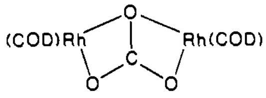
208 *Inorg. Chem.* **1987**, *26*, 208-209

Rh/Rh separations of 3.23 and 3.11 Å, respectively. Rhodium-carbon distances in these two molecules, and in the carbonate, are statistically identical. The Rh-terminal O distances in the carbonate and the acetate are within 3σ of each other. On the other hand, the Rh(μ-OMe) distance (average value 2.057 (5) Å) is significantly shorter than that for the Rh-(μ-O-CO_2) distance (2.129 (4) Å).

Solution Structure. The molecular weight evidence that $(COD)_2Rh_2CO_3$ is the correct degree of aggregation in CH_2Cl_2 solution provides a partial solution to the simple (three chemical shift) ^1H NMR spectrum of the compound. A dirhodium species will not give the 12 (!) separate ^1H NMR chemical shifts expected for the solid-state species. Given the strong preference of Rh(I) for at least four ligands, we propose structure II for the compound



II

in solution. This bridging geometry has been seen previously for both Rh(I)[15] and Cu(II)[18] carbonates, but it still requires some fluxionality to average the inequivalent vinyl groups within each COD in structure II; a transition state with three-coordinate rhodium would suffice. Such a rearrangement has a very low activation energy since the ^1H NMR spectrum of the compound in $CD_2Cl_2/CDCl_3$ shows only modest broadening at the lowest available temperature (−120 °C).

The solution ^{13}C NMR spectrum of the rhodium carbonate shows a single resonance at 167 ppm without any resolved coupling to Rh. This chemical shift corresponds nicely to the handful of other ^{13}C chemical shifts reported for carbonate complexes.[9,15] In contrast, Carmona[19] has recently noted that all CO_2 complexes studied to date by ^{13}C NMR have chemical shifts within the 195-210 ppm region. It thus appears that CO_2 and CO_3 complexes have nonoverlapping chemical shift ranges. Considering the many claimed carbon dioxide complexes (characterized by infrared spectra) shown later to be carbonate complexes, ^{13}C NMR appears to be a very valuable tool in distinguishing between the two[20] when diffraction structural results are unobtainable.

The preparation of a *dimetal* carbonate complex from CO_2 and a *monometal* hydroxy complex has been reported.[11,21] The mechanism suggested in these cases was a bimolecular reaction of two intermediate bicarbonate complexes to eliminate H_2CO_3 and form the observed M_2CO_3 product (eq 1). We have attempted to intercept an analogue of the intermediate bicarbonate complex by reacting CO_2 with $(COD)_2Rh_2(OMe)_2$.[5] Following treatment with 50 atm of CO_2 for 12 h at 25 °C, the μ-OMe complex was recovered unchanged. We suggest that this indicates a reaction mechanism for the $CO_2/(COD)_2Rh_2(OH)_2$ reaction in which the Rh-O bond is retained (eq 2).[22] The mobility of

$$L_nRhOH + CO_2 \rightarrow L_nRh(CO_3H) \xrightarrow{L_nRh(CO_3H)} L_nRh(CO_3)RhL_n + H_2CO_3 \quad (1)$$

$$Rh\text{-}O^{*}H + CO_2 \rightarrow Rh\text{-}O^{*}CO_2H \quad (2)$$

the proton (in contrast to the kinetic inertness of the O-CH_3 bond) is thus essential to CO_2 conversion in the system studied here.

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Supplementary Material Available: Tables of anisotropic thermal parameters and intraligand carbon-carbon distances (3 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Effect of pH on the Chromatographic Resolution of Carboxy Derivatives of Tris(bipyridyl)ruthenium(II) on a Chirally Modified Montmorillonite Column

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The resolution of racemic mixtures of optically active compounds on columns packed with chirally modified montmorillonite clay has recently been demonstrated by Yamagishi and coworkers.[1-4] We report here the effect of pH on the resolution of carboxy-substituted derivatives of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) through such an approach.

Polypyridyl complexes of a number of metal ions exhibit unusual modes of intercalation in smectite clays. For example, Ghosh and Bard have shown that the distribution of Δ,Λ-$Ru(bpy)_3^{2+}$ in the interlamellar region of montmorillonite and hectorite is nonrandom,[5] while Yamagishi has noted that such complexes are adsorbed on clay as a racemic pair.[6] In fact, direct spectral evidence of racemic pairing has recently been reported from this laboratory.[7] These results have spurred interest in the development of chirally modified clay columns capable of resolving optical isomers.

As part of a program to study the relative diffusion rates of optical isomers through chiral-polymer films, we have been interested in resolving racemic mixtures of $Ru(bpy)_2L_2^{2+}$ (**1**) and $Ru(L_2)_3^{2+}$ (**2**), where L_2 = 4,4′-dicarboxy-2,2′-bipyridine. However, resolution through conventional means, e.g. with tartrate or antimonyl tartrate, was unsuccessful, presumably due to the presence of ionizable $-CO_2H$ substituents on bpy. This prompted us to attempt the resolution of **1** and **2** on a chirally modified clay column.

Experimental Section

Materials. Grade GK 129 montmorillonite clay was obtained from Georgia Kaolin Co. and purified as follows: 5 g of clay was stirred in 60 mL of 1 M NaCl for 3 days, following which the clay was purified through several cycles of centrifugation followed by redispersion of the residue in triply distilled water. A final centrifugation at 5000 rpm yielded a pure white supernatant containing 18 g/L sodium montmorillonite. $Ru(phen)_3Cl_2$ was synthesized from $RuCl_3$ and 1,10-phenanthroline[8] and resolved by the method of Dwyer and Gyarfas.[9] The enantiomers were recovered from the solution as their perchlorate salts, and a 0.086 wt % solution of Λ-$Ru(phen)_3(ClO_4)_2{\cdot}2H_2O$ in water yielded an α value of −1.12° (l = 100 mm), corresponding to an enantiomeric excess >95%. $Ru(L_2)_3Cl_2$ (**2**-Cl_2) (L_2 = 4,4′-dicarboxy-2,2′-bipyridine) was obtained by refluxing a solution of $RuCl_3$ (30 mg) and L_2 (100 mg) in 10 mL of DMF for 4 h. Most of the solvent was then

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Table I. Chromatographic Resolution of Carboxy Derivatives of $Ru(bpy)_3^{2+}$ on a Λ-$Ru(phen)_3^{2+}$–Montmorillonite Column[a]

ion	10^6 × mol chromatographed	eluant	10^6 × moles eluted	remarks
$Ru(bpy)_2[bpy\text{-}(CO_2H)_2]^{2+}$ (**1**)	2.5 (in 4 mL of H_2O)	H_2O (25 mL)	2.1	all fractions racemic
	2.5 (in 4 mL of 1 M H_2SO_4)	(a) 1 M H_2SO_4 (11 mL)	1.15	95% ee (Λ)
		(b) 0.025 M NaOH (10 mL)	1.13	95% ee (Δ)
$Ru[bpy\text{-}(CO_2H)_2]_3^{2+}$ (**2**)	2.5 (in 4 mL of 1 M HCl)	(a) 1 M HCl (7 mL)	1.3	15% ee (Λ)
		(b) 1 M HCl (10 mL)	1.15	15% ee (Δ)

[a] A 0.75 cm i.d. glass column, with a coarse frit on one end, was packed with the clay, introduced as a slurry in MeOH. The flow rate was 0.05 mL min^{-1}.

removed under vacuum, following which acetone was added to the flask to precipitate the Ru complex. $Ru(bpy)_2L_2(PF_6)_2$ was prepared by refluxing $Ru(bpy)_2Cl_2$ (260 mg), L_2 (150 mg), and $NaHCO_3$ (150 mg) in 25 mL of 3:2 H_2O/MeOH for 2 h,[10] followed by precipitation of the complex with NH_4PF_6. The water-soluble form, $Ru(bpy)_2L_2Cl_2$ (**1**-Cl_2) was prepared by redissolving the above complex in acetone and precipitating the Cl^--exchanged form with tetrabutylammonium chloride.

Λ-Ru(phen)$_3^{2+}$–Montmorillonite Adduct. The adduct was prepared by adding a solution of Λ-$Ru(phen)_3Cl_2$ (0.85 mmol in 100 mL of water) to a vigorously stirred dispersion of sodium montmorillonite (1.44 g in 80 mL of water). The clay adduct was subsequently centrifuged and repeatedly washed with water (five times) and methanol (five times) to remove all unadsorbed $Ru(phen)_3^{2+}$. A slurry of the adduct (ca. 0.25 g in 8 mL of MeOH) was then poured into a glass column fitted with a coarse frit. The column was readied for chromatography by eluting first with methanol, then with water, and finally with 1 M H_2SO_4.

Instrumentation. Optical rotation measurements were made at the sodium D line by using a Model DIP-140 JASCO digital polarimeter, while UV–vis spectra were recorded on a Model SP8-100 Pye-Unicam spectrophotometer.

Results and Discussion

When 2.5 × 10^{-6} mol of **1** in 4 mL of water was chromatographed on a column containing ca. 0.25 g of Λ-$Ru(phen)_3^{2+}$–montmorillonite, no separation of isomers was found with water as eluant (Table I). However, when an equivalent amount of **1** in 1 M H_2SO_4 was placed on the same column and eluted with aqueous sulfuric acid (1 M), the eluate collected contained 1.15 × 10^{-6} mol of **1** with >95% enantiomeric excess of Λ-**1**.[11,12] Subsequent elution with 0.025 M NaOH yielded an additional 1.13 × 10^{-6} mol of the material having 95% enantiomeric excess of the Δ isomer. Thus **1** was recovered in near-quantitative yield with virtually complete resolution of the enantiomers. Similar experiments with **2** yielded two fractions containing 15% enantiomeric excess of Λ-**2** and Δ-**2**, respectively. In this case, however, the entire amount of **2** was recovered from the column with 1 M HCl as eluant.

The efficacy with which **1** is resolved under acidic conditions is rationalized as follows: Suppression of $-CO_2H$ ionization in 1 M H_2SO_4[13] results in the formation of an electropositive Ru(II) complex, which interacts strongly with the negatively charged clay surface. However, the more favorable interaction of Δ-**1** with adsorbed Λ-$Ru(phen)_3^{2+}$—to form a "racemic pair"—leads to its preferential retention in the column. Subsequent elution with base yields electroneutral Δ-**1**—due to $-CO_2H$ ionization—which interacts only weakly with the clay and can therefore be easily eluted. As compared to **1**, **2** interacts less strongly with the clay surface. This is evident from the fact that the entire amount of the chromatographed material could be recovered from the column with 1 M HCl as eluant. The weaker interaction of **2** with Λ-$Ru(phen)_3^{2+}$–montmorillonite and the resultant loss in resolution efficiency may be due to the larger size of this ion, which hinders access to the interlamellar zone of the modified clay.

The pH effects encountered in the present study suggest that cationic compounds may be more effectively resolved on chirally modified clay columns.[14,15] On the other hand, separation of compounds bearing a permanent positive charge is unattractive, since the clay columns would be destroyed due to formation of stable racemic adducts. Thus those ions whose charge can be varied as a function of pH, e.g. **1**, appear to be the ones most suitable for resolution on such clay columns. The binding strength of the protonated cationic forms must, however, be sufficiently large so as to compete with free protons for the exchangeable sites on clay. We note that the list of compounds that could be subjected to such chromatographic tests includes the amino acids and several key drug intermediates.

In conclusion, the results described above indicate that pH effects can feature prominently in the clay-based separation methodology developed by Yamagishi and co-workers.

Registry No. **1**·2Cl, 68846-36-6; **1**·2PF_6, 64189-98-6; **2**·2Cl, 97333-46-5; Λ-$Ru(phen)_3^{2+}$, 52389-25-0; *d,l*-$Ru(bpy)_2(v\text{-}py)_2^{2+}$, 82769-08-2; montmorillonite, 1318-93-0.

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(11) Note that Λ-$Ru(phen)_3^{2+}$ does not leach out from the column under these conditions.

(12) The enantiomeric excess was estimated on the basis of an $[\alpha]^{25}{}_D$ value of 1200° for the pure enantiomers.

(13) **1** displayed a λ_{max} value of 455 nm at pH 12.0 as compared to λ_{max} values of 478 and 420 nm in 1 M H_2SO_4.

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Electrogeneration of Low-Valent-Oxidation-State Vanadium Porphyrins. Characterization of the First Vanadium(III) Species

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Low-valent metal porphyrin complexes have been extensively studied,[1-7] in particular with a view to understanding the reaction of hemes with molecular oxygen.

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