Complex **3** does not insert into C–H bonds. For example, the central metal does not insert into the methyl groups of dmpe, as does occur with Ru,[34] Ir,[3] and Fe[1c] complexes of methylated phosphines. It is likely that increased phosphine substitution and less effective π-accepting ligands than butadiene are necessary to enhance this type of reactivity.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Natural Sciences and Engineering Research Council of Canada for support of this research. Ms. P. R. Auburn suggested and performed the experiment involving exchange of C_4D_6 with **3**.

Registry No. **1**, 69859-75-2; **2**, 69878-77-9; **3**, 71328-76-2; **4**, 69891-40-3; **5**, 71328-72-8; **6**, 71328-73-9; **7**, 71359-29-0; 1-octene, 111-66-0; cyclohexene, 110-83-8; *cis*-2-pentene, 627-20-3; $ZrCl_4$, 10026-11-6.

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Synthesis of Macrocyclic Complexes of Gold(III) by Condensation of Bis(ethylenediamine)gold(III) Chloride with β-Diketones

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Bis(ethylenediamine)gold(III) chloride in aqueous base reacts with a variety of β-diketones via Schiff base condensation to form 14-membered, tetraaza ring, 12π macrocyclic complexes of gold(III). Reaction intermediates in which condensation of only one β-diketone has occurred can be isolated and condensed with a different β-diketone to provide variety in substituents on the macrocyclic ring. Oxidation of (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) hexafluorophosphate, I, with trityl tetrafluoroborate introduces a double bond in one of the five-membered rings. Gold can be removed from macrocycle I by reduction with Zn in aqueous base, and the free ligand so obtained may be used to prepare macrocyclic complexes of other metal ions. No condensation products could be isolated upon treating $[Au(en)_2]Cl_3$ in aqueous base with 1,1,1,5,5,5-hexafluoropentane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, biacetyl, biguanide, acetone, or 1,1,3,3-tetramethoxypropane.

Efforts by several investigators during the past few years have shown that amine ligands bound to Pt(IV), Ru(II) and -(III), and Os(III) are readily deprotonated in aqueous base and that the resulting coordinated amides show nucleophilic behavior toward certain carbonyl-containing substrates.[1-6] For example, one or more β-diiminate chelate rings are formed when $Pt(NH_3)_6^{4+}$ and $Pt(en)_3^{4+}$ are treated with 2,4-pentanedione in aqueous base.[3] A crystallographic study of one

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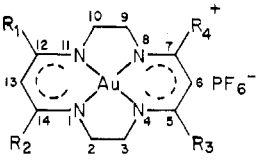
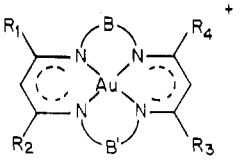
Table I. Characterization of Macrocyclic Gold(III) Complexes



complex	R_1	R_2	R_3	R_4	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
I	CH_3	CH_3	CH_3	CH_3	28.58	28.80	3.78	3.80	9.52	9.38
II	Ph	CH_3	CH_3	CH_3	35.08	34.70	3.73	3.80	8.62	8.30
III	*i*-Pr	CH_3	CH_3	CH_3	31.17	31.38	4.26	4.40	9.09	9.06
IV	*t*-Br	CH_3	CH_3	CH_3	32.39	31.99	4.49	4.44	8.89	8.38
V	CF_3	CH_3	CH_3	CH_3	26.18	25.90	2.99	3.00	8.73	8.48
VI[a]	H	CH_3	H	CH_3	25.72	25.85	3.24	3.28	10.00	9.89
VII[a]	*i*-Pr	CH_3	*i*-Pr	CH_3	33.54	33.28	4.70	4.73	8.70	8.55
VIII	H	CH_3	CH_3	CH_3	27.19	27.45	3.52	3.28	9.76	9.69



complex	R_1	R_2	R_3	R_4	B	B′	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
IX[b]	CH_3	CH_3	CH_3	CH_3	$CH(CH_3)CH_2$	$CH(CH_3)CH_2$	31.17	30.78	4.26	4.32	9.09	8.61
X[c]	CH_3	CH_3	CH_3	CH_3	CH=CH	C_2H_4	31.84	31.97	3.82	3.87	10.61	10.49

[a] Product isolated is a mixture of geometric isomers (see Discussion). [b] Data shown are for the PF_6^- salt. [c] Data shown are for the BF_4^- salt.

of these complexes shows that the β-diiminate chelate ring is planar and has delocalized charge.[3]

During the course of our investigation of condensation reactions of six-coordinate Pt(IV)–amine complexes with β-diketones, we became interested in exploring analogous reactions with square-planar amine complexes in hopes of synthesizing macrocyclic species. In this paper we describe the preparation and characterization of a series of macrocyclic β-diiminate complexes of Au(III) formed by condensation of $Au(en)_2^{3+}$ with various β-diketones in aqueous base.

Experimental Section

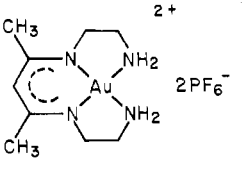
Starting Materials. Tetrachloroauric acid was prepared by dissolving gold wire in aqua regia and was used in preparing the Au(III)–amine complexes. $Au(en)_2Cl_3$ was prepared by treating an ether solution of ethylenediamine with $HAuCl_4$ according to the procedure by Block and Bailar.[7] Attempts to prepare bis(*rac*-1,2-propanediamine)gold(III) chloride by this method gave an oily product. However, a solid product is obtained after the following treatment: The oily material is washed several times with diethyl ether, once with benzene, once with acetone, and again with diethyl ether. The solid product thus obtained is dried under vacuum. Elemental analyses indicate a small amount of impurity, but ^1H and ^{13}C NMR spectra are satisfactory. Anal. Calcd for $[Au(pn)_2]Cl_3$: C, 15.96; H, 4.43; N, 12.40. Found: C, 15.88; H, 4.39; N, 11.58.

Instrumentation. Proton NMR spectra were recorded on a Varian EM-360 CW spectrometer or a Bruker WP-80 FT spectrometer. Carbon-13 spectra were run, using 8K data points, on the Bruker instrument at 20 MHz. Mass spectra were recorded with a Varian-MAT CH-5 instrument. Infrared spectra of complexes in KBr disks were taken on a Perkin-Elmer 421 grating spectrophotometer.

Elemental analyses were carried out locally by using an F and M 185 C, H, N analyzer, or they were sent to Chemalytics, Inc.

(5,7,12,14-Tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-4,6,-11,13-tetraenato)gold(III) Hexafluorophosphate Complexes I, VI, and VII. These macrocyclic complexes were made with only slight modifications (as indicated) of the following general procedure. To a solution of 300 mg of $Au(en)_2Cl_3$ in ~35 mL of H_2O at pH 9–10 (for I and VI) or pH 10–12 (for VII), adjusted by addition of 2 N NaOH, is added slightly more than a twofold molar excess of the appropriate β-diketone. The reaction mixture is stirred at 25 °C (I and VI) or 60 °C (VII) for 15 min (VI), 2 h (I), or several hours (VII) at which times traces of metallic gold can be seen. The reaction mixture is then filtered, and the filtrate for I and VI is treated with solid NH_4PF_6 to precipitate the complex. The precipitate for I and VI is washed with warm (40–50 °C) water and, for I, with cold methanol. Yellow, gummy products are obtained for VII unless the filtered reaction mixture is reduced in volume prior to addition of NH_4PF_6. The precipitate thus obtained is washed twice with water. Recrystallization is accomplished with the following solvent pairs: acetone/diethyl ether for I; acetone/petroleum ether for VI; chloroform/carbon tetrachloride for VII. In each case the precipitate is dissolved in a minimum amount of the first solvent at 50–60 °C. The hot solution is filtered, and the second solvent is added dropwise to the filtrate. After one or two recrystallizations in this manner, followed by drying in vacuo at 50 °C, the complexes gave the elemental analyses shown in Table I. Table I also defines the complexes in terms of their substituents R_1 to R_4. Complex VII is stable for only a few hours in solution at ambient temperature.

(5,7,12,14-Tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-4,6,-11,13-tetraenato)gold(III) Hexafluorophosphate Complexes II–V. These complexes were prepared by a two-step procedure, the first step of which is isolation of the orange tetradentate complex [*N,N′*-bis(2-aminoethyl)-2,4-pentanediiminato]gold(III) hexafluorophosphate hereafter referred to as A. This β-diiminate complex was prepared



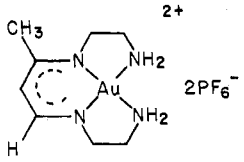
A

according to the procedure reported previously for the iodide salt[3] except that NH_4PF_6 is used, rather than KI, to precipitate the product. Further reaction of the above complex with a different β-diketone affords the unsymmetrical macrocycles II–V.

In a typical preparation, 300 mg of A is dissolved in a minimum amount of water and treated with a slight molar excess of the appropriate β-diketone. The pH is controlled by addition of concentrated

NaOH solution and is maintained sufficiently high to retain the yellow color characteristic of the deprotonated β-diiminate complex A (pH range 9–12). The reaction mixture is stirred at 60–70 °C until most of the product appears to have precipitated as the PF_6^- salt (5 h for II, 3 h for III, 10 h for IV, 3 h for V). The reaction mixture is then cooled to room temperature. The precipitate is collected by filtration and recrystallized in the same fashion as for I, VI, and VII by using the following solvent pairs: $CHCl_3/CCl_4$ for II and V; $CHCl_3$/diethyl ether for III; and $CHCl_3/CCl_4$ or petroleum ether for IV. Results of elemental analyses are given in Table I.

(5,7,14-Trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) Hexafluorophosphate (VIII). This complex was prepared by a procedure similar to that described above for complexes II–V except that B was used as a starting material. B is prepared



B

from $Au(en)_2Cl_3$ and sodium 1,3-butanedionate by using methods analogous to those used to prepare A.[3] Complex VIII is prepared by treating B with 2,4-pentanedione in aqueous solution at pH 12. The reaction appears to be complete after 2 h at ~25 °C. Recrystallization is accomplished with acetone/diethyl ether.

Attempted Condensation of $[Au(en)_2]Cl_3$ with 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione. In a procedure analogous to that used in preparing complexes I, VI, and VII, a solution of $[Au(en)_2]Cl_3$ in water was treated with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfac). The pH was maintained at 6–7 (at higher pH no precipitate could be obtained). After 30 min the pale yellow (nearly white) precipitate which formed was collected by filtration and washed twice with water. The product was recrystallized by dissolving it in dry diethyl ether followed by filtration and addition of dry petroleum ether to the filtrate. The precipitate thus formed was washed with petroleum ether and dried in vacuo, mp 166–167 °C dec. Anal. Calcd for $[Au(en)_2](hfac)_3$ (see Discussion): C, 24.31; H, 2.04; N, 5.97. Found: C, 24.10; H, 1.90; N, 5.72.

Attempted Condensation of A with 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione. The general procedure used in preparing complexes II–V was used here. A yellow precipitate formed immediately; however, the reaction mixture was stirred at pH 9–10 for 30 min. The product was collected by filtration and washed with cold water. Recrystallization was accomplished by dissolving the precipitate in hot chloroform, filtering, and adding petroleum ether to the filtrate. The final precipitate was washed with petroleum ether and dried in vacuo. Anal. Calcd for [*N*,*N*′-bis(2-aminoethyl)-2,4-pentanediiminato]gold(III) bis(hexafluoropentanedionate) (see Discussion): C, 28.74; H, 2.67; N, 7.06; F, 28.71 Found: C, 28.67; H, 2.55; N, 7.04; F, 28.12.

(3,5,7,9(or 10),12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) Hexafluorophosphate (IX). This complex is prepared by the general procedure described above for preparation of complexes I, VI, and VII except that bis(1,2-propanediamine)gold(III) chloride is used. The reaction mixture is maintained at pH 10 and ambient room temperature for 1 h. The crude product obtained by treating the filtered reaction mixture with NH_4PF_6 is recrystallized at room temperature with acetone and diethyl ether. The final product is washed with diethyl ether and dried in vacuo. Results of elemental analyses are given in Table I. The mass spectrum shows a peak at *m/e* 616 and several peaks around *m/e* 470, corresponding to a cation–PF_6 ion pair and the deprotonated macrocyclic cation, respectively.

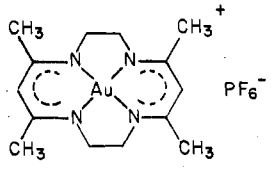
(5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,9,-11,13-pentaenato)gold(III) Tetrafluoroborate (X). This oxidation product of complex I was prepared by a procedure similar to that described by Truex and Holm.[8] A 0.95-g quantity of I is dissolved in the minimum amount of dry, degassed acetonitrile. To this solution, under a nitrogen atmosphere, is added 1.7 g of trityl tetrafluoroborate,[20] and the reaction mixture is stirred at ~50 °C for 24 h. At this point approximately one-third of the solvent is removed by evaporation, and the orange precipitate which forms is collected by filtration (in air) and washed with water and then ethanol. Recrystallization is accomplished by dissolving the product in hot acetonitrile, filtering the resulting solution, and cooling the filtrate to 0 °C. After the final product was dried in vacuo, the elemental analyses given in Table I were obtained. Note that although the starting material, I, is a PF_6^- salt, the product which precipitates is a BF_4^- salt.

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,-11,13-tetraene (XI). The free ligand from complex I can be obtained upon reduction of the Au(III) ion by zinc in basic solution. A 1.5-g quantity of the nitrite salt[21] of I is dissolved in 40 mL of water. To this yellow solution is added simultaneously 4.0 g of zinc dust and 3.0 g of NaOH, and the solution is stirred vigorously. After a few minutes the solution becomes nearly colorless. At this point 100 mL of water is added, and the mixture is filtered. The residue, which contains the ligand along with unreacted Zn and metallic Au, is washed with several small portions of water and then extracted three times with a total of ~100 mL of chloroform. The filtrate from the reaction mixture is also extracted several times with chloroform. These chloroform phases are washed with water prior to combining them with the chloroform solutions used to extract the residue. The combined chloroform solution is dried with molecular sieves, and the solvent is removed in vacuo to yield a pale yellow crude product in approximately 40% yield. The latter is recrystallized once with benzene and petroleum ether and then again with absolute ethanol. The cream-colored product is washed with petroleum ether and dried in vacuo at 40 °C, mp 226–228 °C (sealed tube) (lit.[8] mp 226–228 °C). Anal. Calcd: C, 67.68; H, 9.76; N, 22.56. Found: C, 68.20; H, 10.08; N, 22.78. The parent ion peak at *m/e* 248 is the most intense peak above *m/e* 100 in the mass spectrum of the product.

Results and Discussion

Amine complexes of Au(III), like those of Pt(IV), are acidic as a result of the high polarizing power of the cation.[9] The pK_a of $Au(NH_3)_4^{3+}$ has been reported to be 7.48.[10] Chelating amines have even lower pK_a values, ranging from ~6.5 for $Au(en)_2^{3+}$ to 2.2 for $[Au(Et_4dien)Cl]^{2+}$.[7,11] Thus $Au(en)_2^{3+}$ has potentially nucleophilic coordinated amides present even at neutral pH.

In an earlier paper[3] we reported that reaction of $[Au(en)_2]Cl_3$ with 2,4-pentanedione in aqueous base leads to two products, depending upon the reaction time. Complex A (see Experimental Section) is formed within a few minutes, whereas the predominant product after 2 h is I. $Au(en)_2^{3+}$ reacts also



I

with other β-diketones to form analogous 14-membered-ring macrocyclic complexes having other substituents. Additional variety in the pattern of substitution is afforded by the ability to isolate intermediates such as A which can then undergo further condensation with a different β-diketone. The macrocyclic complexes listed in Table I were prepared during our efforts to determine the synthetic scope of these condensation reactions.

Macrocyclic complexes structurally analogous to I, but containing divalent first-row transition-metal ions, were reported previously by Holm and co-workers.[8] They prepared the complexes by using the free macrocyclic ligand which they were able to synthesize by several routes not involving transition-metal-ion assistance.[8,12,15] Attempts to prepare complexes of this type by template-condensation reactions of ethylenediamine with coordinated β-ketoamines appear to be unsuccessful unless a carbonyl-containing substituent is present at the γ-carbon of the six-membered chelate rings.[8,12–14]

The conditions necessary to prepare gold(III) macrocyclic complexes I–VIII in good yield depend upon the nature of the substituents R_1 to R_4. Higher temperatures, higher pH, and

Table II. NMR Data for Selected Macrocyclic Gold(III) Complexes

complex	nucleus	solvent	chem shifts[a] and signal assignt[b]
I	^1H[c]	Me_2SO-d_6	CH_3, 2.23; CH_2, 3.83; CH, 5.05
	^{13}C	Me_2SO-d_6	CH_3, 20.9; CH_2, 57.8; CH, 99.3; CN, 159.2
II	^1H	$CDCl_3$	CH_3, 2.19, 2.25; CH_2, 3.60 (m), 3.95 (s); CH, 4.95; Ph, 7.40 (m)
	^{13}C	$CDCl_3$	CH_3, 21.4, 21.7; CH_2, 57.8, 58.4, 59.4; CH, 100.3, 101.3; Ph, 127.2, 129.2, 129.9, 135.8; CN, 159.6, 160.4
V	^1H	Me_2SO-d_6	CH_3, 2.25, 2.37; CH_2, 3.86, 3.93; CH, 5.14, 5.62
	^{19}F[d]	Me_2SO-d_6	CF_3, 100.0; PF_6, 92.47 (d)
VI	^1H	acetone	CH_3, 2.35; CH_2, 4.02, 4.06, 4.11; CH, 5.12 (d, J = 6.8 Hz), 7.46 (d, J = 6.8 Hz)
	^{13}C	Me_2SO-d_6	CH_3, 21.1; CH_2, 58.0, 60.0; CH, 96.4; CN, 149.1, 159.8
VII	^1H	$CDCl_3$	CH_3, 1.24 (d), 2.27; CH, 3.15 (m), 4.95; CH_2, 3.88 (m)
X	^1H	Me_2SO-d_6	CH_3, 2.53, CH_2, 4.24; CH, 5.67; CH=CH, 7.09
	^{13}C	Me_2SO-d_6	CH_3, 20.2, 21.3; CH_2, 58.4; CH, 103.4; C=C, 123.2; CN, 151.2, 159.0
XI[e]	^1H	$CDCl_3$	CH_3, 1.80; CH_2, 3.37; CH, 4.42; NH, 11.45 (center)
	^{13}C	$CDCl_3$	CH_3, 19.7; CH_2, 46.9; CH, 94.6; CN, 160.8

[a] In parts per million relative to tetramethylsilane unless otherwise indicated. [b] s = singlet, d = doublet, m = multiplet. [c] In parts per million relative to sodium 3-(trimethylsilyl)-1-propanesulfonate, DSS. [d] In parts per million upfield of a C_6F_6 reference. [e] Free ligand from complex I.

longer reaction times appear to be needed when bulky substituents are present. The complexes vary in stability; some show remarkable stability to acid and base. Complex I, for example, remains unchanged in 1 M HCl or 1 M NaOH for at least 3 days and shows no apparent decomposition (as determined by NMR) after 2 h in concentrated HCl or 4 M NaOH at 100 °C.

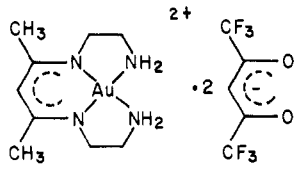
Complexes II–V and VIII were prepared by treating A or B with the appropriate β-diketone as described in the Experimental Section. They may be regarded formally as derivatives of I in which one methyl has been replaced by another substituent. These complexes are readily characterized by their ^1H and ^{13}C NMR spectra (see Table II).

Two geometric isomers, cis ($R_1 = R_4$, $R_2 = R_3$) and trans ($R_1 = R_3$, $R_2 = R_4$), are possible for VI and VII, and both are expected to be formed during the reaction. The overall simplicity of ^1H and ^{13}C spectra for VI and VII led to the conclusion initially that only one isomer is present in the reaction product obtained for each complex. However, closer examination of the ^1H methylene region of VI, using spectrometers operating at different magnetic fields, revealed that the three resonances which initially appeared to be a 1:2:1 triplet are in fact three singlets. Subsequently, the relative intensity of the central component was found to increase with repeated recrystallization of the product. In each spectrum the areas of *all three* signals in the methylene region must be summed in order to account for the eight methylene protons when comparing with areas of all other signals. None of the signals in the methylene region can be attributed to potential impurities such as $Au(en)_2^{3+}$ or B. It is concluded that for VI (and probably also for VII) both isomers are present in approximately a 1:1 mole ratio in the initial product isolated. Subsequent recrystallization increases the proportion of one of these isomers. With the exception of the ^1H methylene region, both ^{13}C and ^1H signals of the two isomers are remarkably coincident. One isomer exhibits two methylene ^1H NMR signals; the other shows only one. No spin coupling is observed in this region. Two methylene signals are expected for *each* isomer on the basis of simple symmetry considerations, excluding spin coupling. Thus unambiguous assignments of these methylene signals to specific isomers are not possible from these data. It should be noted that complex VIII, which has features in common with both isomers of VI and for which four methylene signals might be expected, shows only two methylene signals (with some apparently poorly resolved spin splitting). Attempts to separate the isomers of VI by TLC on silica gel, using eluants covering a wide range of polarities, have not been successful.

Complex IX represents our only successful attempt to introduce substituents into the five-membered rings of the macrocycle. The starting material $Au(pn)_2^{3+}$ was prepared by using racemic pn, and the product obtained is probably a mixture of several diastereomeric macrocyclic species.

Complex X is an oxidation product of I. It was prepared by the method described by Truex and Holm to introduce double bonds into the Ni(II) and Cu(II) analogues of I.[8] The procedure uses trityl tetrafluoroborate to extract a hydride ion which is followed by loss of a proton to generate a double bond. Although the oxidation product cannot clearly be distinguished from I by elemental analysis, the presence of one double bond is demonstrated by the ^1H and ^{13}C NMR spectra of X (see Table II). Attempts to oxidize I to the fully conjugated, 16π antiaromatic system containing a double bond in each five-membered ring were unsuccessful when excess trityl tetrafluoroborate and methods described previously[8] were used. This was accomplished previously for Ni(II) and Cu(II) complexes analogous to I by Truex and Holm,[8] but the Ni(II) and Cu(II) analogues of X were not isolated.

In an attempt to prepare a macrocyclic complex having $R_1 = R_2 = CH_3$, $R_3 = R_4 = CF_3$, we treated the tetradentate complex A with 1,1,1,5,5,5-hexafluoropentane-2,4-dione as described in the Experimental Section. Elemental analyses of the yellow product, however, were inconsistent with that expected for the macrocyclic complex. Instead the analyses (see Experimental Section) agree with formulation C.



C

Proton NMR spectra of C in Me_2SO or acetone solutions show broad signals in the range expected for NH's. These signals are absent in spectra of all the macrocyclic complexes. Furthermore, in spite of the differences in anions, proton NMR signals of C in Me_2SO closely match those of the iodide salt of A (chemical shifts of the latter given in parentheses): CH_3, 2.27 (2.30); CH_2, triplets at 3.08 and 3.83 (triplets at 3.13 and 3.87); CH, 5.12 (5.23) ppm relative to Me_4Si. The proton signal at 5.37 ppm, assigned to the $hfac^-$ moiety in C, does not closely match the corresponding signal at 5.90 ppm of Hhfac in Me_2SO to which some triethylamine is added. It is of interest to note here that other investigators have found Hhfac and Htfac tend to form uncoordinated anions under certain conditions, and the methine proton NMR signals of the anion are shifted as much as 0.7 ppm to high field.[16–18]

The ^{19}F NMR spectrum of C shows a single resonance at 86.6 ppm relative to C_6F_6 in Me_2SO solution. Hhfac in Me_2SO (with or without triethylamine) gives a signal at 86.7 ppm under the same conditions. However in macrocycle V, the CF_3 resonance appears at 100.0 ppm. This is also con-

sistent with the proposed nonmacrocyclic structure for C.

The ^{13}C NMR spectrum of C in acetone solution compares favorably with the spectrum of the iodide salt of A in Me_2SO solution (chemical shifts of the latter in parentheses): CH_3, 21.0 (20.9); CH_2, 49.0 and 60.8 (48.3 and 59.4); CH, 100.7 (99.4); CN, 159.6 (158.2) ppm relative to Me_4Si. Signals at 85.6 (CH) and 174.7 (CO) ppm attributable to the $hfac^-$ moiety compare favorably with signals at 85.4 and 172.8 ppm for Hhfac in acetone with added triethylamine.

Infrared spectra of C show a band at 1650 cm^{-1} assigned to a carbonyl stretch. This band is also found for Hhfac but not for any of the macrocyclic complexes including V. Mass spectra of C show peaks at m/e 208 and 207, corresponding to ions of Hhfac and hfac, respectively. Another peak at m/e 380 is attributed to the cation. Final confirmation for formulation C involved treating C with pentane-2,4-dione. A yellow reaction product was obtained and precipitated as the iodide salt. This proved to be the iodide salt of complex I (NMR).

Thus it appears that Hhfac does not undergo Schiff base condensation with A as do the other β-diketones reported herein. The $hfac^-$ may interact with the cation in some manner other than purely ionic, however, since the proton signal of the $hfac^-$ moiety in C occurs at 0.5 ppm higher field than in free Hhfac.[19] Possibly the interaction involves hydrogen bonding between cation and anion.

Attempts to prepare a macrocyclic complex having $R_1 = R_2 = R_3 = R_4 = CF_3$ by treating $Au(en)_2^{3+}$ with Hhfac were also unsuccessful. The pale yellow material isolated gave an elemental analysis (see Experimental Section) consistent with the formulation $Au(en)_2^{3+}\cdot 3hfac^-$, hereafter designated as product D. This formulation is substantiated by ^1H, ^{19}F, and ^{13}C NMR spectra, mass spectra, and infrared spectra. Product D shows peaks in the mass spectrum at m/e 207 and 208, an IR band at 1650 cm^{-1}, and a single ^{19}F NMR signal at 86.7 ppm relative to C_6F_6 in Me_2SO solution, all of which are consistent with the presence of unreacted $hfac^-$ (see above).

A signal at 50.0 ppm relative to Me_4Si in the ^{13}C NMR spectrum of D in Me_2SO solution is assigned to the methylene carbons of the cation, since $[Au(en)_2]Cl_3$ in D_2O solution has a corresponding resonance at 50.6 ppm. A ^{13}C signal at 83.9 ppm for D is attributed to the CH of the $hfac^-$ moiety and may be compared to the 85.4-ppm signal of Hhfac in Me_2SO with added triethylamine. The quartets arising from the CF_3 and CO carbons of $hfac^-$ in D occur at 118.4 and 172.4 ppm, respectively.

As in the case of product C, broad signals arising from NH's are seen in the proton NMR spectrum of D. Also, as is the case for C and other examples of "outer-sphere" β-diketonate anions,[16-18] the methylene proton resonance signal of the anion is shifted to high field (5.4 ppm). This implies some interaction of $hfac^-$ in D with the cation as in the case of product C.

Additional support for the proposed structure for D comes from the fact that D reacts readily with pentane-2,4-dione to form the $hfac^-$ salt of macrocycle I (identified by proton NMR). This salt can be converted to the corresponding PF_6^- salt which gives a satisfactory elemental analysis.

The free macrocyclic ligand from complex I, originally synthesized by Holm and co-workers by other methods,[8,12,15] can readily be obtained by reduction of the Au(III) ion in I with powdered Zn in basic solution. Elemental analyses and the melting point for the product obtained agree well with those reported earlier[8] (see Experimental Section). Treatment of the product with copper(II) acetate[8] results in formation of the emerald green Cu(II) macrocycle.[22] Thus the template reaction of 2,4-pentanedione with $Au(en)_2^{3+}$, followed by removal of gold, provides a facile means of synthesizing this macrocyclic ligand for use with other metal ions.

Additional Attempted Condensation Reactions Using $Au(en)_2^{3+}$. When $Au(en)_2^{3+}$ or complex A is treated with biacetyl or with 2,2,6,6-tetramethylheptane-3,5-dione in aqueous base, there is no evidence that a condensation reaction takes place. Even under conditions of higher pH, higher temperatures, and longer reaction times, only starting materials or decomposition products are obtained upon workup of the reaction mixture. This was also found to be the case for $Pt(NH_3)_6^{4+}$, as reported previously.[3] Also, in our hands, attempts to condense $Au(en)_2^{3+}$ with biguanide, 1,1,3,3-tetramethoxypropane, and acetone failed to result in any isolable condensation products.

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Registry No. I, 65681-95-0; I, nitrite salt, 71393-39-0; II, 71393-41-4; III, 71393-43-6; IV, 71393-45-8; V, 71393-47-0; VI (trans isomer), 71393-49-2; VI (cis isomer), 71393-51-6; VII (trans isomer), 71393-53-8; VII (cis isomer), 71393-55-0; VIII, 71393-57-2; IX, 71382-93-9; X, 71393-59-4; XI, 71382-91-7; A, 71393-61-8; B, 71393-63-0; $[Au(en)_2](hfac)_3$, 71393-64-1; [*N*,*N*′-bis(2-aminoethyl)-2,4-pentanediiminato]gold(III) bis(hexafluoropentanedionate), 71393-65-2; $Au(en)_2Cl_3$, 15278-22-5; $[Au(pn)_2]Cl_3$, 17653-70-2; 2,4-pentanedione, 123-54-6; 1-phenyl-1,3-butanedione, 93-91-4; 5-methyl-2,4-hexanedione, 7307-03-1; 5,5-dimethyl-2,4-hexanedione, 7307-04-2; 1,1,1-trifluoro-2,4-pentanedione, 367-57-7; 3-oxobutanal, 625-34-3.

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(22) Anal. Calcd: C, 54.26; H, 7.16; N, 18.08. Found: C, 54.13; H, 7.09; N, 18.20. Mp 297.5–298 °C (sealed tube) (lit.[8] mp 298–299 °C).