can be determined at various R values by measuring the decrease in optical rotation as a function of time (Table II).

If the proposed mechanism is operating, the rate of racemization should vary with R (inversely proportional to concentration of metal ion) according to the function: $k' = 3ka\ (1/R - 3/R^2)$. This function is zero at $R = 3$, has a maximum at $R = 6$, and slowly tapers off at higher R values. A plot of k'/ka against R for the various runs shows excellent agreement with the theoretically constructed curve (Figure 1).

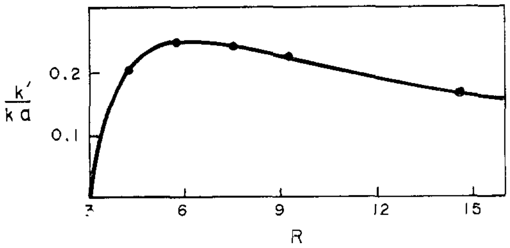

Figure 1.—Effect of ligand to metal ratio, R, on the rate of racemization of 1. The points represent experimental runs, and the curve is constructed theoretically from $k'/ka = 3(1/R - 3/R^2)$.

This strongly supports our proposed mechanism and the reaction is an interesting example of a racemization path, where the action of the metal ion is truly catalytic and where the substrate itself acts as the basic racemization agent.

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Dimethylmercury and Tetraborane(10)

By F. M. Miller and D. M. Ritter[1]

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Dimethylmercury[2] will alkylate tetraborane(10)[3] to give 2-methyltetraborane(10).[4] The best yield (68%) at optimum conversion (27%) was obtained after 5 min at 50° in a volume of 200 ml when the ratio of dimethylmercury to tetraborane was 2.50:0.42 (in mmol).[5] From this was recovered by glpc tetraborane (0.25), 2-methyltetraborane (0.12), methyldiboranes (0.09), and trimethylborane (0.01). Reactants in the ratio 2.38:0.78 underwent a 10% conversion at 25° after 1.6 hr with a 62% yield of 2-methyltetraborane. After 5 hr at 25° reactants in the ratio 3.78:1.37 gave a 42% conversion and a 56% yield. About the same amount of dimethylmercury and larger proportions of tetraborane gave approximately the same conversion, but the yield of methyltetraborane diminished. The reaction appeared to proceed in the dimethylmercury as solvent, and the more dilute the solution, the better was the yield. When all substances were present as vapor only, there was no reaction.

Under similar conditions trimethylbismuth[6] gave 5% conversion to 2-methyltetraborane. Trimethylgallium[7] converted 50% of tetraborane to trimethylborane.

Pentaborane(11) with dimethylmercury after 1 hr gave pentaborane(9), tetraborane(10), and the products expected from the latter. In 12 hr diborane(6) was 16% converted to methyldiboranes.

The results reported here are reminiscent of the cases where trimethylgallium and diborane(6) gave gallium metal and methyldiboranes[8] and where bis(trifluoromethylmercury) and diborane in dimethyl sulfide solvent gave the dimethyl sulfide adduct of trifluoromethylborane.[9]

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[1] Author to whom inquiries should be addressed. Work supported by funds from National Science Foundation Grants GP-3459 and GP-7888.

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Protonic Complexes of Oxo Ligands with Tetrachloroauric Acid

By Richard A. Potts

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At the turn of the century Pickard and Kenyon[1] prepared a series of compounds of tertiary phosphine oxides with acids and salts. Complexes of phosphine oxides with various metal ions[2-4] and nonmetals (halogens)[5] have now been widely studied. Pickard and Kenyon's complexes with acids, however, have received less attention. Collamati[6] studied the compound tetrachloroauric acid–bis(triphenylphosphine oxide), $HAuCl_4 \cdot 2(C_6H_5)_3PO$, and found that the phosphine oxide molecules are not coordinated to the gold(III) but are bonded to the hydrogen ion as in the

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TABLE I

ANALYTICAL AND PHYSICAL DATA

Compound	Mp, °C	Analytical data							
		Calcd, %			Found, %			Mol wt[a]	
		C	H	Au	C	H	Au	Calcd	Found
$[H((C_6H_5)_3PO)_2]AuCl_4$	175–178	48.24	3.49	21.98	47.96	3.40	21.99	896.2	579.8
$[H((C_6H_5)_3AsO)_2]AuCl_4$	174–177	43.94	3.18	20.02	43.81	3.08	19.68	984.1	630.8
$[H((CH_3)_2SO)_2]AuCl_4$	106–108[b]	9.68	2.65	39.71	9.56	2.69	39.37	496.1	291.7
$[H(C_5H_5NO)_2]AuCl_4$	91–93	22.66	2.09	37.17	22.84	2.10	37.13	530.1	346.4
$[H((CH_3)_3NO)_2]AuCl_4$	156–169	14.70	3.92	40.20	14.67	3.92	40.17	490.1	318.6

[a] The molecular weights reported are interpolated for a concentration of 0.05 *M*. [b] Melts with decomposition and evolution of the gas dimethyl sulfide.

compound $HCl \cdot 2(C_6H_5)_3PO$.[7] The purpose of this paper is to describe the preparation and characterization of protonic complexes of tetrachloroauric acid with other oxo ligands.

Experimental Section

Materials.—The triphenylphosphine oxide, triphenylarsine oxide hydrate, pyridine N-oxide, and triphenylphosphine sulfide were purchased from the Aldrich Chemical Co. Trimethylamine oxide dihydrate was purchased from Eastman Organic Chemicals. The methanol-d_1 (99%) was purchased from Diaprep, Inc.

The pyridine N-oxide was recrystallized from toluene and then handled in a dry nitrogen atmosphere. The tetrachloroauric acid hydrate was prepared by dissolving a weighed amount of gold metal in aqua regia, replacing the solution by repeated partial evaporation, adding concentrated hydrochloric acid, and finally evaporating to dryness in a desiccator.

Preparation of the Complexes.—The complexes $[H((C_6H_5)_3PO)_2]AuCl_4$, $[H((C_6H_5)_3AsO)_2]AuCl_4$, $[H(C_5H_5NO)_2]AuCl_4$, and $[H((CH_3)_3NO)_2]AuCl_4$ were prepared by a method similar to that described by Pickard and Kenyon.[1] Concentrated solutions of tetrachloroauric acid hydrate and the ligand in absolute methanol produced the yellow crystalline compounds upon mixing and cooling. The compounds were filtered, washed quickly with cold methanol, and air dried. The pyridine N-oxide complex was prepared in a dry nitrogen atmosphere.

The complex $[H((CH_3)_2SO)_2]AuCl_4$ was prepared by adding the dimethyl sulfoxide to a concentrated solution of tetrachloroauric acid hydrate in absolute methanol. The compound was precipitated by the addition of diethyl ether and recrystallized from ethyl acetate.

All of these compounds are stable in air. All were obtained in yields of 70% or better. A ligand to acid ratio in slight excess of 2:1 was used.

The deuterated compound, $[D((C_6H_5)_3PO)_2]AuCl_4$, was prepared by recrystallizing the protonated compound from a solution of methanol-d_1 through which deuterium chloride had been passed. This operation was carried out in a dry nitrogen atmosphere since the deuterium is exchanged very rapidly.

The compound sodium tetrachloroaurate(III)–tetrakis(triphenylphosphine oxide), $NaAuCl_4 \cdot 4(C_6H_5)_3PO$, was prepared as described in the literature;[6] mp 217–220°.

Analyses.—Analytical data for the above compounds appear in Table I. Carbon and hydrogen analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Analysis for gold was performed gravimetrically by precipitating gold metal with a hydroquinone solution.

Physical Measurements.—Infrared spectra were obtained with a Perkin-Elmer 221 spectrophotometer containing a sodium chloride prism-grating interchange over the range 4000–600 cm^{-1}. Samples were mulled in Nujol and placed on sodium chloride plates covered with polyethylene film. Hexachlorobutadiene was utilized as the mulling agent when important absorptions fell under the Nujol–polyethylene frequencies. Ultraviolet–visible spectra were obtained from 210 to 800 nm on a Beckman DB spectrometer with an attached strip chart recorder. The spectra were determined by placing a solution of the sample in absolute methanol in a 1-cm quartz cell and recording it against the solvent. Molecular weights were determined cryoscopically in dried and freshly distilled nitrobenzene.

Results and Discussion

The analyses indicate that there are 2 mol of ligand/mol of tetrachloroauric acid in these compounds. These results are similar to that reported for the compound tetrachloroauric acid bis(triphenylphosphine oxide).[6] For this compound it was suggested that the two phosphine oxide ligands are not coordinated to the gold(III) but are hydrogen bonded to the proton. A six-coordinated gold(III) species is rather unlikely. The new complexes reported here with triphenylarsine oxide, dimethyl sulfoxide, pyridine N-oxide, and trimethylamine oxide fall into the same general pattern.

The ultraviolet spectra of all of these compounds show one strong absorption with a maximum between 315 and 320 nm and a maximum molar absorptivity of from 3.5×10^3 to 5.0×10^3. These values are almost identical with those reported in the literature for the tetrachloroaurate(III) anion (aqueous solution).[8] This similarity suggests that the gold(III) is unaffected by the inclusion of the two ligand molecules in the compound. One spectrum was obtained of the compound tetrachloroauric acid–bis(dimethyl sulfoxide) dissolved in dimethyl sulfoxide. This spectrum showed a maximum absorbance at 326 nm and a molar absorptivity of 4.1×10^3 indicating that even under these conditions no donor molecule is associated with the tetrachloroaurate anion.

The two ligand molecules may have two other possible major roles in these compounds. They either may be simply filling holes in the crystal lattice or may be hydrogen bonded with the proton. Evidence against the first is derived from molecular weight data. The molecular weights reported in Table I are about half the calculated values. This suggests that the molecules dissociate into two particles instead of four which would be the case if the two ligand molecules were not associated with one of the other two species. A study of the variation of molecular weights with the change of concentration was conducted. For the concentration range of 0.01–0.06 *M* the molecular weights increased only slowly (about 10%) with increase in concentration.

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TABLE II

INFRARED FREQUENCIES[a]

Compound	P-O, N-O, As-O, S-O str freq		H-bond freq		
	Complex	Free Ligand			
$[H((CH_3)_2SO)_2]AuCl_4$	937 s	1053 s	1240 w,b	1150 w, b	750 s, b
$[H((C_6H_5)_3PO)_2]AuCl_4$	1100 s	1192 s	1225 w, b		850 s, b
$[D((C_6H_5)_3PO)_2]AuCl_4$	762 s	1192 s			<600 s, b
$NaAuCl_4\cdot 4(C_6H_5)_3PO$	1206 m, 1185 s	1192 s			
$[H((C_6H_5)_3AsO)_2]AuCl_4$	770 s	881 s	1280 w, b		1030 s, b
$[H(C_5H_5NO)_2]AuCl_4$	1245 s	1265 s (CS_2)[b]	1280 w, b		770 s, b
$[H((CH_3)_3NO)_2]AuCl_4$	937 m	940 s ($CHBr_3$)[c]	1065 m, b		860 s, b

[a] All values are in wave numbers. Abbreviations: s, strong; m, medium; w, weak; b, broad. [b] Reference 10. [c] Reference 12.

The role of the two ligand molecules seems then to be the stabilization of the acid proton by hydrogen bonding. The infrared data displayed in Table II support this conclusion. The P–O, As–O, and S–O stretching frequencies have all shifted to lower frequencies which is characteristic of complex formation through the oxygen atom. In the deuterated compound the band at 1100 cm^{-1} is greatly diminished and a new strong band appears at 762 cm^{-1}. If this frequency is the P–O stretching frequency, it suggests that this vibration is strongly coupled with the proton. The sodium salt which crystalizes with four phosphine oxide molecules shows infrared frequencies almost identical with those of the free ligand. These data perhaps suggest that the ligands are simply filling holes in the crystal structure. However, in light of some recent studies indicating complex formation between phosphine oxides and alkali metal ions,[4,9] this conclusion should not be accepted without further evidence. The N–O stretching frequencies are affected as when complexed to other species.[10,11] The N–O frequencies of the complexes are compared to the free-ligand frequencies in solution where there should be less association.[10,12]

A second set of absorptions in the infrared also points to hydrogen bonding between the ligands and the proton in these compounds. A strong and broad but well-defined band appears in the region 750–1030 cm^{-1} accompanied by one or more much weaker and broad bands in the region 1065–1280 cm^{-1}. Upon deuteration of the phosphine oxide complex, both of the broad bands disappear and only the tail of a strong, broad band below 600 cm^{-1} was observed. These bands must then be associated with the hydrogen bond vibrations. Hadzi[7] attributes similar infrared activity to the formation of symmetrical hydrogen bonds. The infrared spectra of the complexes reported here are indeed very similar to but better defined than those reported for such compounds as $HCl\cdot 2(C_6H_5)_3PO$. With the hydrogen halides a 1:1 adduct is also reported with the halide ion associated with the proton. With tetrachloroauric acid the noncoordinating, large anion $AuCl_4^-$ allows the maximum coordination of the proton and assists in the stabilization of the large cation.

The preparation of a similar compound with the ligand triphenylphosphine sulfide, $(C_6H_5)_3PS$, was attempted. The compound trichloro(triphenylphosphine sulfide)gold(III), $(C_6H_5)_3PSAuCl_3$,[13] was isolated. This result might have been predicted if one considers that the soft sulfide donor has the choice of the hard proton or the soft gold(III).

These results lend support to the existence of protonic complexes in these compounds. The formulas of these compounds should then be written to indicate the ligands, point of attachment, such as $[H((C_6H_5)_3PO)_2]$-$AuCl_4$.

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Octahedral Metal Carbonyls. XVI.[1] A Kinetic Investigation of the Second Step of the Reaction of *o*-Phenanthrolinetetracarbonylmolybdenum with Lewis Bases

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Angelici and Graham have investigated the kinetics of reactions of $(phen)M(CO)_4$ (phen = *o*-phenanthroline; M = Cr, Mo, W) with Lewis bases (L) to give, as sole products, $(phen)(L)M(CO)_3$ complexes[3,4]

$$(phen)M(CO)_4 + L \longrightarrow (phen)(L)M(CO)_3 + CO \qquad (1)$$

For M = Mo, W, these reactions were found to proceed by way of a two-term rate law[4]

$$rate = k_1[(phen)M(CO)_4] + k_2[(phen)M(CO)_4][L] \qquad (2)$$

A mechanism involving two parallel processes, rate-

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