are presently investigating the photochemistry of several polynuclear transition-metal anions intercalated within hydrotalcite layered supports.

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Notes

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Conversion of Carbon Dioxide to Carbonate Using a Rhodium μ-Hydroxy Species

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Chemical conversion of carbon dioxide is a resource utilization problem of worldwide interest.[1,2] Nucleophilic attack on CO_2 is a frequently successful strategy, being the basis for C–C bond formation by the enzyme Rubisco (addition of CO_2 to ribulose bisphosphate to give a six-carbon product).[3] When the nucleophile is OH^- (or H_2O), carbonic anhydrase catalyzes the conversion of CO_2 to the HCO_3^-/CO_3^{2-} equilibrium system. This latter enzyme is currently thought to involve bicarbonate production by addition of a Zn^{II}–OH unit to triatomic CO_2.[4]

Numerous studies of relevance to the carbonic anhydrase function have been reported.[1] These generally involve reaction of CO_2 with a hydroxy ligand bound to a *single*, coordinatively saturated (18-valence-electron) metal cation. Detailed kinetic studies are consistent with direct formation of a C–O bond without the intermediacy of prior coordination of CO_2 to the metal. The work reported here describes the result of reaction of a *bridging* hydroxyl group with CO_2.

Experimental Section

General Procedures and Materials. All manipulations were carried out by using standard Schlenk and glovebox procedures under prepurified nitrogen or vacuum. Solvents were dried and deoxygenated by Na/benzophenone (THF) or P_2O_5 (CH_2Cl_2 and CD_2Cl_2). ^1H spectra were recorded on a Nicolet 360-MHz spectrometer at 25 °C and referenced to Me_4Si. ^{13}C NMR spectra were recorded on a Varian XL 300 at 25 °C and referenced to solvent. Mass spectra were recorded on a Kratos MS-80. Bone Dry CO_2 (Matheson) was used as received.

$(COD)_2Rh_2(OH)_2$. $(COD)_2Rh_2(OH)_2$ was prepared according to the published synthesis,[5] modified by dissolving the final product in benzene and filtering to remove traces of KOH and KCl.

$(COD)_6Rh_6(CO_3)_3$. A degassed THF solution (20 mL) of $(COD)_2Rh_2(OH)_2$ (500 mg, 1.1 mmol) was exposed to CO_2 (3 mmol, 1 atm). After being stirred for 30 min, the clear yellow solution became cloudy and, upon standing for an additional 3 h, deposited a bright yellow powder. Decanting the THF solvent yielded 275 mg (52%) of pure, air-stable $(COD)_6Rh_6(CO_3)_3$. IR (Fluorolube mull): 1530, 1365 cm^{-1} (identified by comparison with the spectra of $(COD)_6Rh_6(^{13}CO_3)_3$ and $(COD)_2Rh_2Cl_2$). ^1H NMR (CD_2Cl_2, 360 MHz): 4.00 (s), 2.55 (m), 1.70 (m) ppm. The electron-impact mass spectrum of this material shows peaks above *m/e* 390, due to $(COD)Rh_2(CO_3)_nO^+$ (n = 1, 2) and $(COD)_2Rh_2O_m(CO_3)_{2-m}{}^+$ (m = 0–2).

Table I. Crystal Data for $[((COD)Rh)_2CO_3]_3$

empirical formula	$C_{51}H_{72}O_9Rh_6$
color	yellow
cryst dimens, mm	0.15 × 0.15 × 0.15
space group	$P\bar{1}$
cell dimens (at −156 °C; 36 reflecns)	
a, Å	13.238 (3)
b, Å	15.553 (4)
c, Å	12.894 (3)
α, deg	107.61 (1)
β, deg	91.39 (1)
γ, deg	100.40 (1)
molecules/cell	2
vol, Å^3	2479.77
calcd density, g/cm^3	1.937
wavelength, Å	0.71069
mol wt	1446.56
linear abs coeff, cm^{-1}	19.8
no. of unique intensities	6488
no. with $F > 0.0$	6021
no. with $F > 3.0\sigma(F)$	5465
final residuals	
$R(F)$	0.0361
$R_w(F)$	0.0388
goodness of fit for last cycle	0.90
max Δ/σ for last cycle	0.05

$(COD)_6Rh_6(^{13}CO_3)_3$. The ^{13}C-enriched compound was prepared (as above) on a vacuum line by using $^{13}CO_2$ prepared from 90% enriched $Ba^{13}CO_3$ and concentrated H_2SO_4. ^{13}C NMR (CD_2Cl_2, 74 MHz): 167.0 (s), 75.5 (br m), 31.0 (s) ppm. IR (Fluorolube mull): 1464, 1315 cm^{-1}.

Molecular Weight Determination. Molecular weights were determined by using the method of Signer[6] in CH_2Cl_2 at 25 °C. In a typical experiment, 10 mg of $(COD)_6Rh_6(CO_3)_3$ was dissolved in approximately 3.5 mL of CH_2Cl_2. Triphenylphosphine was used as the reference compound. Readings were taken daily until an equilibrium was achieved (about 12 days). The ^1H NMR spectrum of the molecular weight sample was recorded at the end of this time period; it revealed that no decomposition had occurred. Three measurements were taken, giving molecular weights of 433, 522, and 461.

Crystallography of $(COD)_6Rh_6(CO_3)_3$. A suitable, almost equidimensional crystal grown by slow evaporation from a THF solution was selected and transferred to the goniostat and cooled to −156 °C for characterization and data collection using graphite-monochromated radiation and a diffractometer of local construction. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited no symmetry of systematic extinctions. The choice of the centrosymmetric triclinic space group, $P\bar{1}$, was confirmed by the successful solution and refinenent of the structure. Characteristics of the data collection[7] ($6° \leq 2\theta \leq 45°$), processing, and refinement are given in Table I.

The structure was solved by a combination of direct-methods and heavy-atom Fourier techniques. Six Rh atoms were located by means of MULTAN78, and the remainder of the atoms were located in successive difference maps. Hydrogen atoms were visible in a difference map. All hydrogen atoms were introduced in calculated positions with d(C–H) = 0.95 Å and individual isotropic thermal parameters equal to 1 greater than the isotropic parameter of the attached carbon atom. Due to program limitations and a lack of interest in the hydrogen positions, the

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Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $[((COD)Rh)_2CO_3]_3$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2		10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Rh(1)	8758.6 (4)	2162.0 (4)	1058.7 (4)	10	C(34)	10240 (6)	587 (5)	3276 (6)	18
Rh(2)	8679.3 (4)	1785.1 (3)	3488.9 (4)	10	C(35)	5853 (5)	1729 (5)	−777 (5)	14
Rh(3)	5246.2 (4)	2021.8 (4)	742.7 (4)	10	C(36)	5867 (6)	2532 (5)	−1221 (6)	21
Rh(4)	5146.6 (4)	1832.2 (4)	3388.8 (4)	11	C(37)	4920 (6)	2976 (5)	−923 (6)	21
Rh(5)	7249.5 (4)	4495.3 (4)	4975.0 (4)	11	C(38)	4568 (5)	2924 (5)	165 (6)	15
Rh(6)	7465.5 (4)	4928.7 (4)	2548.4 (4)	11	C(39)	3806 (5)	2232 (5)	306 (6)	16
O(7)	7867 (3)	1363 (3)	1909 (3)	10	C(40)	3236 (5)	1401 (5)	−598 (6)	17
C(8)	6907 (5)	1495 (4)	2007 (5)	10	C(41)	3950 (6)	942 (5)	−1395 (6)	17
O(9)	6340 (4)	1349 (3)	1145 (4)	15	C(42)	5000 (6)	1033 (5)	−826 (5)	15
O(10)	6639 (3)	1709 (3)	2969 (4)	14	C(43)	5381 (6)	1271 (5)	4635 (6)	19
O(11)	5154 (3)	2729 (3)	2414 (3)	11	C(44)	4795 (6)	1658 (5)	5604 (6)	20
C(12)	5761 (5)	3530 (4)	2931 (5)	12	C(45)	3798 (6)	1939 (5)	5282 (6)	21
O(13)	6041 (4)	4072 (3)	2385 (4)	17	C(46)	3860 (5)	2176 (5)	4221 (6)	18
O(14)	5968 (4)	3687 (3)	3941 (4)	16	C(47)	3539 (5)	1521 (5)	3172 (6)	16
O(15)	8098 (3)	4359 (3)	3581 (4)	12	C(48)	3133 (5)	516 (5)	2967 (6)	20
C(16)	8371 (5)	3580 (5)	3112 (6)	14	C(49)	3823 (6)	77 (5)	3553 (6)	19
O(17)	8742 (4)	3179 (3)	3713 (4)	14	C(50)	4935 (5)	570 (5)	3685 (6)	15
O(18)	8267 (4)	3286 (3)	2066 (4)	16	C(51)	6444 (5)	4183 (5)	6222 (5)	17
C(19)	9179 (5)	2960 (4)	42 (5)	14	C(52)	6337 (5)	5069 (5)	6227 (6)	17
C(20)	8937 (5)	2391 (5)	−1153 (6)	17	C(53)	6921 (6)	5955 (5)	7065 (6)	19
C(21)	9060 (6)	1403 (5)	−1349 (6)	22	C(54)	7921 (6)	6339 (5)	6639 (6)	17
C(22)	8821 (6)	1069 (4)	−368 (6)	17	C(55)	8390 (5)	5583 (4)	5899 (6)	14
C(23)	9581 (6)	1113 (5)	433 (6)	17	C(56)	8534 (5)	4778 (5)	6103 (6)	15
C(24)	10722 (6)	1522 (5)	481 (6)	17	C(57)	8261 (6)	4557 (5)	7145 (6)	20
C(25)	10892 (5)	2464 (5)	290 (6)	17	C(58)	7156 (6)	3993 (5)	7016 (6)	22
C(26)	10047 (5)	2977 (5)	696 (5)	13	C(59)	8739 (5)	6028 (5)	2927 (6)	14
C(27)	9105 (5)	509 (4)	3001 (5)	14	C(60)	8888 (5)	5398 (5)	1926 (6)	15
C(28)	8334 (5)	496 (4)	3737 (5)	14	C(61)	8788 (6)	5562 (5)	833 (6)	20
C(29)	8580 (6)	534 (5)	4914 (6)	19	C(62)	7688 (6)	5177 (5)	266 (6)	22
C(30)	8722 (6)	1530 (5)	5693 (6)	19	C(63)	6888 (6)	5158 (5)	1074 (6)	19
C(31)	9203 (5)	2218 (4)	5139 (5)	13	C(64)	6792 (5)	5894 (5)	1980 (5)	15
C(32)	10033 (6)	2160 (5)	4502 (6)	15	C(65)	7510 (6)	6833 (5)	2231 (6)	16
C(33)	10663 (5)	1395 (5)	4313 (6)	16	C(66)	8401 (5)	6937 (5)	3057 (6)	16

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

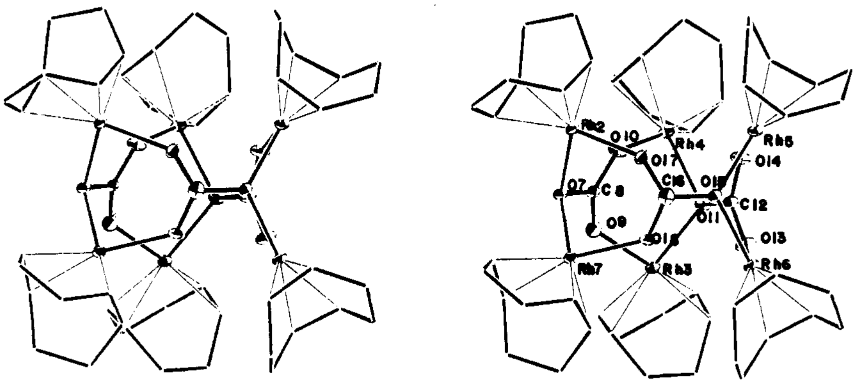

Figure 1. Stereo ORTEP drawing of $[(COD)_2Rh_2CO_3]_3$ with the pseudo-threefold symmetry axis vertical. Cyclooctadiene carbons have been represented as points for clarity.

hydrogen atoms were not refined. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms. A total of 5465 reflections having $F > 3\sigma(F)$ were used. The final difference Fourier was essentially featureless; the largest peak was 0.84 e/Å^3. The ten most intense residual peaks were within 1.2 Å of the Rh atoms. The results of the X-ray study are given in Tables II and III and Figures 1 and 2. Additional details are available as supplementary material.

Results

Synthesis and Characterization. A THF solution of $(COD)_2Rh_2(OH)_2$ reacts rapidly with CO_2 (1 atm) at 25 °C, depositing a fine yellow solid. The ^1H NMR spectrum (CD_2Cl_2) of this material shows three resonances for the cyclooctadiene ligand. The solid-state infrared spectrum shows band at 1530 and 1365 cm^{-1}, consistent with (yet not uniquely diagnostic of) the presence of a carbonate moiety.[8] This is further supported by the ^{13}C NMR spectrum (CD_2Cl_2) of this material (synthesized by using 90% ^{13}C-enriched CO_2), which shows a single resonance at 167 ppm;[9] no ^{13}C–Rh coupling is evident ($J < 2$ Hz). Elucidation

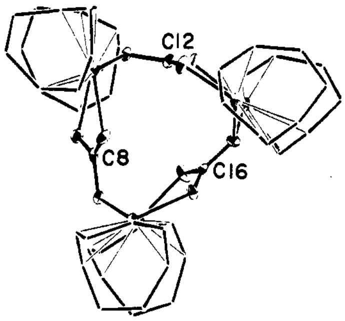

Figure 2. ORTEP drawing of $[(COD)_2Rh_2CO_3]_3$ viewed down the pseudo-threefold axis.

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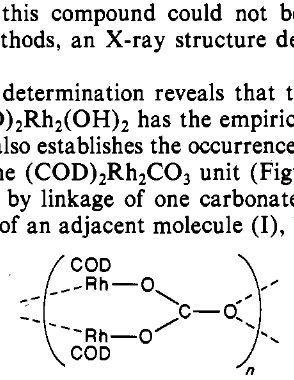
Table III. Selected Bond Distances (Å) and Angles (deg) for $[((COD)Rh)_2CO_3]_3$

	Distances		
Rh(1)–Rh(2)	3.358 (1)	Rh(4)–C(46)	2.100 (7)
Rh(3)–Rh(4)	3.516 (1)	Rh(4)–C(47)	2.088 (7)
Rh(5)–Rh(6)	3.516 (1)	Rh(4)–C(50)	2.083 (7)
Rh(1)–O(7)	2.120 (4)	Rh(5)–O(14)	2.084 (5)
Rh(1)–O(18)	2.061 (5)	Rh(5)–O(15)	2.118 (4)
Rh(1)–C(19)	2.083 (6)	Rh(5)–C(51)	2.080 (7)
Rh(1)–C(22)	2.108 (7)	Rh(5)–C(52)	2.115 (7)
Rh(1)–C(23)	2.094 (7)	Rh(5)–C(55)	2.081 (6)
Rh(1)–C(26)	2.086 (6)	Rh(5)–C(56)	2.103 (7)
Rh(2)–O(7)	2.138 (4)	Rh(6)–O(13)	2.085 (5)
Rh(2)–O(17)	2.084 (4)	Rh(6)–O(15)	2.137 (4)
Rh(2)–C(27)	2.078 (7)	Rh(6)–C(59)	2.102 (7)
Rh(2)–C(28)	2.097 (7)	Rh(6)–C(60)	2.102 (7)
Rh(2)–C(31)	2.086 (6)	Rh(6)–C(63)	2.078 (7)
Rh(2)–C(32)	2.075 (7)	Rh(6)–C(64)	2.109 (7)
Rh(3)–O(9)	2.074 (5)	O(7)–C(8)	1.326 (8)
Rh(3)–O(11)	2.120 (4)	O(10)–C(8)	1.260 (8)
Rh(3)–C(35)	2.088 (7)	O(11)–C(12)	1.324 (8)
Rh(3)–C(38)	2.094 (7)	O(13)–C(12)	1.265 (8)
Rh(3)–C(39)	2.085 (7)	O(14)–C(12)	1.263 (8)
Rh(3)–C(42)	2.113 (7)	O(15)–C(16)	1.300 (8)
Rh(4)–O(10)	2.088 (5)	O(17)–C(16)	1.272 (8)
Rh(4)–O(11)	2.141 (4)	O(18)–C(16)	1.281 (8)
Rh(4)–C(43)	2.089 (7)		
	Angles		
O(7)–Rh(1)–O(18)	87.26 (17)	Rh(5)–O(14)–C(12)	130.7 (4)
O(7)–Rh(2)–O(17)	93.42 (17)	Rh(5)–O(15)–Rh(6)	111.44 (19)
O(9)–Rh(3)–O(11)	91.13 (18)	Rh(5)–O(15)–C(16)	119.2 (4)
O(10)–Rh(4)–O(11)	88.04 (17)	Rh(6)–O(15)–C(16)	113.5 (4)
O(14)–Rh(5)–O(15)	88.15 (17)	Rh(2)–O(17)–C(16)	130.7 (4)
O(13)–Rh(6)–O(15)	90.09 (17)	Rh(1)–O(18)–C(16)	127.2 (4)
Rh(1)–O(7)–Rh(2)	104.13 (18)	O(7)–C(8)–O(9)	118.0 (6)
Rh(1)–O(7)–C(8)	114.3 (4)	O(7)–C(8)–O(10)	115.3 (6)
Rh(2)–O(7)–C(8)	109.7 (4)	O(9)–C(8)–O(10)	126.5 (6)
Rh(3)–O(9)–C(8)	132.6 (4)	O(11)–C(12)–O(13)	117.6 (6)
Rh(4)–O(10)–C(8)	124.9 (4)	O(11)–C(12)–O(14)	115.7 (6)
Rh(3)–O(11)–Rh(4)	111.22 (19)	O(13)–C(12)–O(14)	126.6 (6)
Rh(3)–O(11)–C(12)	122.4 (4)	O(15)–C(16)–O(17)	118.3 (6)
Rh(4)–O(11)–C(12)	108.9 (4)	O(15)–C(16)–O(18)	116.9 (6)
Rh(6)–O(13)–C(12)	129.3 (4)	O(17)–C(16)–O(18)	124.8 (6)

of the composition of this complex is complicated by the electron-impact mass spectrum, which shows several peaks above *m/e* 550; the molecular weight of $(COD)_2Rh_2CO_3$ is 482. Since the exact nature of this compound could not be determined by spectroscopic methods, an X-ray structure determination was carried out.

The structure determination reveals that the carboxylation product of $(COD)_2Rh_2(OH)_2$ has the empirical formula $(COD)_2Rh_2CO_3$ but also establishes the occurrence of a head-to-tail aggregation of the $(COD)_2Rh_2CO_3$ unit (Figure 1). This aggregation occurs by linkage of one carbonate oxygen to both rhodium centers of an adjacent molecule (I), but it stops short of infinite polymerization. Instead, this repeat unit forms a cylindrical trimer. The wall of this barrel-shaped molecule is comprised of a $(Rh_2CO_3)_3$ surface of atoms that is further wrapped with a lipophilic sheath of six cyclooctadiene molecules (Figure 2). One η^4-COD ligand is attached to each rhodium. Within any one carbonate group, two oxygens bridge two rhodiums in the manner of conventional carboxylate bridges and the third oxygen forms a single-atom bridge between two rhodium atoms of the next Rh_2CO_3 unit. Each pair of metals is thus part of a six-atom ORh_2O_2C ring, a situation previously unobserved for rhodium.



I

The $(olefin)_2Rh(O)_2$ coordination geometry at each metal is conventional (planar). Rhodium–carbon distances (average value 2.092 Å) span a range of only 4σ; they are thus identical. Diene ring C–C distances for single and double bonds average 1.523 and 1.402 Å, respectively, and each spans a range of only 3σ (difference). Rh–(μ_3-O) distances (average value 2.129 Å) are consistently longer than Rh–(μ-O) distances (average value 2.079 Å). Within the carbonate moiety, C–(μ_3-O) distances are longer than C–(μ-O) distances (average values are 1.317 and 1.267 Å, respectively). The (μ-O)–C–(μ-O) angles open to an average value of 126.0°, in contrast to the average (μ_3-O)–C–(μ-O) angle of 117.0°. The carbonate groups are each coplanar to within ±0.02 Å, while the attached rhodiums lie out of such planes by as much as 1.58 Å. The ORh_2O_2C rings are not planar but are significantly folded about the Rh–Rh line. It is this feature that allows the repeat unit to form a closed cylinder with only three repetitions.

Most remarkable is the fact that the repeat unit exhibits two very different Rh/Rh separations, one being 3.35 Å and the other two being 0.16 Å longer.[10] Such flexibility is not characteristic of authentic chemical bonds, and we take these data as proof of the lack of metal–metal bonding in this and related compounds. Thus, we view the dinuclear character of the repeat unit as due to constraints of the mechanical linkage of bridging carbonates and not to any Rh–Rh bonding.

Solution Behavior. Solution molecular weight measurements in CH_2Cl_2 at 25 °C yield values of 433, 522, and 461, for an average molecular weight of 472. These results indicate complete dissociation of the solid-state hexameric structure into $(COD)_2Rh_2CO_3$ units (mol wt 482) in dichloromethane.

Discussion

The study reported here reveals a facile insertion of CO_2 into the $Rh_2(\mu\text{-}OH)_2$ unit to yield a carbonate complex of remarkable structural and dynamic complexity. We conclude that the rhodium complex contains carbonate, not bicarbonate, because there is a lack of IR or NMR evidence for a hydroxyl group and because the crystallographic study shows no O···O contact characteristic of hydrogen bonding; all bicarbonate complexes characterized crystallographically show intermolecular hydrogen bonding.[11] The complexity of the problem is magnified because the solution and solid-state structures are different.

Solid-State Structure. The μ_4-η^3-carbonate moiety seen in the solid state for $(COD)_6Rh_6(CO_3)_3$ has been seen previously in the salt $[Cu_4(dpt)_4(CO_3)Cl_2]Cl_4{\cdot}7.5H_2O$[12] (dpt = bis(3-aminopropyl)amine) as well as in the copper mineral malachite.[13] We were originally led to determine the crystal structure of the rhodium(I) carbonate because the infrared bands of the carbonate unit were not definitive for its binding mode. Indeed, while the bands observed for $(COD)_6Rh_6(CO_3)_3$ (1530 and 1365 cm^{-1}) duplicate nicely those of $[Cu_4(dpt)_4(CO_3)Cl_2]Cl_4{\cdot}7.5H_2O$,[14] they are not sufficiently different from those (1535 and 1328 cm^{-1}) of $H_2(P(i\text{-}Pr)_3)_2Rh(\mu\text{-}\eta^2,\eta^2\text{-}CO_3)Rh(PhC_2Ph)P(i\text{-}Pr)_3$[15] to exclude linkage of that sort.

The ORh_2O_2C ring in $(COD)_6Rh_6(CO_3)_3$ may be viewed as a hybrid of the μ-OMe and μ-O_2CMe components found in $[(COD)RhOMe]_2$[16] and in $[(norbornadiene)RhO_2CMe]_2$,[17] with

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(9) Carbonate and bicarbonate both show ^{13}C chemical shifts in this region. See: Strom, E. T.; Woessner, D. E.; Smith, W. B. *J. Am. Chem. Soc.* **1981**, *103*, 1255.

(10) All Rh/Rh separations are substantially larger than the "bite" distance of the μ-carbonate.

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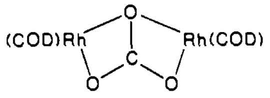
Rh/Rh separations of 3.23 and 3.11 Å, respectively. Rhodium-carbon distances in these two molecules, and in the carbonate, are statistically identical. The Rh-terminal O distances in the carbonate and the acetate are within 3σ of each other. On the other hand, the Rh(μ-OMe) distance (average value 2.057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

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

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

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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