change with the solvent in $S_4N_4 \cdot AlBr_3$ and the inability to recover aluminum chloride from attempted sublimation all suggest less ready dissociation in the aluminum halide–tetrasulfur tetranitride adducts than has been observed in the analogous boron trichloride adduct (*i.e.*, a higher formation constant most probably arising from a smaller rate of dissociation).

Experimental Section

General.—Tetrasulfur tetranitride was prepared as previously described[10] and recrystallized from benzene to give material of mp 178°. Aluminum halides were sublimed *in vacuo* immediately prior to use. All solvents were reagent grade, were refluxed over phosphorus pentoxide for 6 hr prior to distillation and were subsequently stored in the drybox. All reactions and work-up procedures were carried out in a Vacuum Atmosphere Corp. Dry Lab, equipped with Dry Train Model HE-93-B. Analyses for carbon, hydrogen, nitrogen, and halogen were performed by commercial laboratories. Sulfur was analyzed in triplicate by conversion to barium sulfate.[11] Aluminum was determined by neutron activation analysis of ^{28}Al.

$S_4N_4 \cdot AlCl_3$.—Aluminum chloride (0.88 g, 6.8 mmol) was added to 50 ml of dry 1,2-dichloroethane, followed by 1.21 g (6.6 mmol) of tetrasulfur tetranitride. The reaction mixture turned dark red immediately. After 5 hr of stirring, no undissolved tetrasulfur tetranitride remained. The deep red solution was filtered and reduced in volume (*in vacuo*) until precipitation began. The solution was then heated to redissolve the product and cooled overnight whereupon dark red crystals were obtained. These were collected by filtration and dried *in vacuo* to give a crystalline product which decomposed at 100° in a sealed tube. The infrared spectra (Nujol mull) showed absorption at 1045 (s), 990 (m), 960 (s), 925 (m), 860 (s), 750 (m), 720 (w), 700 (m), 675 (w), 620 (m), 570 (w, sh), 540 (w, sh), 500 (s), 470 (s, sh), 400 (s), 360 (w), 340 (w), 320 (w) cm^{-1}. *Anal.* Calcd for $S_4N_4AlCl_3$: S, 40.4; N, 17.6; Al, 8.5; Cl, 33.6. Found: S, 40.5; N, 16.0; Al, 8.5; Cl, 34.2.

On exposure of 0.6075 g (1.94 mmol) of the adduct to air, it turned yellow and became sticky. After several days, extraction of this material with benzene gave 0.3372 g (1.83 mmol) of tetrasulfur tetranitride. On contact with water, the adduct underwent rapid decomposition to a dark green intractable slime.

$S_4N_4 \cdot AlCl_3 \cdot SbCl_5$.—Antimony pentachloride (0.90 g, 3.0 mmol) was added to 0.858 g (2.65 mmol) of $S_4N_4 \cdot AlCl_3$ in 20 ml of dry carbon tetrachloride and stirred at room temperature for 5 hr. Filtration gave a light brown powder which was washed repeatedly with dry carbon tetrachloride and dried *in vacuo*. *Anal.* Calcd for $S_4N_4 \cdot AlCl_3 \cdot SbCl_5$: S, 20.8. Found: S, 21.1.

The ir spectra showed bands at 1080 (s), 1010 (w), 995 (m), 825 (m), 800 (m), 740 (w), 720 (w, sh), 530 (s), 360 (s, multiple absorption) cm^{-1}. The powder was placed in a sublimation apparatus and heated to 120° whereupon traces of $S_4N_4 \cdot SbCl_5$ (identified by ir spectra) collected on the cold finger. No $S_4N_4 \cdot AlCl_3$ was observed and the residue consisted mainly of an intractable polymer.

When $S_4N_4 \cdot SbCl_5$ (1.50 g, 3.17 mmol) was stirred with 0.50 g (3.17 mmol) of $AlCl_3$ in 20 ml of dry carbon tetrachloride a similar brown powder resulted whose ir spectrum was superimposable upon that of the previous mixed adduct.

$S_4N_4 \cdot AlBr_3$.—Freshly sublimed aluminum bromide (6.49 g, 24.7 mmol) was reacted with 4.53 g (24.6 mmol) of tetrasulfur tetranitride in 50 ml of dry 1,2-dibromoethane. The reaction mixture slowly turned dark red and, after work-up as described for the chloride, gave orange crystals which decomposed at 122°. The infrared spectra (Nujol mull) showed adsorption at 1035 (s), 950 (s), 850 (s), 830 (s), 770 (m), 715 (w), 515 (s), 480 (s), 440 (w), 380 (s), 350 (w) cm^{-1}. *Anal.* Calcd for $S_4N_4 \cdot AlBr_3$: S, 28.3; N, 12.4; Al, 6.0; Br, 53.3. Found: S, 28.4; N, 12.0; Al, 5.6; Br, 53.4.

A sample (0.1724 g, 0.386 mmol) on exposure to air for several days gave 0.0646 g (0.351 mmol) of tetrasulfur tetranitride on extraction with benzene.

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Complexes Formed by the Reactions of Tetraoxobis(pyridine)ruthenium(VIII) with 2,2′-Bipyridine and 1,10-Phenanthroline in Methanol

BY TOSHIO ISHIYAMA* AND YOSHIO KODA

Received February 25, 1972

No hydroxoruthenium(II) complexes with pyridine, 2,2′-bipyridine, or 1,10-phenanthroline have previously been reported. Dwyer, *et al.*,[1–3] reported that tetrakis(pyridine)(2,2′-bipyridine)ruthenium(II) perchlorate, $[Ru(py)_4bipy](ClO_4)_2$, was isolated by the addition of pyridine to a hot concentrated solution of acid, $H[RuCl_4bipy]$, and reported that two pyridine molecules in $[Ru(py)_4bipy]^{2+}$ were readily replaced by a variety of other ligands although it was difficult to replace more than two. They also reported that *cis*-bis(pyridine)bis(1,10-phenanthroline)ruthenium(II) perchlorate, *cis*-$[Ru(py)_2phen_2](ClO_4)_2$, was formed by the reaction of $[RuCl_2phen_2]$ with pyridine. In previous papers[4–7] it was reported that $[RuO_4(py)_2]$, $[RuO_4bipy]$, and $[RuO_3phen]_2O$ were obtained by the reactions of ruthenium tetraoxide with pyridine, 2,2′-bipyridine and 1,10-phenanthroline in carbon tetrachloride, respectively, and it was also reported that $[RuO_2(bipy)_2]$, $[RuO_2bipy \cdot phen]$, and $[RuO_2(phen)_2]$ were obtained by the reduction and substitution reactions of $[RuO_4bipy]$ and $[RuO_3phen]_2O$ with 2,2′-bipyridine and 1,10-phenanthroline in methanol, respectively. In the present paper two new complexes, $[Ru(OH)_2(py)_2bipy] \cdot 3H_2O$ and $[Ru(OH)_2(py)_2phen] \cdot 1.5H_2O$, are reported, together with the infrared and electronic spectra and magnetic properties of the starting complex, $[RuO_4(py)_2]$, reported previously.[4]

Experimental Section

Materials.—Ruthenium(III) chloride monohydrate (extra pure grade) supplied by Mitsuwa Chemicals was used as received. Pyridine was treated with potassium permanganate, distilled, treated with potassium hydroxide, and redistilled. Both 2,2′-bipyridine and 1,10-phenanthroline were supplied by Wako Pure Chemical Industries Ltd. The former was purified by recrystallization from distilled water, and the latter from ethanol after it had been dried by heating at 110° for 3 hr. Commercial methanol was dried by treatment with magnesium ribbon and iodine and distilled. Lithium perchlorate (extra pure grade) supplied by Mitsuwa Chemicals was purified by recrystallization from methanol after heating at 110° for 3 hr.

Syntheses. (1) **Tetraoxobis(pyridine)ruthenium(VIII), $[RuO_4(py)_2]$.**—This compound was synthesized according to the method reported previously.[4]

(2) **Dihydroxobis(pyridine)(2,2′-bipyridine)ruthenium(II),**

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TABLE I

ANALYTICAL DATA OF HYDROXORUTHENIUM(II) COMPLEXES WITH PYRIDINE, 2,2′-BIPYRIDINE, AND 1,10-PHENANTHROLINE

Complex	Yield, %	Analytical data, % Calcd Ru	Calcd C	Calcd H	Calcd N	Calcd H_2O	Found Ru	Found C	Found H	Found N	Found H_2O	Mol wt Calcd (anhydride)	Mol wt Found
$[Ru(OH)_2(C_5H_5N)_2(C_{10}H_8N_2)]\cdot 3H_2O$	86	20.1	47.7	5.2	11.1	10.7	19.1	46.3	4.8	10.7	11.1	449.5	500
$[Ru(OH)_2(C_5H_5N)_2(C_{12}H_8N_2)]\cdot 1.5H_2O$	90	20.2	52.7	4.6	11.2	5.4	19.6	53.9	4.3	10.8	5.0	473.5	500

$[Ru(OH)_2(py)_2bipy]\cdot 3H_2O$, and Dihydroxobis(pyridine)(1,10-phenanthroline)ruthenium(II), $[Ru(OH)_2(py)_2phen]\cdot 1.5H_2O$.—To a solution of 1 g of $[RuO_4(py)_2]$ in 150 ml of methanol, 2.5 g of 2,2′-bipyridine or 1,10-phenanthroline was added. The reaction mixture was refluxed with occasional shaking on a water bath for about 2 hr until the solution turned orange-brown. The solution was then evaporated to dryness, and the residue was repeatedly washed with diethyl ether and then dissolved in distilled water. An insoluble material was filtered off. The solution was concentrated, and the crystals which formed were recrystallized from distilled water and dried *in vacuo;* yield of dihydroxobis(pyridine)(2,2′-bipyridine)ruthenium(II) was 86%, and of dihydroxobis(pyridine)(1,10-phenanthroline)ruthenium(II) was 90%. Both complexes are insoluble in carbon tetrachloride, benzene, ether, ethyl acetate, and dioxane but are soluble in water, methanol, acetic acid, acetone, dimethylformamide, and dimethyl sulfoxide.

Analysis of the Complexes.—The determination of ruthenium in complexes was made spectrophotometrically by measuring the absorbance at 465 mμ after the decomposition of the complexes by heating at 350° and then by alkali fusion.[8] The determination of pyridine in the complexes was attempted by the method reported previously in the case of $[RuO_4(py)_2]$.[4,9] Pyridine was detected by this method, but the liberation of pyridine in the complexes was incomplete. The water content of the complexes was determined by measuring the weight loss in the temperature range 100–130° with a thermobalance. Molecular weights were measured with a Model S-601 vapor pressure osmometer of Shibayama Scientific Instrument Co. Samples of the complexes were heated in advance for 3 hr at 110° to remove water of crystallization. It was ascertained by measuring the infrared absorption spectra that the structure of the complexes was not altered by this treatment.

Analyses are reported in Table I. The results of elemental analysis of $[RuO_4(py)_2]$ are consistent with the formula proposed previously.[4]

Absorption Spectra.—The infrared absorption spectra were obtained on an infrared spectrophotometer, Model IR-S of the Japan Spectroscopic Co., by the KBr disk method. The visible and ultraviolet absorption spectra were measured with a Beckmann Model D.U. spectrophotometer.

Magnetic Measurements.—The magnetic susceptibility was measured at 25° with a Cahn R.G. electrobalance by the Faraday method.[10]

Polarographic Measurements.—The polarographic measurements were carried out at 25° with a Yanagimoto automatic recording polarograph (Type PA 101). A conventional H-type electrolytic cell was used with a saturated mercurous sulfate reference electrode, and an agar plug saturated with potassium sulfate was used for the junction. Lithium perchlorate was used as the supporting electrolyte. The measurements were performed as described previously.[7]

Results and Discussion

Compositions of the Complexes.—From the results of the elemental analysis, the mole ratios of ruthenium: pyridine:(2,2′-bipyridine or 1,10-phenanthroline) seem to be 1:2:1. The molecular weight data indicate that both complexes, $[Ru(OH)_2(py)_2bipy]$ and $[Ru(OH)_2(py)_2phen]$, are mononuclear.

Oxidation States of the Complexes.—In the two new complexes, $[Ru(OH)_2(py)_2bipy]$ and $[Ru(OH)_2(py)_2phen]$, no reduction waves were observed in 0.5 mol/l. $LiClO_4$–methanol solutions. It has been reported by Niedrach and Tevebaugh[11] that ruthenium(IV) is stepwise reduced to Ru(III) and to Ru(II) in perchloric acid solution. The fact that no reduction waves were observed under the same experimental conditions as those of previously reported complexes, $[RuO_2(bipy)_2]$ and $[RuO_2(phen)_2]$,[7] shows that the oxidation number of ruthenium in the two new complexes is 2 for each, indicating that tetraoxobis(pyridine)ruthenium(VIII) was reduced to hydroxoruthenium(II) complexes by reaction with 2,2′-bipyridine and 1,10-phenanthroline in methanol.

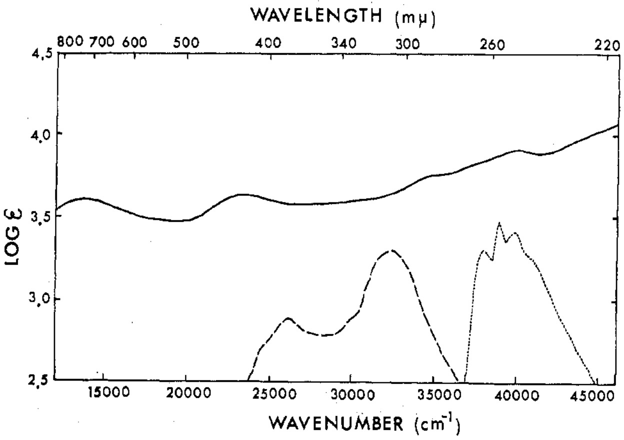

Figure 1.—Electronic spectra of $[RuO_4(py)_2]$ (——) and its components py (····) and RuO_4 (– – – –) in H_2O.

Infrared Absorption Spectra.—The main infrared absorption bands of the three present complexes, $[RuO_4(py)_2]$, $[Ru(OH)_2(py)_2bipy]$, and $[Ru(OH)_2(py)_2phen]$, are shown in Table II, together with those of the free ligands. The C=N stretching peaks of the complexes are all shifted to the higher frequency side by coordination. This behavior is interpreted as an indication that the bond order of the carbon–nitrogen link is increased.[12,13] In the present ruthenium–pyridine complexes, characteristic triplets are clearly observed in the region from 1100 to 1000 cm^{-1}, probably due to the C–H stretching of the coordinated pyridine molecules. Similar bands have also been observed for several copper–pyridine complexes.[14] The absorption bands at 3380 and 3390 cm^{-1} of $[Ru(OH)_2(py)_2bipy]$ and $[Ru(OH)_2(py)_2phen]$, respectively, were assigned to the O–H stretching vibration. Similar observations have been reported for the previously reported complexes, $[RuO_2(OH)_2bipy]$ and $[Ru(OH)_3phen]_2O$.[7] The infrared absorption spectrum of the ruthenium(VIII) oxide complex with pyridine contains no peak attributable to the O–H stretching frequency,

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TABLE II

THE CHARACTERISTIC INFRARED ABSORPTION BANDS OF OXORUTHENIUM(VIII) AND HYDROXORUTHENIUM(II) COMPLEXES WITH PYRIDINE, 2,2′-BIPYRIDINE, AND 1,10-PHENANTHROLINE (cm^{-1})

Assignments	py	bipy	phen	$[RuO_4(py)_2]$	$[Ru(OH)_2(py)_2bipy]$	$[Ru(OH)_2(py)_2phen]$
ν(O—H)					3380 vs	3390 vs
ν(C═N)	1575 s	1582 s	1621 s	1608 s	1605 s	1630 m
		1560 m			1565 m	
ν(C═C)			1585 m			
			1560 m			1572 m
	1072 s	1076 s		1072 s	1072 m	1095 w
	1045 s	1043 s		1050 m	1048 w	1055 w
	1018 s	1000 s		1020 m	1023 m	1038 m
ν(C—H)			762 s			775 m
		759 s			780 s	
			730 s			730 s
	695 s			700 s	705 m	715 sh

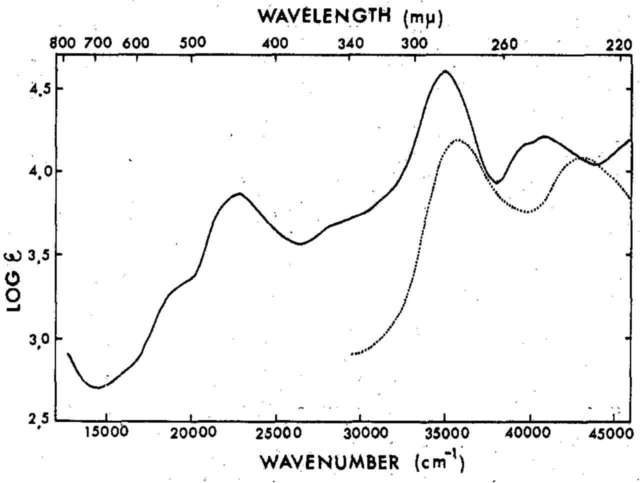

Figure 2.—Electronic spectra of $[Ru(OH)_2(py)_2bipy]$ (——) and 2,2′-bipyridine (····) in H_2O.

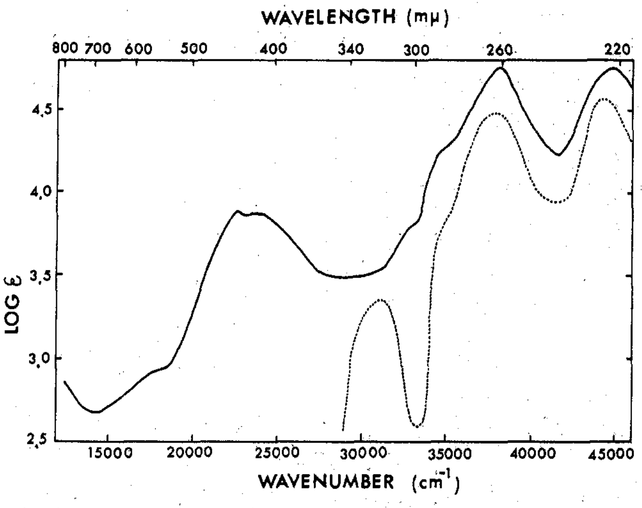

Figure 3.—Electronic spectra of $[Ru(OH)_2(py)_2phen]$ (——) and 1,10-phenanthroline (····) in H_2O.

indicating that no hydroxo group is present in the ruthenium(VIII) oxide complex.

Electronic Absorption Spectra.—The visible and ultraviolet absorption spectra of oxoruthenium(VIII) and hydroxorutheneium(II) complexes with pyridine, 2,2′-bipyridine, and 1,10-phenanthroline ($[RuO_4(py)_2]$, $[Ru(OH)_2(py)_2bipy]$, and $[Ru(OH)_2(py)_2phen]$) were measured in water. They are shown in Figures 1–3, together with those of pure ligands in water.

Tetraoxobis(pyridine)ruthenium(VIII) has three peaks and a shoulder at 720, 420, 257, and 295 mμ, respectively (Figure 1). The two peaks observed in the visible region may both be assigned to the charge transfer from ligand to metal. Two absorption bands observed in the visible region for ruthenium tetraoxide have been attributed to the charge transfer from oxygen to ruthenium.[15] The shoulder and the peak at 295 and 257 mμ, respectively, can both be assigned to the intraligand transition ($\pi \rightarrow \pi^*$), corresponding to the 265, 256, and 250 mμ bands in pyridine.[16]

Dihydroxobis(pyridine)(2,2′-bipyridine)ruthenium(II) has six absorption bands at 535, 445, 350, 285, 252, and 244 mμ (Figure 2). The shoulders and the peak at 535, 350, and 445 mμ, respectively, may all be assigned as metal-to-ligand charge-transfer transitions ($t_{2g} \rightarrow \pi^*$). Two peaks and a shoulder at 285, 244, and 252 mμ, respectively, appear to be intraligand transitions corresponding to the 279 and 233 mμ for free 2,2′-bipyridine. The spectrum of $[Ru(OH)_2(py)_2bipy]$ resembles that of $[Ru(bipy)_3]Cl_2$[17] except for the band in the vicinity of 420 mμ of $[Ru(bipy)_3]Cl_2$.

Dihydroxobis(pyridine)(1,10-phenanthroline)ruthenium(II) has seven absorption bands at 550, 445, 415, 310, 290, 262, and 223 mμ (Figure 3). The shoulder and two peaks at 550 and 445 and 415 mμ, respectively, may all be assigned to the metal-to-ligand charge-transfer transitions ($t_{2g} \rightarrow \pi^*$). The two shoulders at 310 and 290 and two peaks at 262 and 223 mμ appear to be intraligand transitions corresponding to 320, 290, 265, and 230 mμ bands of free 1,10-phenanthroline. The spectrum of $[Ru(OH)_2(py)_2phen]$ resembles that of *cis*-$[Ru(py)_2(phen)_2](ClO_4)$[18] except for the shoulder in the vicinity of 550 mμ of $[Ru(OH)_2(py)_2phen]$.

Magnetic Properties.—The observed diamagnetism of $[RuO_4(py)_2]$ indicates the absence of unpaired electrons, presumably because the 4d electrons are absent in Ru(VIII) oxide complex.

The two new hydroxoruthenium(II) complexes contain two hydroxo groups, two pyridine molecules and one 2,2′-bipyridine or 1,10-phenanthroline molecule in octahedral coordination around the central ruthenium atom. The observed diamagnetism of the complexes indicates that the ruthenium atoms have a spin paired d^6 (Ru^{II}) configuration.

A cis–trans isomeric pair of $[RuCl_2(py)_2bipy]$ has been prepared and characterized by infrared, visible, and ultraviolet absorption spectra and nmr spectra.

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The isomeric nature of the present complexes, [Ru(OH)$_2$(py)$_2$bipy] and [Ru(OH)$_2$(py)$_2$phen], will be discussed in the following paper by the comparison of the results of the cis–trans isomeric pair.

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The Syntheses of Some New Silver Olefin Compounds of the Type (Olefin)(β-diketonato)silver(I)

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It has been well established that the silver(I) cation has a strong propensity to react with olefins to form labile, relatively weakly bonded olefin complexes.[1] Most of the available isolable Ag(I) olefin compounds are salts in which the anion is perchlorate, nitrate, or tetrafluoroborate. We were interested in obtaining some nonionic silver(I) olefin compounds that would be isolable and soluble in relatively nonpolar solvents such as dichloromethane or cyclohexane. This paper reports a series of compounds with such characteristics.

The compounds which have been characterized are of the type [Ag(hfacac)(olefin)] (hfacac is the conjugate base of hexafluoroacetylacetone; olefins are 1,5-cyclooctadiene (C_8H_{12}), 1,3,5,7-cyclooctatetraene (C_8H_8), cyclohexene (C_6H_{10}), cycloheptene (C_7H_{12}), and cyclooctene (C_8H_{14})) and [Ag(tfacac)(olefin)] (tfacac is the conjugate base of trifluoroacetylacetone; olefins are 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene).

Experimental Section

J. T. Baker 1,5-cyclooctadiene, Columbia Organic 1,3,5,7-cyclooctatetraene, and Aldrich cyclooctene, cycloheptene, and cyclohexene were used in the preparation of the olefin compounds. Nmr spectra were recorded on a Varian A-60 spectrometer and are reported in Table I. Molecular weights were determined cryoscopically. Elemental analyses were performed by Instranal Labs. Silver analyses were performed gravimetrically by precipitation of the bromide salt. Conductance measurements were performed with an Industrial Instruments Model 16B2.

Preparation of Ag(hfacac)(C_8H_8).—A 5.92-g (34.9-mmole) amount of silver nitrate was dissolved in 30 ml of water and 4 ml of 1,3,5,7-cyclooctatetraene was added. To this solution was added a solution of Na$^+$ hfacac$^-$, prepared by addition of 1.125 g (28.14 mmol) of sodium hydroxide to 5.876 g (28.14 mmol) of Hfacac in water, yielding a flocculent white precipitate. (Occasionally a dark oil forms which may be due to a slight excess of sodium hydroxide. This oil can be extracted from the aqueous solution with benzene and recrystallized yielding the desired product.) Filtration and subsequent recrystallization from benzene–cyclohexane yielded 5.029 g (12.0 mmol) of the desired product. *Anal.* Calcd for $AgC_{13}H_9O_2F_6$: C, 37.25; H, 2.17; Ag, 25.75; mol wt 419. Found: C, 37.22; H, 2.26; Ag, 25.71; mol wt 354 (benzene).

Preparation of Ag(hfacac)(C_8H_{12}).—Procedure identical with that of [Ag(hfacac)(C_8H_8)] except that recrystallization was from chloroform. *Anal.* Calcd for $AgC_{13}H_{13}O_2F_6$: C, 36.90; H, 3.10; Ag, 25.50; mol wt 423. Found: C, 36.78; H, 3.22; Ag, 25.51; mol wt 391 (benzene), 734 (cyclohexane), 435 (bromoform). Conductivity data: Ag(hfacac)(C_8H_{12}), 84 mhos; NaI, 1125 mhos (10^{-3} *M* nitromethane solutions).

Preparation of Ag(hfacac)(C_8H_{14}).—The procedure was identical with that of Ag(hfacac)(C_8H_8) except that addition of Na$^+$-hfacac$^-$ to the aqueous solution containing Ag$^+$ and cyclooctene yielded an oil. This oil was extracted with benzene–cyclohexane and filtered, and the solution was allowed to evaporate yielding the desired product in 59% yield. *Anal.* Calcd for $AgC_{13}H_{15}O_2F_6$: C, 36.72; H, 3.56; mol wt 425. Found: C, 36.15; H, 3.47; mol wt 425 (bromoform).

Preparation of Ag(hfacac)(C_6H_{10}), Ag(hfacac)(C_7H_{12}), Ag(tfacac)(C_8H_{12}), and Ag(tfacac)(C_8H_8).—The procedure was identical with the preparation of Ag(hfacac)(C_8H_8). The compounds were recrystallized from chloroform, dichloromethane, dichloromethane, and benzene and the yields were 45, 31, 29, and 52%, respectively. Satisfactory carbon and hydrogen analyses were not obtainable since these compounds lose olefin readily. The integrated nmr signals of freshly prepared samples were consistent with the given stoichiometries.

Discussion

The preparation of the compounds reported in this work can be summarized by the equations

$$\mathrm{Ag^+NO_3^-} + \text{olefin} \xrightarrow{\mathrm{H_2O}} \mathrm{[Ag(olefin)]^+NO_3^-}$$

$$\mathrm{[Ag(olefin)]^+NO_3^-} + \mathrm{Na^+Xacac^-} \xrightarrow{\mathrm{H_2O}} \mathrm{[Ag(olefin)(Xacac)]}\downarrow + \mathrm{Na^+NO_3^-}$$

where X = hf or tf.

The qualitative stability of these compounds is dependent upon the type of β-diketonate anion present in the compound. For example, Ag(hfacac)(cyclooctadiene) can be stored for weeks at 0° without any appreciable change, while Ag(tfacac)(cyclooctadiene) loses olefin fairly rapidly and decomposes in a few days. We have attempted to prepare analogous compounds using the conjugate base of acetylacetone, but these failed. It may be that the qualitative stability of these compounds are inversely proportional to the basicity of the acetylacetonate derivative used.[2]

The vibrational spectra of the silver olefin compounds have been compared to those of the known compounds Cu(hfacac)$_2$ and Cu(tfacac)$_2$. All of the major bands associated with the hfacac and tfacac anion appear in the spectra of the silver compounds. The purpose of Table II is to provide evidence that the hfacac is bonded to silver *via* the oxygen atoms, rather than the γ-carbon atom. The first three compounds in Table II are thought to be bonded to the metal *via* the oxygens. The absorptions in the 1500–1700-cm^{-1} region are thought to be due to the ν(C$\overset{\cdot\cdot\cdot}{-}$O) and ν(C$\overset{\cdot\cdot\cdot}{-}$C) modes.[3] Pd(acac)$_2$(P(C$_6H_5$)$_3$) has been shown to have one acac group attached to the metal *via* the oxygen atoms and the other *via* the γ-carbon atom.[4] The ir spectrum of

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[1] D. C. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev.*, **6**, 215 (1970), and references quoted therein.

[2] The variation of substituents on the acetylacetonate ligand and its effects upon stability constants, force constants, and adduct formation in copper(II) acetylacetonates are discussed in the following two references: (a) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962); (b) W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).

[3] These frequencies are thought to be coupled. See K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970, pp 247–256.

[4] See Table II, ref *d*.