Acknowledgments. The authors wish to acknowledge Mr. K. P. Wagner for aid in obtaining pure $Mn(CO)_5CF_3$. This work was supported by the National Science Foundation (Grant GP-27636). D. L. L. acknowledges an NDEA Title IV fellowship (Grant 69-03546.1).

Registry No. $Mn(CO)_5CF_3$, 13601-14-4; $Mn(CO)_5CH_3$, 13601-24-6.

Contribution from the Department of Chemistry, The Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

Preparation and Properties of Ethoxycarbonyl(tetraphenylporphinato)rhodium(III)

Irwin A. Cohen* and Ben C. Chow

Received May 2, 1973

Recent interest in unusual rhodium[1,2] porphyrins and the possible applications of these compounds as model systems for vitamin B_{12} have prompted us to report the synthesis of a novel porphine containing a rhodium-bound alkoxycarbonyl group.

The general area of alkoxycarbonyl complexes of transition metals has recently been reviewed by Angelici[3] and he has presented many examples (including rhodium complexes) of the general reaction

$$L_nMCO^{z+} + OR^- \rightarrow L_nMCOOR^{(z-1)+}$$

Angelici has also pointed out that the reactivity of a metal-bound CO in the analogous reaction with amines can often be correlated with the force constant or stretching frequency of the CO in question. Generally, CO groups exhibiting absorptions below 2000 cm^{-1} are not reactive. Inasmuch as Cl(TPP)RhCO[4] exhibits a CO stretching absorption at 2100 cm^{-1}, we expected it to be susceptible to attack by an alkoxy anion.

Friedrich and Moskophidis[5] have examined the reaction between cobalt corrinoids and carbon monoxide in alcoholic solution. They observed the formation of the alkoxycarbonyl derivative of the Co(III) corrinoid but not of the Co(II) species.

Experimental Section

Dichlorotetracarbonyldirhodium was prepared by the method of McCleverty and Wilkinson.[6]

The reaction of $(TPP)H_2$ and $[Rh(CO)_2Cl]_2$ was carried out by the methods of Fleischer and coworkers.[7-9] The previously reported product, ClTPPRhCO, was purified by an indirect route because it was not stable enough to withstand chromatography. Crude Cl(TPP)RhCO was dissolved in 2:1 $CHCl_3$-C_2H_5OH and allowed to evaporate slowly to dryness producing a residue possessing an infrared spectrum containing no carbonyl absorption at 2100 cm^{-1} and a visible spectrum with peaks at 422, 538, and 571 nm, identical with that of a sample of the reported compound (TPP)RhCl. This residue was redissolved in benzene and chloroform and chromatographed on alumina to obtain pure (TPP)RhCl. The carbonylation of (TPP)RhCl to produce a pure sample of the known compound Cl(TPP)RhCO was carried out in methylene chloride under 1 atm of CO at room temperature for 12 hr. The product crystallized quantitatively and was suction filtered, washed with a few milliliters of ether or hexane, and air-dried. The CO absorption was observed at 2100 cm^{-1}.

Ethoxycarbonyl(tetraphenylporphinato)rhodium(III) ((TPP)Rh-$COOC_2H_5$). A 10-mg sample of Cl(TPP)RhCO was dissolved in 150 ml of methylene chloride and a dilute solution of sodium ethoxide in ethanol was added until the reaction mixture turned orange-red. The solvents were immediately removed under reduced pressure at 60°. The residue was washed with a few milliliters of water and ethanol, chromatographed twice with benzene-chloroform on alumina, and recrystallized from chloroform-ethanol. Spectral peaks were observed at 418 and 526 nm in $CHCl_3$ and 1700 cm^{-1} in KBr. *Anal.* Calcd for $C_{44}H_{28}N_4RhCOOC_2H_5$: C, 71.58; H, 4.19; N, 7.11; Rh, 13.06. Found: C, 71.37; H, 4.33; N, 7.00; Rh, 12.72. The nmr spectrum ($CDCl_3$) showed peaks at τ 1.2 (sharp s, pyrrole H), 1.8 (m, phenyl H), 2.2 (m, phenyl H), 8.7 (q, CH_2), and 10.8 (t, CH_3).

Instrumentation. Infrared and visible spectra were recorded on a Perkin-Elmer Model 521 and a Cary Model 14, respectively. Molecular weights in Fisher Spectrograde methylene chloride were determined on a Hitachi Perkin-Elmer Model 115 vapor pressure osmometer at 31.5° using benzil as a standard. Solute concentrations were in the 10 mm range. Magnetic susceptibilities were measured on polycrystalline powders by the Faraday method using a Cahn RG electrobalance. The molar diamagnetic susceptibility of $(TPP)H_2$ was measured as -386×10^{-6} cgsu/mol. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E spectrometer by direct introduction of the sample above 250°. The pyrolysis products were introduced as gases, the pyrolysis being conducted outside the spectrometer. The nmr spectrum was recorded at 220 MHz on a Varian spectrometer.

Results and Discussion

Duplication of the conditions employed by Fleischer[7-9] and coworkers for the reaction between $[Rh(CO)_2Cl]_2$ and $(TPP)H_2$ in refluxing benzene or glacial acetic acid produced the previously reported products, $H_2ORh(TPP)Cl$, EtOHRh(TPP)Cl, and ClRh(TPP)CO. In addition, a small amount of material exhibiting an infrared absorption at 1700 cm^{-1} was also obtained and the low frequency for the carbonyl absorption led us to suspect that an alkoxylcarbonyl may have been produced. Because of the poor yield of that material a direct synthesis was sought and accomplished by the reaction of ClRh(TPP)CO and $NaOC_2H_5$ in ethanol which essentially quantitatively produced $(TPP)RhCOOC_2H_5$. This product exhibits a strong CO stretching absorption at 1700 cm^{-1}, far below that expected for a terminal CO group. The molecular weight observed in CH_2Cl_2 requires a monomeric formulation and thus eliminates the possible bridging of CO groups between two rhodium porphine molecules. The maintenance of the oxidation state of the rhodium at III is indicated by the diamagnetism of the product. The high-field position found for the ethyl group in the nmr spectrum is due to the anisotropic effect of the porphine ring current and is similar to that observed for the axial acyl group in $(TPP)RhCOCH_3$.[1]

The mass spectrum of $(TPP)RhCOOC_2H_5$ is presented in Table I. It is noteworthy that no fragments are observed which correspond to $(TPP)RhCO^+$, $(TPP)RhOC_2H_5{}^+$, and $COOC_2H_5{}^+$. The large peak for $CO_2{}^+$ is derived from the alkoxycarbonyl as indicated by the absence of a peak at *m/e* 32 indicating the absence of air. Presumably then the peak at *m/e* 28 is likewise due to CO^+ rather than $N_2{}^+$. In

---

* To whom correspondence should addressed at the Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, N. Y. 11210

(1) B. R. James and D. V. Stynes, *J. Chem. Soc., Chem. Commun.*, 1261 (1972).

(2) Z. Yashida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972).

(3) R. J. Angelici, *Accounts Chem. Res.*, 5, 335 (1972).

(4) TPP is the dianion of tetraphenylporphine.

(5) W. Friedrich and M. Moskophidis, *Z. Naturforsch. B*, 26, 879 (1971).

(6) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8, 211 (1966).

(7) E. B. Fleischer and N. Sadasivan, *Chem. Commun.*, 159 (1967).

(8) N. Sadasivan and E. B. Fleischer, *J. Inorg. Nucl. Chem.*, 30, 591 (1968).

(9) E. B. Fleischer, R. Thorp, and D. Venerable, *Chem. Commun.*, 475 (1969).

Table I. Major Ions Observed in Mass Spectrum of $(TPP)RhCOOC_2H_5$

m/e	Ion	Rel intens
788	$(TPP)RhCOOC_2H_5^+$	28
715	$(TPP)Rh^+$	100
614	$(TPP)H_2^+$	29
357.5	$(TPP)Rh^{2+}$	33
316.5–318.5	$((TPP)Rh - C_6H_5 - XH)^{2+}$	39–15
279.5	$((TPP)Rh - 2(C_6H_5) - 2H)^{2+}$	23
44	CO_2^+	43
32	O_2^+	0
28	$CO^+ + N_2^+$	28

a separate experiment, the gaseous pyrolysis products of $(TPP)RhCOOC_2H_5$ *in vacuo* were examined and the evolution of CO_2 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 CO_2 rapidly.

Alkoxycarbonyl 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 alkoxycarbonyls. This reaction is observed for $(TPP)RhCOOC_2H_5$ in dry organic solvents. In $CHCl_3$, gaseous HCl reacts as

$$(TPP)RhCOOC_2H_5 + HCl \rightarrow Cl(TPP)RhCO + C_2H_5OH$$

However, when aqueous concentrated HCl is added to a THF solution of $(TPP)RhCOOC_2H_5$, the porphine product is not the metal carbonyl, but rather $H_2O(TPP)RhCl$.

Inasmuch as carbamoyl complexes can usually be derived from metal carbonyls which produce stable alkoxycarbonyls,[3] it is not surprising that the reaction of Cl(TPP)RhCO with $LiN(C_2H_5)_2$ in $HN(C_2H_5)_2$ produced a rhodium porphine with a carbonyl absorption at 1697 cm^{-1}, presumably $(TPP)RhCON(C_2H_5)_2$. That compound also reacts with dry HCl to form Cl(TPP)RhCO in analogy to the reaction of the alkoxycarbonyl. No reaction was observed between Cl(TPP)RhCO and $NaSC_2H_5$ in a mercaptan solution.

Acknowledgment. This work was supported by the Public Health Service through Grant AM-11355.

Registry No. $[(TPP)RhCOOC_2H_5]$, 42892-90-0; Cl(TPP)RhCO, 42892-91-1.

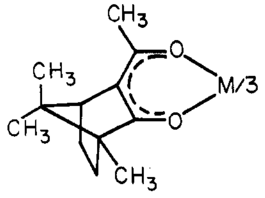
Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66044

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

Grover W. Everett, Jr.,* and Ann Johnson

Received June 5, 1973

Recent publications from this laboratory[1,2] and others[3] 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 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 determination[5] 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).



I

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 Na_2CO_3 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 ($\tau \sim 7.9$) in diastereomers A and B clearly demonstrates that these have a trans arrangement of ligands (C_1 symmetry). The single pmr signal observed in this region for diastereomers C and D is consistent with a cis geometry (C_3 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 those[1] of Δ-*trans*-$Co((+)atc)_3$ and Δ-*trans*-$Cr((+)atc)_3$ is deemed satisfactory. Also a fair match between the pat-

---

[1] R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).

[2] G. W. Everett, Jr., and R. M. King, *Inorg. Chem.*, **11**, 2041 (1972).

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

[4] G. W. Everett, Jr., and R. R. Horn, submitted for publication.

[5] W. D. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7620 (1970).

[6] J. G. Brushmiller, private communication.