid, which latter can be isolated readily in good yield.

Studies of the capacity of I to coördinate with metal salts give unexpected results. Thus, because the capacity of tertiary arsines to reduce copper(II) salts is well known,[7] and because, also, complexes of copper(II) with tertiary arsines appear to be unknown, it is not surprising to find that interaction of I with copper(II) salts leads rapidly to their reduction to the copper(I) salts. From solutions so prepared sodium perchlorate precipitates a pale cream crystalline perchlorate (III, X = ClO_4, n = 1). Analysis shows this to be a complex salt derived by coördination of two molecules of the arsine oxide II with each copper(I) ion. Thus, the process of interaction of copper(II) salt with I apparently leads to reduction of the copper(II) ions to copper(I) ions, the molecules of I being simultaneously oxidized to the arsine oxide II, two molecules of which then promptly coördinate with the copper(I) ions. The failure of the arsine oxide II molecules to hydrolyze to cacodylic acid in presence of the copper(I) ions with which they coördinate is noteworthy.

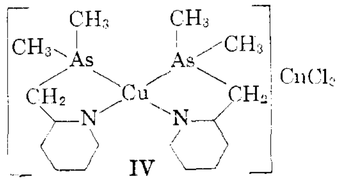
The complex salt (III, X = ClO_4, n = 1) is diamagnetic and the bond hybridization probably sp^3



III

Proof of the tetrahedral disposition of the copper coördination covalences would be afforded by the resolution of the salt. However, attempts to achieve resolution failed. Resolution of a 4-covalent complex copper(I) salt, and thus verification of the tetrahedral disposition of the four covalences, does not yet appear to have been reported. It is worthy of comment that the only material difference between a 4-covalent copper(I) complex ion and the corresponding copper(II) complex ion would be that the latter has one electron less. Spatially, however, such a loss means adjustment of tetrahedrally disposed bonds [copper(I)] to a planar distribution [copper(II)]. It then will be perceived readily that in the presence of even the minutest amount of copper(II) complex salt, reversible electronic interchange between complex copper(II) ions on the one hand and complex copper(I) ions on the other, must lead to racemization of any optically active forms. It would appear to us that successful resolution of a complex copper(I) cation would require the use of a carefully designed quadridentate compound whose own structure would preclude any possibility of the four donor atoms being simultaneously coplanar.

Aeration for a considerable time of a suspension of the pale-cream salt (III, X = ClO_4, n = 1) in aqueous sodium perchlorate solution leads to slow oxidation and eventual deposition of blue crystalline bis-(α-picolyldimethylarsine oxide)-copper(II) perchlorate, (III, X = ClO_4, n = 2)—a process in which the organic moiety remains intact. It is also worthy of note that bis-(α-picolyldimethylarsine)-copper(I) dichlorocuprate(I) (IV) can be



IV

readily prepared from the arsine and copper(I) chloride dissolved in saturated potassium chloride solution. It can be recrystallized from chloro-

---

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

[3] For a bibliography, *cf.* R. S. Nyholm and G. J. Sutton, *ibid.*, 560 (1958)

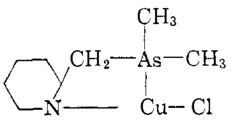
[4] Because there is some present lack of precise definition of the term "chelate compound," it is suggested that the known, useful, self-explanatory term "metallocyclic" be used to describe such a coördination complex whose molecules contain a ring of atoms of which one is the metal atom.

[5] *Cf.* W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 959 (1954).

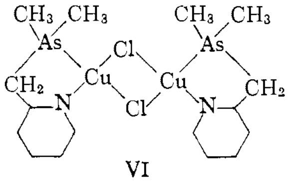
[6] K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).

[7] *Cf. e.g.*, A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 38 (1951).

form–ether, is diamagnetic and shows conductivity behavior in nitrobenzene solution which indicates that it is a uni-univalent electrolyte and not the non-electrolyte V or the bridged complex VI. On exposure to air this complex salt gradually turns green, probably because of oxidation, but we have been unable to isolate any copper(II) complex salt after oxidation by any chemical method. It should also be reported that all attempts to prepare copper(II) complex salts with I in anhydrous solvents proved fruitless.



V



VI

Addition of the arsine I to a solution of silver chloride in saturated sodium chloride solution leads to precipitation of the sparingly soluble light-sensitive white crystalline bis-(α-picolyldimethylarsine)-silver(I) dichloroargentate(I). A white complex gold(I) salt can be obtained similarly by treatment of chloroauric acid with the arsine, but it is unstable. We were unable to obtain consistent analytical figures from the various samples made and studied.

Addition of an alcoholic solution of the arsine to aqueous potassium tetrachloropalladate(II) solution leads to fading of its color, and then addition of sodium perchlorate solution causes bis-(α-picolyldimethylarsine)-palladium(II) perchlorate to separate as a pale-yellow precipitate. The pale-cream bis-(α-picolyldimethylarsine)-platinum(II) perchlorate can be prepared similarly.

Reaction of the arsine I with an aqueous solution of potassium pentachloroaquoruthenate(III) leads to formation of a deep brown-green solution. If this solution is heated at 100° for a few minutes, then cooled in ice, it yields bright-green crystalline dichloro-bis-(α-picolyldimethylarsine)-ruthenium(III) chloride trihydrate (VII). This water-soluble salt shows electrical conductivity behavior consistent with that of a uni-univalent electrolyte. If the time of heating at 100° in the above-described experiment is extended to an hour or more, there is formed the bright orange ruthenium(II) non-valent complex dichloro-bis-(α-picolyldimethylarsine)-ruthenium(II) (VIII). This can be oxidized with chlorine or cerium(IV) sulfate to the readily isolable green salt VII, or the sparingly soluble perchlorate can be precipitated.

In the process of heating at 100° described above, conversion to VIII is not quantitative and the residual aqueous solution is always dark orange-brown. We have been unable, however, to isolate any other well-defined complex compound from it.

In view of the relative stability of the complex salts obtainable by interaction of 2,2′-bipyridine or tetramethyl-*o*-phenylene-bis-arsine with suitable iron, nickel and cobalt salts, it is surprising to find that, despite numerous attempts at preparation, compounds of definite composition containing I could not be obtained. The arsine does not apparently react with iron(II) chloride in alcohol and heating under nitrogen leads only to deposition of a small amount of a rust-colored powder.

In view of the lower potential of the iron(II)/iron(III) couple (−0.77 v.) relative to the copper(I)/copper(II) couple (−0.167 v.) and the inability of I to form stable complexes with copper(II), it would not be anticipated that iron(III) salts would form stable coördination complex salts with I. It was thought possible, however, that a process similar to that leading to the complex copper(I) salts (III, $n = 1$) might occur and give iron(II) complex salts containing the bidentate II. Addition of the arsine to a solution of anhydrous iron(III) chloride in absolute ethanol leads to precipitation of a rust-colored powder. However, analysis shows this to be of uncertain composition.

Reaction of the arsine I in dry ethanol under nitrogen with nickel(II) chloride or cobalt(II) chloride apparently fails to occur. Allowing the solution of reactants to stand exposed to air for some time leads to slow separation of a pale yellow powder in the case of the nickel salt, but no definite formula could be deduced for it from the analytical figures obtained.

Experimental

α-Picolyldimethylarsine (I).—While a current of dry nitrogen was passed continuously through the apparatus, dry ether (400 ml.) and finely-divided lithium (4.6 g.) were placed in a 2-liter 3-necked flask fitted with a dropping funnel, mechanical stirrer and reflux condenser protected from moisture. The solution was stirred and dry bromobenzene (53 g.) in dry ether (80 ml.) was added at such a rate that the ether gently refluxed. A dark brown color developed and the mixture was stirred until all the lithium had dissolved (about 1.5 hr.). Dry α-picoline (31 g.) was then added slowly and the mixture stirred for 1 hr., during which time the dark red picolyllithium was formed. After this time dimethyliodoarsine (70 g.) in dry ether (50 ml.) was added slowly. As the arsine was added the ether refluxed and the dark red color of the picolyllithium faded, becoming light yellow-brown. The mixture was stirred for 1 hr., then allowed to stand overnight under nitrogen. Water (70 ml.) and hydrochloric acid (50 ml. of 10 *N*) were then stirred in. The solution became warm and the ether refluxed. The light brown acidic solution was separated and the ether layer washed again with hydrochloric acid (40 ml. of 5 *N*). The combined acid extracts were washed with two portions of ether (50 ml.), and then neutralized with potassium carbonate (120 g.). A dark oil separated and lithium carbonate crystallized. The oily arsine was extracted with ether and the mixture filtered through a sintered glass filter (under nitrogen). The ether layer was separated and the aqueous solution extracted twice with ether (100 ml.). The combined ethereal extracts were dried over anhydrous sodium sulfate. The ether was then removed and the residual mixture of α-picolyldimethylarsine and unchanged picoline was fractionated *in vacuo*. The arsine (21 g.) distilled as a colorless oil, b.p. 86–90° (2 mm.) (67–69° (0.4 mm.)).

α-Picolyldimethylarsine picrate was crystallized in elongated needles from aqueous alcohol, m.p. 106°.

Anal. Calcd. for $C_{14}H_{15}N_4O_7As$: C, 39.4; H, 3.6. Found: C, 39.3; H, 3.5.

The arsine has to be kept in an inert atmosphere out of light. On exposure to air it rapidly oxidized. The primary product of oxidation, however, was unstable and decomposed to picoline and colorless crystalline cacodylic acid, m.p. 199°.

Anal. Calcd. for $C_2H_7AsO_2$: C, 17.4; H, 5.1. Found: C, 17.7; H, 5.2.

On exposure to light the arsine became a very dark brown. It had a pungent and objectionable odor, characteristic of tertiary arsines.

Bis-(α-picolyldimethylarsine)-copper(I) Dichlorocuprate-(I) (IV).—Copper(I) chloride (1 g.) was dissolved in saturated aqueous potassium chloride solution (15 ml.) containing one drop of concentrated hydrochloric acid. To this solution was added α-picolyldimethylarsine (2 g.) in alcohol (5 ml.). A white, crystalline precipitate quickly deposited. The mixture was heated on the water-bath for 1 hr. under nitrogen. After this time the precipitate was filtered and extracted with three portions of chloroform (20 ml.). The chloroform extracts were dried over anhydrous sodium sulfate and evaporated to a volume of about 15 ml. The product crystallized on addition of ether. It was washed with ether and dried *in vacuo.*

Anal. Calcd. for $Cu_2C_{16}H_{24}N_2As_2Cl_2$: Cu, 21.6; C, 32.4; H, 4.1. Found: Cu, 21.8; C, 32.1; H, 4.1.

This complex salt was diamagnetic. It was insoluble in water and alcohol but quite soluble in chloroform and nitrobenzene. It slowly oxidized on exposure to air. Its molecular conductivity in nitrobenzene solution was 19 reciprocal ohms (measured for a $M/2{,}000$ solution).

Bis-(α-picolyldimethylarsine Oxide)-copper(I) Perchlorate, Monohydrate (III, X = ClO$_4$, n = 1).—α-Picolyldimethylarsine (0.80 g.) in alcohol (5 ml.) was added to a warm solution of copper(II) sulfate pentahydrate (0.5 g.) in water (20 ml.). The color became a deep blue as soon as the solutions were mixed but quickly faded to a pale blue-green, almost colorless, solution. The mixture was heated on the water-bath for 10 minutes, filtered and a 10% solution of sodium perchlorate added to the filtrate. The pale cream, practically white, product was then readily induced to crystallize. It was washed with cold water, recrystallized from hot water and air-dried.

Anal. Calcd. for $[CuC_{16}H_{24}N_2As_2O_2]ClO_4 \cdot H_2O$: Cu, 10.5; C, 31.6; H, 4.3. Found: Cu, 10.4; C, 31.3; H, 4.3.

This complex salt was diamagnetic.

Bis-(α-picolyldimethylarsine Oxide)-copper(II) Perchlorate, Dihydrate.—Bis-(α-picolyldimethylarsine oxide)-copper(I) perchlorate (0.5 g.) was suspended in cold water (10 ml.) containing sodium perchlorate (0.5 g.) and air was bubbled through the suspension for several days. Gradually the amount of white material decreased and deep-blue, elongated needles of the oxidized species appeared. After 12 days these were filtered, washed with cold water and alcohol and air-dried.

Anal. Calcd. for $[CuC_{16}H_{24}N_2As_2O_2]Cl_2O_8 \cdot 2H_2O$: Cu, 8.8; C, 26.5; H, 3.9; N, 3.9. Found: Cu, 8.9; C, 26.8; H, 3.8; N, 3.9.

Bis-(α-picolyldimethylarsine)-silver(I) Dichloroargentate-(I).—Silver nitrate (0.7 g.) was added to a saturated aqueous solution of sodium chloride (12 ml.). To this mixture then was added a solution of α-picolyldimethylarsine (0.8 g.) in alcohol (5 ml.). The mixture was heated on the water-bath for 1 hr. under nitrogen and then filtered while still hot. Crystallization of the product was induced by cooling the filtrate and scratching the sides of the vessel. It formed colorless rods. It was washed with cold water and dried *in vacuo.*

Anal. Calcd. for $Ag_2C_{16}H_{24}N_2As_2Cl_2$: Ag, 31.7; C, 28.2; H, 3.6. Found: Ag, 31.3; C, 28.2; H, 3.6.

The complex salt was *diamagnetic;* it darkened on exposure to light.

Bis-(α-picolyldimethylarsine)-palladium(II) Perchlorate.—α-Picolyldimethylarsine (0.4 g.) in alcohol (4 ml.) was added to a solution of potassium tetrachloropalladate(II) (0.33 g.) in water (12 ml.). The initially red-brown solution immediately lightened to a clear yellow. The mixture was heated on the water-bath for 10 minutes under nitrogen, filtered and 10% sodium perchlorate solution added to the filtrate, when pale yellow crystals of the product were obtained. These were washed with cold water and alcohol and dried *in vacuo.*

Anal. Calcd. for $PdC_{16}H_{24}N_2As_2Cl_2O$: Pd, 15.3; C, 27.4; H, 3.5; N, 4.0. Found: Pd, 15.0; C, 27.2; H, 3.4; N, 4.0.

Bis-(α-picolyldimethylarsine)-platinum(II) Perchlorate.—Potassium tetrachloroplatinate(II) (0.42 g.) was dissolved in water (10 ml.) and α-picolyldimethylarsine (0.4 g.) in alcohol (3 ml.) added under nitrogen. The color of the solution quickly faded to a pale yellow. The solution was filtered and 10% sodium perchlorate solution added to the filtrate, with scratching of the sides of the vessel. Pale cream crystals of the product were obtained. These were washed with cold water and dried *in vacuo.*

Anal. Calcd. for $PtC_{16}H_{24}N_2As_2Cl_2O_8$: Pt, 24.8; C, 24.4; H, 3.1; N, 3.6. Found: Pt, 24.6; C, 24.4; H, 3.1; N, 3.6%.

Dichloro-bis-(α-picolyldimethylarsine)-ruthenium(III) Chloride Trihydrate (VII).—Potassium pentachloroaquoruthenate(III) (0.75 g.) was dissolved in water (15 ml.) and α-picolyldimethylarsine (0.8 g.) in alcohol (3 ml.) was added. The solution was heated on the water-bath for a few minutes under nitrogen, filtered and cooled in ice. Bright green plates of the product soon deposited. These were washed with a little cold water and dried over fused calcium chloride.

Anal. Calcd. for $[RuC_{16}H_{24}N_2As_2Cl_2]Cl \cdot 3H_2O$: Ru, 15.5; C, 29.2; H, 4.6; N, 4.3. Found: Ru, 15.3; C, 29.4; H, 4.4; N, 4.4.

The molecular conductivity in water at 20° was 113 reciprocal ohms (measured for a $M/1{,}000$ solution). The complex was quite soluble in water and very soluble in alcohol or chloroform, giving bright green solutions. It could be reduced with iron(II) sulfate to the non-electrolyte, dichloro-bis-(α-picolyldimethylarsine)-ruthenium(II). The reduction was reversible.

Dichloro-bis-(α-picolyldimethylarsine)-ruthenium(III) perchlorate could be precipitated from an aqueous solution of the above chloride by sodium perchlorate, or could be prepared from the reduced species, dichloro-bis-(α-picolyldimethylarsine)-ruthenium(II), suspended in 0.5 *N* nitric acid and oxidized with cerium(IV) ammonium nitrate, followed by precipitation with sodium perchlorate. It was washed with cold water and dried *in vacuo.*

Anal. Calcd. for $[RuC_{16}H_{24}N_2As_2Cl_2]ClO_4$: Ru, 15.3; C, 28.8; H, 3.6. Found: Ru, 15.1; C, 29.1; H, 3.8.

Dichloro-bis-(α-picolyldimethylarsine)-ruthenium(II) (VIII).—Potassium pentachloroaquoruthenate(III) (0.75 g.) was dissolved in water (15 ml.) and α-picolyldimethylarsine (0.8 g.) in alcohol (3 ml.) added. The solution turned green immediately on the addition of the arsine. The mixture was heated on the water-bath for 1 hr. in the presence of sodium hypophosphite solution (0.3 ml. of 20%) under nitrogen. Bright orange-red crystals of the product soon appeared. The solution slowly lightened to a yellow-brown as the reduction proceeded. The product was filtered after 1 hr., washed with warm water and dried *in vacuo.*

Anal. Calcd. for $[RuC_{16}H_{24}N_2As_2Cl_2]^0$: Ru, 17.9; C, 33.9; H, 4.3; N, 4.9. Found: Ru, 18.1; C, 33.8; H, 4.2; N, 4.8.

The complex was insoluble in cold water but slightly soluble in hot. It was quite soluble in alcohol or chloroform to give a bright orange solution. The complex was *diamagnetic.* The conductivity of an $M/1000$ solution in nitrobenzene was 0.8 reciprocal ohm.

Acknowledgment.—The authors gratefully acknowledge their indebtedness to Miss B. Stevenson for the C, H and N microanalyses recorded in this paper.

SYDNEY, AUSTRALIA