CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOT, ISRAEL

Chiral d^8 Metal Ion Coordination Compounds. The Preparation of *d*-3-Trifluoroacetylcamphorato Complexes of Rhodium, Palladium, and Nickel

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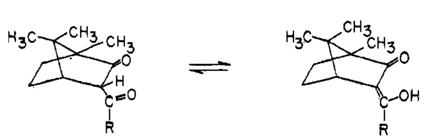
Received July 7, 1971

Chiral *d*-3-trifluoroacetylcamphorato chelates of Rh(I), Pd(II), and Ni(II) are obtained by a mild homogeneous exchange reaction with barium(II) *d*-bis(3-trifluoroacetylcamphorate) in organic solvents in high yields. The barium chelate is prepared from *d*-3-bromocamphor and ethyl trifluoroacetate in a one-step Grignard reaction without isolation of the free ligand. Access to this class of compounds is thus considerably facilitated.

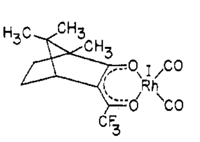
Introduction

Stable metal chelates of 3-acylcamphor compounds[2-6]



I I

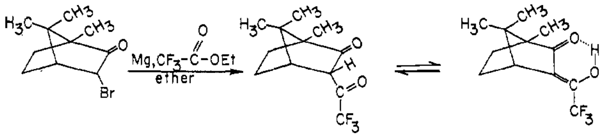
have been prepared more than half a century ago.[2,5,7] However, the theoretical and practical importance of this class of chiral compounds, containing the chelating unit of the enolizable β-diketone in a rigid asymmetric environment of known absolute configuration,[8] has only recently been recognized. The occurrence of some stereoselectivity in the formation of diastereomeric tris(bidentate) chelates of trivalent Cr, Co, V, and Rh ions with I (R = H, CH_3) has been demonstrated previously and subsequently elucidated by ORD, pmr, and X-ray studies.[9] The ability of rare earth metal ion tris chelates of I (R = CH_3, CF_3) to expand their coordination number has been used for the determination of association constants with lone electron pair containing organic compounds by glc.[6] The potential interest of this approach to the resolution of racemic solutes with chiral coordination compounds, based on diastereomeric interaction between solute and solution, has been recognized.[6] Consequently, the Eu(III) tris chelate (R = *tert*-C_4H_9) has very recently been recommended as a chiral pmr shift reagent for enantiomeric substrates.[4] Finally, as reported from this laboratory,[10] the affinity of d^8 transition metal ions toward two-π-electron systems has been applied to selective olefin separations with square-planar dicarbonylrhodium(I)-β-diketone chelates. Owing to its stability and due to the electron-withdrawing properties of the trifluoromethyl group the chelate IIa gave the most satisfactory results. Because of the current interest in these compounds, the synthesis of *d*-3-trifluoroacetylcamphorato chelates has been investigated, and a very convenient method has been developed.



IIa

Results

d-3-Trifluoroacetylcamphor had first been prepared by Feibush, Sievers, and Springer[6] by using the procedure of Malmgren[5a]



The isolation of the β-diketone, however, is complicated by the presence of camphor formed as by-product.

We previously found that the sodium salt of *d*-3-trifluoroacetylcamphor, obtained with sodium metal in benzene and recrystallized from benzene–heptane, easily reacts with transition metal halides such as $Pd(C_6H_5CN)_2Cl_2$ in aprotic solvents to give the corresponding chelate

$$Pd(C_6H_5CN)_2Cl_2 + 2Na(tfacCam)^{11} \longrightarrow Pd(tfacCam)_2 + 2NaCl + 2C_6H_5CN$$

This reaction, however, has some experimental disadvantages and a more straightforward route was sought.

In the preparation of the 3-acylcamphor compounds (R = H, CH_3) formation of the sodium salt in aqueous solution has been advantageously used for separation from by-products.[2,5] Attempts to utilize this step directly for chelate formation, without isolation of the 3-acylcamphor, failed in the case of 3-trifluoroacetylcamphor, since its sodium salt tends to decompose in aqueous solution. The barium salt, however, which is insoluble in water and ether, is readily formed in excellent yields. The ligand can thus be conveniently trapped from the reaction mixture with barium ions and at the same time separated from water and ether-

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[3] M. O. Forster, *Proc. Chem. Soc., London*, **17**, 167, 257 (1901).

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[5] (a) S. M. Malmgren, *Ber.*, **36**, 2608 (1903); (b) J. W. Brühl, *ibid.*, **37**, 746, 761 (1904).

[6] (a) B. Feibush, R. E. Sievers, and C. S. Springer, Jr., paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; (b) B. Feibush, M. F. R. Richardson, R. E. Sievers, and C. S. Springer, Jr., submitted for publication.

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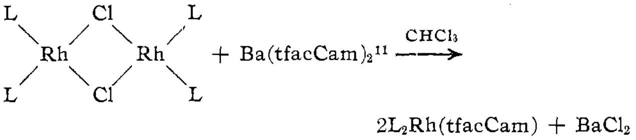
[11] tfacCam = *d*-3-trifluoroacetylcamphorate.

soluble by-products. In addition, the recrystallized barium bis chelate (from ethanol) is fairly soluble in chloroform and undergoes a clean and almost quantitative homogeneous displacement reaction with organometallic halides in this solvent, *e.g.*

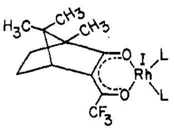


$$[L_2RhCl]_2 + Ba(tfacCam)_2{}^{11} \xrightarrow{CHCl_3} 2L_2Rh(tfacCam) + BaCl_2$$

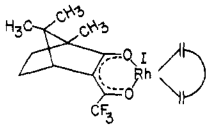
The driving force of this reaction is the formation of $BaCl_2$, which can be removed by filtration and detected with sulfate ion.

The advantage of this method is evident from the fact that the free ligand itself, which is accessible only with difficulty, need not be isolated, and it furthermore avoids conditions which might decompose or racemize the desired organometallic complex, such as basic or acidic aqueous media.

The following series of chiral organometallic rhodium(I) square-planar chelates of 3-trifluoroacetylcamphor has been prepared by the barium method



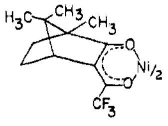
IIa, L = CO
b, L = C_2H_4



IIIa, diolefin = 1,5-cyclooctadiene (COD)
b, diolefin = *endo*-dicylopentadiene (DCP)
c, diolefin = norbornadiene (NOR)

All complexes are air-stable and soluble in organic solvents and readily undergo vacuum sublimation without serious decomposition at temperatures between 60 and 130°. The presence of the chelated ring is evidenced by ir bands between 1300 and 1650 cm^{-1}.[12] The structure of the complexes is further supported by their nmr and mass spectra and is closely related to that of the corresponding acac species.[13] It should be noted, however, that no mass peak due to the ligand anion, $(tfacCam)^-$, appears in the mass spectra. The mass 248 of the ligand itself, HtfacCam, formed by hydrogen abstraction, is present instead. Optical rotations for chelates obtained from optically pure *d*-3-bromocamphor are listed in Table I. The value for IIIb is dependent on the method of isolation employed. Since chiral *endo*-dicyclopentadiene, complexed with Rh^I-(tfacCam), gives rise to diastereoisomerism, partial resolution may occur during crystallization. Application of the chiral chelates II and III for the study of asymmetric induction in catalytic olefin reactions and for detection of diastereoisomerism, upon complexation with chiral olefins, by glc, ^1H nmr, and ^{19}F nmr, is currently being investigated.

The barium method may also be applied to other syntheses. Thus, $Pd(C_6H_5CN)_2Cl_2$ reacts with $Ba(tfacCam)_2$ in chloroform to give $Pd(tfacCam)_2$ (IV), and $NiCl_2 \cdot 6H_2O$ reacts with $Ba(tfacCam)_2$ in ethanol to give $Ni(tfacCam)_2$ (V). The nickel chelate is monomeric in dimethylformamide and soluble in all common organic solvents. Its properties are essentially different from those of trimeric nickel(II) bis(3-formylcamphorate), which is amorphous and insoluble.[12] Lone-pair substrates, preferentially cyclic ethers, complex with V as established by glc.[14] Since solutions of the chelate are in addition paramagnetic, pmr shifts (upfield) are observed. Its application as a cheap chiral shift reagent is however limited, because serious line broadening occurs, due to the unfavorable electronic relaxation time of the nickel ion involved. The stereochemistry of the chelate has not been investigated yet.



V

Experimental Section

General Information.—Mass spectra were recorded with an Atlas CH 4 instrument applying 70-eV electron energy. Optical rotations were measured at 23° on a Perkin-Elmer 141 polarimeter; 10^{-2} *M* chelate solutions in chloroform or acetone were used throughout. Melting points are uncorrected. Molecular weight determinations and elemental analyses were carried out by the Microanalytical Laboratories of the Weizmann Institute and Dornis & Kolbe, Mülheim, West Germany.

Materials.—*d*-3-Bromocamphor was purchased from Aldrich Co. and ethyl trifluoroacetate was obtained from Fluka Co. Rhodium chloride hydrate and $Rh_2(CO)_4Cl_2$ were obtained from Johnson, Matthey Ltd. All other reagents and solvents were of analytical grade and obtained from local stores.

Preparation of Barium(II) *d*-Bis(3-trifluoroacetylcamphorate), $Ba(tfacCam)_2$.—The mixture of 23.1 g (0.1 mol) of *d*-3-bromocamphor (dried over P_2O_5), 14.2 g (0.1 mol) of ethyl trifluoroacetate, and 2.3 g (0.1 mol) magnesium in 250 ml of dry ether was refluxed for 90 min. The clear solution was then poured into 100 ml of 10% hydrochloric acid solution. The ether layer was separated and shaken with 100 ml of 5% sodium hydroxide solution. The ether and alkaline water phases were immediately treated simultaneously with 100 ml of 10% barium chloride solution, whereby a voluminous white precipitate was formed during shaking. This was collected by suction and washed with ether, followed by iron-free water. Washing with water was continued until the filtrate was alkali and barium ion free. The product was air-dried and Soxhlet-extracted with 250 ml of ethanol. After storing the extract at 0° for 8 hr 21.5 g (72%) of $Ba(tfacCam)_2$ was isolated as a white amorphous solid with mp 285°, soluble in acetone. The crude product could be used directly for exchange reactions without further purification; $[\alpha]^{23}{}_D$ +180° (10^{-2} *M* in acetone).

Preparation of the Rhodium(I) *d*-3-Trifluoroacetylcamphorato Complexes IIa, b and IIIa–c.—A 63-mg sample (0.1 mmol) of $Ba(tfacCam)_2$ was dissolved in 30 ml of boiling chloroform. A 0.1-mmol amount of the corresponding ligand–rhodium(I)–chloride dimer—$(C_2H_4)_4Rh_2Cl_2$,[15a] $(CO)_4Rh_2Cl_2$,[15b] $(COD)_2Rh_2Cl_2$,[13a] $(DCP)_2Rh_2Cl_2$,[13a] and $(NOR)_2Rh_2Cl_2$,[15c] dissolved in 5 ml chloroform—was filtered into the solution (25°). After 90 min the reaction mixture was filtered from the barium chloride formed, and the solvent was removed *in vacuo*. The yellow residue is taken up in *n*-pentane, and the yellow chelates (see Table I) were obtained either by recrystallization at −75° or by allowing the pentane to evaporate slowly at room temperature and atmospheric pressure. Further purification may be accomplished by chromatography on inactive alumina with chloroform and/or sublimation between 60 and 130° with a high vacuum.

Preparation of Palladium(II) *d*-Bis(3-trifluoroacetylcamphorate), $Pd(tfacCam)_2$.—A 632-mg sample (1 mmol) of $Ba(tfacCam)_2$ was suspended in 150 ml of chloroform and 384 mg (1 mmol) of

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(12) R. L. Lintvedt and A. M. Fatta, *Inorg. Chem.*, **7**, 2489 (1968).

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TABLE I

ANALYTICAL DATA OF COMPLEXES IIa, b AND IIIa–c

Complex	Mp, °C	Empirical formula	Mol wt Calcd	Mol wt Mass spec[c]	% C Calcd	% C Found	% H Calcd	% H Found	Optical rot.,[a] deg	Yield, %
$(CO)_2Rh(tfacCam)$ (IIa)	131	$RhC_{14}H_{14}F_3O_4$	406.162	406	41.40	42.04	3.47	3.50	+106	92
$(C_2H_4)_2Rh(tfacCam)$ (IIb)	145 dec	$RhC_{16}H_{22}F_3O_2$	406.246	406	47.30	48.18	5.46	5.58	+102	75
(COD)Rh(tfacCam) (IIIa)	163	$RhC_{20}H_{26}F_3O_2$	458.318	458	52.41	52.51	5.72	5.59	+80	Quant
(DCP)Rh(tfacCam) (IIIb)	130–142[b]	$RhC_{22}H_{26}F_3O_2$	482.338	482	54.78	55.07	5.43	5.56	+87[b]	Quant
(NOR)Rh(tfacCam) (IIIc)	87	$RhC_{19}H_{22}F_3O_2$	442.276	442	51.59	52.28	5.01	5.29	+82	Quant

[a] Complex solutions 10^{-2} *M* in chloroform (23°). [b] Sublimed sample. [c] Molecular ion peak.

$Pd(C_6H_5CN)_2Cl_2$[16] was added. The mixture was refluxed for 4 hr, stirred for another 8 hr at room temperature, and then filtered. The solvent was evaporated *in vacuo* and the residue was extracted with boiling *n*-hexane. The hexane solution was filtered, concentrated, and left at 0° for a prolonged period, whereby large red-brown crystals of the palladium chelate were formed; mp 237° dec; yield 77%; $[\alpha]^{23}D$ +182° (10^{-2} *M* in chloroform). *Anal.* Calcd for $PdC_{24}H_{28}F_6O_4$: C, 47.95; H, 4.69. Found: C, 48.32; H, 4.72.

Preparation of Nickel(II) *d*-Bis(3-trifluoroacetylcamphorate), $Ni(tfacCam)_2$.—A 632-mg sample (1 mmol) of $Ba(tfacCam)_2$ was dissolved in 150 ml of boiling ethanol, and 238 mg (1 mmol) of $NiCl_2 \cdot 6H_2O$, dissolved in 25 ml of ethanol, was filtered in. The mixture was stirred for 10 min at 60° and then the barium chloride formed was filtered off. The solvent was removed *in vacuo*, the residue was taken up in 15 ml of *n*-hexane, and the extract was filtered. The hexane was removed *in vacuo* and the green residue was dissolved in 5 ml of ethanol. The ethanol was allowed to evaporate slowly, whereby large green crystals were formed. The crystals are efflorescent and should therefore be stored under ethanol. The green chelate had no melting point up to 300° but loses water at 100°. It can be completely dehydrated in an oven at 100° and high vacuum and is very soluble in common organic solvents; yield, quantitative; $[\alpha]^{23}D$ +215° (10^{-2} *M* in chloroform). *Anal.* Calcd for $NiC_{24}H_{28}F_6O_4$: C, 52.11; H, 5.10; Ni, 10.61; mol wt 553. Found: C, 51.37; H, 5.29; Ni, 10.58; mol wt 562 (vaporimetric in DMF).

Acknowledgments.—The author is indebted to Professor E. Gil-Av and Dr. B. Feibush for their interest in this work, to the Stiftung Volkswagen for a grant, and to Johnson, Matthey Ltd. for a loan of rhodium.

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Properties of Palladium(II) Complexes of Peptides and Histidine in Basic Solutions[1]

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Received May 26, 1971

By comparison with properties of a related series of ligands, the change in net circular dichroism (CD) sign from negative to positive occurring upon addition of base with p*K* = 11.7 in the quadridentate Pd(II) complex of GlyGly-L-Ala is identified as replacement of bound carboxylate by hydroxide in the tetragonal coordination plane. A similar transformation occurs in the Cu(II) complex with p*K* = 13.1. Instead of the usual negative, a net positive CD is observed for several tetragonal peptide complexes where the carboxyl terminal L-alanyl residue is bound only *via* the deprotonated amide nitrogen with an unbound carboxylate group. Nmr chemical shift nonequivalence of glycyl methylene protons observed in the zwitterion form of L-AlaGly does not occur in the terdentate Pd(II) complex but appears upon displacement of the bound carboxylate group by hydroxide and in $Pd(en)(AlaGly)^0$, where there are four nitrogen donor atoms about Pd(II). Absorption and CD spectra are reported for complexes of Pd(en)(L ligand) where the optically active ligand possesses two nitrogen donors. Comparisons from among the compounds permit assignment of the transformation occurring upon addition of base to $Pd(en)(L\text{-}His)^+$ (His = histidine) with p*K* = 10.83 to ionization of the pyrrole hydrogen.

Introduction

Tetragonal transition metal ions form complexes with peptides the structures of which are well understood. For example, after the addition of 3 equiv of base to a solution containing equimolar amounts of $PdCl_4^{2-}$ and tripeptide, an end point is reached by pH 6. At this point the ligand is tetradentate, being bound in the coordination plane by one amino, two deprotonated amide, and one carboxylate oxygen donor atoms to yield a complex of net unit negative charge. The complex exhibits an absorption maximum at 300 nm with $\epsilon \sim 1300$, and the circular dichroism (CD) values of a variety of peptide complexes of Pd(II) have been reported.[2] Ni(II) and Cu(II) form similar tetragonal complexes.[3,4] In this paper we study the behavior of tripeptide complexes of these transition metal ions upon the addition of a fourth equivalent of base. There has been uncertainty concerning the structures of the complexes under these conditions. Absorption, CD, and proton magnetic resonance (pmr) spectra of carefully chosen complexes are utilized to define the nature of the transformations taking place. The Pd(II) com-

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(1) This paper is abstracted from the Ph.D. Thesis (1971) of T. P. Pitner, who was holder of a NASA predoctoral fellowship. The research was supported by a grant from the National Science Foundation.

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