

Table I. Major Ions Observed in Mass Spectrum of (TPP)RhCOOC₂H₅

<i>m/e</i>	Ion	Rel intens
788	(TPP)RhCOOC ₂ H ₅ ⁺	28
715	(TPP)Rh ⁺	100
614	(TPP)H ₂ ⁺	29
357.5	(TPP)Rh ²⁺	33
316.5-318.5	((TPP)Rh - C ₆ H ₅ - XH) ²⁺	39-15
279.5	((TPP)Rh - 2(C ₆ H ₅) - 2H) ²⁺	23
44	CO ₂ ⁺	43
32	O ₂ ⁺	0
28	CO ⁺ + N ₂ ⁺	28

a separate experiment, the gaseous pyrolysis products of (TPP)RhCOOC₂H₅ *in vacuo* were examined and the evolution of CO₂ was not observed until the sample temperatures reached 250°, indicating the stability of the Rh-C bond in this compound. Above 250° the solid sample generates CO₂ rapidly.

Alkoxy carbonyl complexes universally react with strong acids to re-form the alcohol and the metal carbonyl.³ In fact, that reaction is often considered diagnostic for alkoxy carbonyls. This reaction is observed for (TPP)RhCOOC₂H₅ in dry organic solvents. In CHCl₃, gaseous HCl reacts as (TPP)RhCOOC₂H₅ + HCl → Cl(TPP)RhCO + C₂H₅OH

However, when aqueous concentrated HCl is added to a THF solution of (TPP)RhCOOC₂H₅, the porphine product is not the metal carbonyl, but rather H₂O(TPP)RhCl.

Inasmuch as carbamoyl complexes can usually be derived from metal carbonyls which produce stable alkoxy carbonyls,³ it is not surprising that the reaction of Cl(TPP)RhCO with LiN(C₂H₅)₂ in HN(C₂H₅)₂ produced a rhodium porphine with a carbonyl absorption at 1697 cm⁻¹, presumably (TPP)RhCON(C₂H₅)₂. That compound also reacts with dry HCl to form Cl(TPP)RhCO in analogy to the reaction of the alkoxy carbonyl. No reaction was observed between Cl(TPP)RhCO and NaSC₂H₅ in a mercaptan solution.

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Diastereomer Separation and Configurational Assignments for a Chiral Rhodium(III) β-Diketonate Complex

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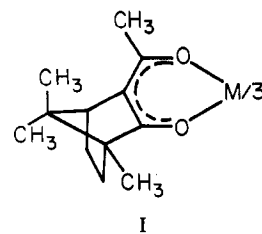
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Recent publications from this laboratory^{1,2} and others³ have described the separation and identification of the four possible diastereomers each of tris[(+)-3-acetylcamphorato]-cobalt(III), -chromium(III), and -ruthenium(III), abbreviated M((+)atc)₃, I. Electrolytic oxidation and reduction of the

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(3) C. S. Springer, Jr., R. E. Sievers, and B. Feibush, *Inorg. Chem.*, **10**, 1242 (1971).



Ru(III) diastereomers were found to proceed with retention of configuration, thereby permitting CD studies of the individual Ru(IV) and Ru(II) diastereomers.⁴ One of the primary objectives in examining this series of complexes has been to establish Cotton effect-configuration relationships for tris(β-diketonate) complexes of a variety of transition metal ions. Absolute configurations of all diastereomers of the Co(III), Cr(III), and Ru(II), -(III), and -(IV) complexes have been established by a combination of methods including nmr, CD, X-ray powder diffraction,¹⁻⁴ and a single-crystal X-ray structure determination⁵ of one member of the series. Herein we report isolation and identification of the four diastereomers of the corresponding Rh(III) complex, Rh((+)-atc)₃ (I, M = Rh).

Experimental Section

Rh((+)atc)₃ was prepared by modification of a procedure used to prepare tris(acetylacetonato)rhodium(III).⁶ In approximately 15 ml of (+)-3-acetylcamphor was suspended 0.5 g of rhodium trichloride hydrate (Alfa Inorganics) and 0.3 g of KOH. The mixture was heated at 80° for around 20 hr; then the excess ligand was removed by distillation *in vacuo*. The thick brown material which remained was chromatographed on a silica gel column (30 cm × 3 cm, Mallinckrodt Silic AR CC4) using benzene. The first predominant band (yellow-orange) contained the desired product. After removing benzene, the product was recrystallized by dissolving it in a minimum amount of ethanol and then adding this solution dropwise to a 1% aqueous Na₂CO₃ solution. The product was then adsorbed onto a preparative layer silica gel plate (Brinkmann Instruments, 20 × 20 cm, 2 mm thick) and developed with chloroform. Four pale yellow bands (most easily seen under uv lamp) labeled A-D in decreasing order of elution separated after three developments. Samples were removed from the chromatographic plates using methods described previously.^{1,2} Further chromatography of isomers A and D (from chromatographic bands A and D, respectively) was necessary to obtain them free of traces of isomers B and C. No quantitative attempt was made to determine the relative diastereomer abundances.

Physical measurements were carried out using methods and instruments described previously.^{1,2} Photoisomerization attempts were made using a 15-lamp RPR "merry-go-round" device and a high-intensity preparative reactor.

Results and Discussion

The multiplicity of proton nmr signals arising from the 3-acetylmethyl group (τ ~7.9) in diastereomers A and B clearly demonstrates that these have a trans arrangement of ligands (C₁ symmetry). The single pmr signal observed in this region for diastereomers C and D is consistent with a cis geometry (C₃ symmetry). CD spectra in cyclohexane solution (Figure 1) reveal that A and B have opposite helicities; the same is true of the two cis isomers, C and D. X-Ray powder patterns of the four diastereomers (Table I) were taken in hopes that they would match those of isostructural diastereomers of Co((+)atc)₃, Cr((+)atc)₃, or Ru((+)atc)₃. The match between the interplanar spacings of isomer A of Rh((+)atc)₃ and those¹ of Δ-*trans*-Co((+)atc)₃ and Δ-*trans*-Cr((+)atc)₃ is deemed satisfactory. Also a fair match between the pat-

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(6) J. G. Brushmiller, private communication.

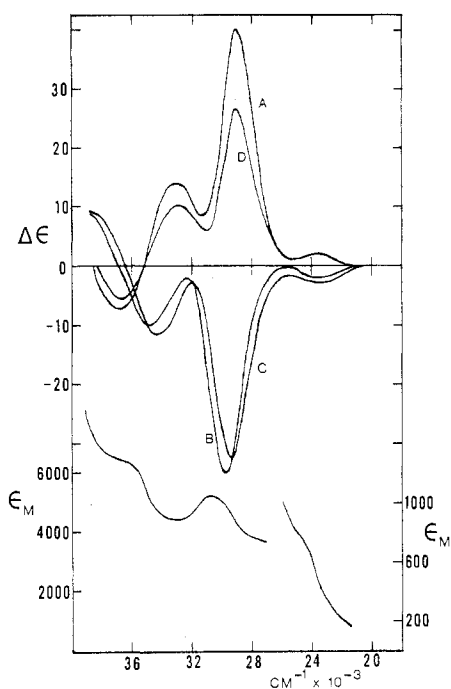


Figure 1. CD spectra of $\text{Rh}(\text{atac})_3$ diastereomers in cyclohexane solution. Letters in the figure correspond to those in the text. The absorption spectrum of isomer B was done in cyclohexane solution.

Table I. X-Ray Powder Diffraction Data for $\text{Rh}(+)\text{atac}_3$ Diastereomers

Isomer	Interplanar spacings, Å
A	12.31 vs, 9.48 mw, 8.29 s, 6.90 s, 6.52 s, 6.45 s, 5.87 m, 5.48 mw, 5.07 w, 4.77 w, 4.50 ms
B	12.23 vs, 10.09 ms, 8.99 ms, 8.34 s, 7.88 s, 7.39 w, 6.96 s, 6.55 m, 6.15 s, 5.68 mw, 5.47 ms, 5.14 w, 4.93 w, 4.72 w, 4.49 s
C	13.33 ms, 11.48 w, 9.50 s, 8.89 mw, 8.16 mw, 7.48 mw, 6.63 m, b, 5.94 s, 5.60 m, 5.32 m, 4.43 mw
D	15.56 w, 13.64 m, 12.20 vs, b, 11.38 m, 10.63 w, 9.70 ms, 8.66 s, b, 7.98 vs, b, 7.60 ms, 6.83 vs, b, 6.36 vs, 6.16 s, 5.80 ms, 5.56 ms, 5.30 w, 5.16 w, 4.83 ms, 4.65 ms

terns of isomer C and those of $\Lambda\text{-cis-Co}(+)\text{atac}_3$ and $\Lambda\text{-cis-Cr}(+)\text{atac}_3$ is found. If it can be assumed that isomorphous diastereomers have identical absolute configurations, then the following configurational assignments for the diastereomers of $\text{Rh}(+)\text{atac}_3$ are consistent with the nmr, CD, and X-ray data: A, $\Delta\text{-trans-Rh}(+)\text{atac}_3$; B, $\Lambda\text{-trans-Rh}(+)\text{atac}_3$; C, $\Lambda\text{-cis-Rh}(+)\text{atac}_3$; D, $\Delta\text{-cis-Rh}(+)\text{atac}_3$. These assignments are in line with the observation discussed earlier² that the order of the tlc elution of diastereomers in the series $\text{M}(+)\text{atac}_3$ is $\Delta\text{-trans} > \Lambda\text{-trans} > \Lambda\text{-cis} > \Delta\text{-cis}$ and is independent of the eluting solvents used.

Ligand field absorption bands are largely obscured in these $\text{Rh}(\text{III})$ diastereomers. The shoulder at ca. $25,000\text{ cm}^{-1}$ (Figure 1) may arise from a d-d transition, and a weak CD is associated with this band. CD bands in the ultraviolet region clearly show the relative helicities of the four diastereomers. In principle, absolute configurations could be deduced from signs of Cotton effects in this region using exciton theory;^{7,8} however criteria⁷ for use of this method do not appear to be satisfied for $\text{Rh}(+)\text{atac}_3$. On an empirical basis the CD spectra shown in Figure 1 should serve as models to which CD

spectra of other chiral tris(β -diketonato)rhodium(III) complexes may be compared for the purpose of making configurational assignments. For example, Dunlop, *et al.*,⁹ obtained two of the four possible diastereomers of tris[(+)-hydroxymethylenecamphorato]rhodium(III). These were assigned the $\Delta\text{-trans}$ and $\Lambda\text{-trans}$ configurations on the basis of pmr and steric arguments. The isomer assigned the Λ configuration shows a negative Cotton effect in the ORD spectrum around $28,000\text{ cm}^{-1}$, in agreement with our results for Λ isomers of $\text{Rh}(+)\text{atac}_3$. Also Fay, *et al.*,¹⁰ observed a negative Cotton effect in the low-energy region of the ORD spectrum of the first eluted fraction during a partial resolution of tris(acetylacetonato)rhodium(III). The results presented in this paper indicate that the more abundant enantiomer in this first eluted fraction has the Λ configuration.

A recent report¹¹ on the reversible photoisomerization of $[(\text{-})_{546}\text{-Rh}^{\text{III}}\text{-D}(\text{-})\text{-PDTA}]^-$ prompted us to test the photolability of $\text{Rh}(+)\text{atac}_3$. Solutions of isomer A (10^{-3} M) in cyclohexane were irradiated for periods of 2–3.5 hr at 2537, 3000, and 3500 Å. No isomerization detectable by tlc occurred, however. Irradiation of isomer A by means of a high-intensity preparative photochemical reactor resulted in apparent decomposition of the complex. Also no thermal isomerization could be detected when toluene solutions of diastereomers A and D were maintained at $100\text{--}120^\circ$ for periods up to 1 week.

Registry No. A, 42744-93-4; B, 42744-94-5; C, 42744-95-6; D, 42719-80-2.

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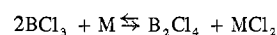
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A Novel Vapor Pump Applied to the Synthesis of Diboron Tetrachloride

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To date the preferred preparation of B_2Cl_4 seems to be electrochemical wherein chlorine is excited from BCl_3 by means of an electrical discharge and scavenged by reaction with the electrode material resulting in the net reaction



This preparation as originally described by Stock, Brandt, and Fischer¹ used zinc electrodes immersed in liquid BCl_3 . It was then improved by Wartik, Moore, and Schlesinger,² who described a high-voltage ac discharge between mercury electrodes in the presence of BCl_3 vapor. The uses of micro-

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