been noted for related systems previously by Keppert[17] (Figure 4). NMR spectra[13] have shown no evidence for an equilibrium mixture. The "skew-trapezoidal" geometry should be characterized by an intensity ratio only slightly lower than 4/1. The actual value will depend upon the angle between the ligands. An earlier calculation[8] indicates that a 3/1 ratio corresponds to a 160° angle between the ligands; i.e., the ligand should be 20° out of plane.

In summary, this study definitely shows that dibenzoylmethane is characterized by resonance-enhanced Rayleigh depolarized scattering which increases modestly as scattered-light wavelengths decrease from 514.5 to 457.9 nm. The complexes also show similar amounts of resonance-enhanced scattering and the constancy of the $I_{\text{complex}}/I_{\text{ligand}}$ ratio shows that the dibenzoylmethane is relatively unaffected in its optical properties by complexation. The 3/1 $I_{\text{complex}}/I_{\text{ligand}}$ ratio strongly suggests that the complex is approximately "trans" in geometry with only moderate distortion from ligand–ligand coplanarity observed. The relaxation times calculated from the half-widths at half-height of the central Rayleigh peaks show that the ligand and complexes are not strongly associated with the solvent or each other. This latter condition is necessary for the simple relation of the light-scattering intensities to molecular optical anisotropies.

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Registry No. DBZM, 120-46-7; $(C_4H_9)_2Sn(DBZM)_2$, 22673-17-2; $(C_6H_{11})_2Sn(DBZM)_2$, 80327-43-1.

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Absorption and Circular Dichroism Studies of Rhodium(I) Complexes Containing Chiral Isocyanides[1]

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Absorption and CD spectra of mono- and dinuclear Rh(I) complexes containing chiral isocyanide ligands such as (1*R*,2*R*)- or (1*S*,2*S*)-diisocyanocyclohexane (ICH) and (*R*)- or (*S*)-phenylethyl isocyanide (PEI) were examined. The ICH complexes showed an intermolecular metal–metal interaction in the solid state but not in solution. A metal–metal interaction in the PEI complexes was observed in the solid state and in a mixture of CH_3CN and H_2O. The CD spectra of ICH and PEI complexes showed a characteristic band at 310 nm, in which the CD band with plus sign was assigned to *S* configuration and that with minus sign to *R* configuration.

Square-planar d^8 rhodium complexes of isocyanide, $Rh(RNC)_4^+$, have been found to show oligomerization in solution and redox chemistry.[2] There has been considerable interest in the electronic properties of their compounds. Many studies on their electronic spectra are known,[2] but there are few electronic and circular dichroism studies on the complexes containing chiral isocyanides. This paper reports the synthesis of some rhodium(I) complexes coordinated by chiral isocyanides such as (*R*)- and (*S*)-phenylethyl isocyanide (PEI) and (1*R*,2*R*)- and (1*S*,2*S*)-diisocyanocyclohexane (ICH), and their spectroscopic studies.

Results and Discussion

Preparation. Mono- and dinuclear Rh(I) complexes containing chiral isocyanides, $Rh(PEI)_4Cl$ and $[Rh_2(ICH)_4]X_2$, were prepared by the reaction of $[Rh(COD)Cl]_2$ with the corresponding isocyanide. They are reddish violet or yellow crystalline solids. The reddish violet color was reminescent of a metal–metal interaction.

Electronic Spectra. Absorption spectral data of $Rh(PEI)_4Cl$ and $[Rh_2(ICH)_4]X_2$ in solution and in the solid state are given in Table I together with those of related complexes. Figures 1 and 2 show absorption spectra of some Rh(I) complexes.

Absorption spectra of all dinuclear complexes in solution show the transition at ca. 400 nm, which is identified as d_{z^2}–π^* metal to ligand charge-transfer absorption. The positions of these transitions are independent of solvents and concentrations in the range from 1.3×10^{-5} to 6.2×10^{-2} M. Furthermore, the spectra are closely similar to those of mononuclear complexes at concentration. These observations suggest that dinuclear Rh(I) complexes do not exhibit intra- and intermolecular metal–metal interaction in solution. However, dinuclear complexes of 1,3-diisocyanopropane derivatives[3] and 1,3-*cis*-diisocyanocyclohexane[2j,4] exhibit the presence of intra- and intermolecular metal–metal interaction in solution. This difference is unexpected on the basis of the molecular models (vide infra).

In the electronic spectrum of reddish violet solid, $[Rh_2(1S,2S\text{-}ICH)_4](PF_6)_2$, in a pressed KBr pellet, there exists a

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Table I. Absorption Spectral Data of Rhodium(I) Complexes

complex	color	method	λ_{max}, nm ($10^{-3}\ \epsilon_{max}$)[a]
$[Rh_2(1R,2R\text{-ICH})_4](BPh_4)_2 \cdot 2H_2O$	yellow	CH_3CN	229 (40.8), 308 (39.0), 338 sh (4.51), 390 (13.3), 443 (0.53)
$[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$	yellow	CH_3CN	221 (52.3), 308 (47.5), 337 sh (5.02), 390 (15.4), 445 (0.58)
		KBr	228 (–), 314 (–), 336 sh (–), 339 (–), 452 (–)
$[Rh_2(1S,2S\text{-ICH})_4]Cl_2 \cdot 4H_2O$	reddish violet	MeOH	207 (22.9), 308 (24.4), 335 sh (3.49), 391 (7.41), 442 (0.35)
$[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2 \cdot H_2O$	reddish violet	CH_3CN	220 (11.8), 308 (33.3), 335 sh (4.28), 390 (9.59), 441 (0.46)
		KBr	230 (–), 318 (–), 338 sh (–), 393 (–), 512 (–)
$[Rh_2(1S,2S\text{-ICH})_4](ClO_4)_2 \cdot 5H_2O$	reddish violet	CH_3CN	220 (13.6), 306 (36.4), 335 sh (4.35), 390 (11.7), 442 (0.61)
$Rh(S\text{-PEI})_4Cl$	reddish violet	CH_3CN	224 (8.34), 310 (27.5), 336 sh (3.23), 385 (7.08), 441 (0.31)
		KBr	314 (–), 338 sh (–), 388 (–), 440 (–), 500 (–)
$[Rh_2(\text{bridge})_4](BPh_4)_2 \cdot CH_3CN$[b]	violet	CH_3CN	318 (31.5), 344 (5.5), 380, 553 (14.5)
$[Rh(PhNC)_4][BPh_4]$[c]	violet	CH_3CN	241 (60.5), 335 (40.2), 411 (5.00), 463 (0.63)

[a] sh = shoulder peak. [b] bridge = 1,3-diisocyanopropane. K. R. Mann, J. A. Thick, R. A. Bell, C. C. Coyle, and H. B. Gray, *Inorg. Chem.*, 19, 2462 (1980). [c] K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray, and J. G. Gordon II, *Inorg. Chem.*, 17, 828 (1978).

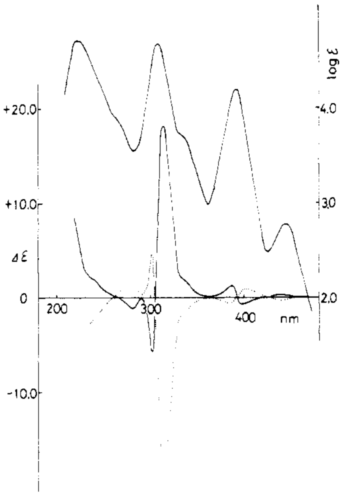

Figure 1. Absorption and circular dichroism spectra of dinuclear Rh(I) complexes in CH_3CN: $[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$ (—) and $[Rh_2(1R,2R\text{-ICH})_4](BPh_4)_2 \cdot 2H_2O$ (···).

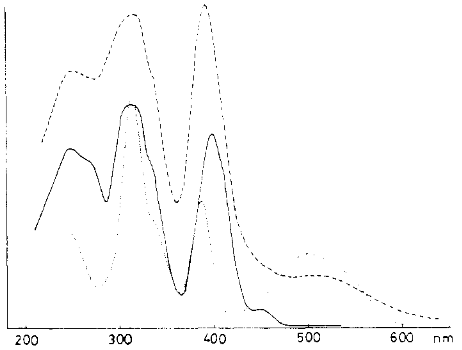

Figure 2. Absorption spectra of mono- and dinuclear Rh(I) complexes in KBr: $Rh(S\text{-PEI})_4Cl$ (···), $[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$ (—), and $[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2 \cdot H_2O$ (- - -).

band at 512 nm, assignable to a metal–metal interaction. The spectra of the Cl^- and ClO_4^- salts are quite similar to that of the PF_6^- salt, but the spectrum of the BPh_4^- salt is closely similar to that in solution. It has been established from X-ray crystallographic studies that the metal–metal distances of the complexes containing a metal–metal interaction are in the range from 3.1 to 3.5 Å.[2a,i,5–7]

Consideration of a molecular model of the dinuclear complex suggests that an intramolecular Rh–Rh distance falls in the range from ca 5.5 to 6.0 Å.[2e] An intramolecular Rh–Rh distance of $[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2$ was roughly estimated to be ca 4.7 Å by the powder X-ray method,[8] suggesting the absence of an intramolecular metal–metal distance. Thus the presence of the aforementioned metal–metal interaction is dinuclear complexes in the solid state should result from an intermolecular interaction. The difference between two values (5.5–6.0 Å and ca. 4.7 Å) may suggest the presence of conformational strain.

The unidentate complex $Rh(PEI)_4Cl$ in organic solvents such as CH_3CN and CH_3OH did not oligomerize over a wide range of concentrations, but oligomerization was observed in a mixture of CH_3CN and H_2O and in the solid state (Figure 2). In a mixture of CH_3CN and H_2O (1:4), the band at 385 nm, which dominates the low-concentration spectra, decreases in intensity and two new bands grow in, first at 522 and then at 640 nm. On the basis of equations specifying the equilibria derived by Mann et al., we examined a plot of $[Rh]/A_{522nm}{}^{1/2}$ vs. $A_{522nm}{}^{1/2}$ over the concentration range 10^{-4} M < [Rh] < 3×10^{-3} M.[2a] We obtained K_1 = 8000 (2700) M^{-1} and ϵ_2 = 9400 (1100) from the slope and intercept. The absorption peak at 522 nm is identified as due to a dimer. An absorption at 640 nm, assigned to the trimer, is present only at very high concentrations.

Oligomerization also increases with an increase of the ratio of H_2O to CH_3CN. The equilibrium constant K_2 is estimated to be 9200 M^{-1} for a ratio of 1:9 of CH_3CN and H_2O. This complex showed higher oligomerization ability than $Rh(t\text{-BuNC})_4Cl$ (K_2 = 250 M^{-1}) in H_2O.[2a] A study of differences of oligomerization ability arising from isocyanide ligands will be reported elsewhere.

Circular Dichroism Spectra. CD spectra data of $[Rh_2(1S,2S\text{- or }1R,2R\text{-ICH})_4]X_2$ and $Rh(S\text{- or }R\text{-PEI})_4Cl$ are listed in Table II. The spectra of the bidentate complexes in organic solvents showed a characteristic intense band at 310 nm, but those of the unidentate ones showed a low-intensity band. The CD band having a positive peak in this range is assigned to the *S,S* configuration for dinuclear complexes and to the *S* one for mononuclear one. The band having a negative peak is assigned to the *R,R* and *R* configurations, respectively (Figure 1 and Table II). The CD spectrum of $Rh(S\text{-PEI})_4Cl$ in $CH_3CN–H_2O$ (1:4) showed a new positive peak at 520 nm. The band at 520 nm increases and that at 307 nm, having a positive value, decreases with an increase in concentration, being responsible for the molecular association. The spectrum in a KBr disk is similar to that in solution. In the CD spectrum of the dinuclear complex $[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2$ in the solid state, a new band having a negative value appears at 510 nm due to an intermolecular metal–metal interaction. There is no information on a band of different sign near 500 nm arising

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(8) The powder X-ray analysis was measured by a Rigaku Geigerflex apparatus. The 2θ value was calculated as 19°.

Table II. CD Spectral Data of Rhodium(I) Complexes

complex	method	CD peak, nm ($\Delta\epsilon$)
$[Rh_2(1R,2R\text{-ICH})_4](BPh_4)_2\cdot 2H_2O$	CH_3CN	279 (+1.37), 302 (+4.61), 314 (−17.3), 386 (−0.49), 399 (+0.89), 444 (−0.10)
$[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$	CH_3CN	240 sh (+1.97), 281 (−1.18), 302 (−5.64), 314 (+18.1), 338 sh (+1.73), 386 (+1.21), 399 (−0.70), 444 (+0.12)
	KBr	280 sh (−), 300 (−), 317 (+), 395 (+), 410 (−), 447 (+)
$[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2\cdot H_2O$	CH_3CN	240 sh (+1.60), 282 (−0.31), 300 (−1.23), 316 (+11.3), 336 sh (+1.23), 366 (+0.31), 390 (+0.47), 409 (−0.33), 448 (+0.05)
	KBr	319 (+3.05), 340 sh (+0.91), 393 (+0.25), 417 (−0.07), 449 (+0.05), 510 (+0.03), 610 (−0.01)
$[Rh_2(1S,2S\text{-ICH})_4](ClO_4)_2\cdot 5H_2O$	CH_3CN	240 (+1.58), 281 (−0.26), 289 (+0.18), 301 (−2.61), 314 (+13.1), 337 sh (+1.76), 384 (+0.33), 404 (−0.28), 445 (+0.08)
$[Rh_2(1S,2S\text{-ICH})_4]Cl_2\cdot 4H_2O$	CH_3OH	226 (−0.17), 248 (+2.18), 291 sh (+0.38), 313 (+4.88), 357 sh (+0.06), 382 (−0.66), 395 (+0.35), 440 (+0.02)
$Rh(R\text{-PEI})_4Cl$	CH_3CN	215 (+5.79), 264 (−0.05), 278 (+0.14), 310 (−0.36), 385 (+0.37), 435 (+0.01)
$Rh(S\text{-PEI})_4Cl$	CH_3CN	214 (−4.66), 242 (+0.02), 279 (−0.06), 307 (+0.62), 327 (−0.12), 384 (−0.25), 462 (−0.10)
	$CH_3CN\text{-}H_2O^b$	216 (−2.93), 241 (+0.53), 280 (−0.10), 313 (+0.44), 329 (−0.10), 382 (−0.19), 521 (−0.21)
	KBr	309 (+), 356 (+), 390 (−), 510 (−)

[a] sh = shoulder peak. [b] $CH_3CN:H_2O = 1:4$.

from an intermolecular metal–metal interaction in mono- and dinuclear complexes.

Experimental Section

Infrared, absorption, and CD spectra were recorded on Shimazu IR-27G, Hitachi 330, and JASCO J-20 spectrophotometers, respectively. The conductivity was measured in Me_2SO by an Ando LCR-10. Dimethyl sulfoxide was distilled under reduced pressure after drying over $CaSO_4$ to give specific conductance, $k = 2.25 \times 10^{-7}$ S cm^{-1}. Chiral isocyanides were prepared by a procedure described in the literature.[4,9]

Preparation of Rhodium(I) Complexes. (1*S*,2*S*)-1,2-Diisocyanocyclohexane (0.66 g, 5 mmol) was added with stirring to a solution of $[Rh(COD)Cl]_2$ (0.48 g, 1.0 mmol) in CH_2Cl_2 (30 mL). The mixture was treated with hexane (10–20 mL) to give a purple-red precipitate (0.71 g, 81%), which was filtered off, washed with hexane, and dried in vacuo. IR(KBr): 2163 cm^{-1} (N≡C). Anal. Calcd for $C_{32}H_{48}N_8O_4Cl_2Rh_2$: C, 43.41; H, 5.46; N, 12.65; Cl, 8.01. Found: C, 43.41; H, 5.55; N, 13.11; Cl, 8.73.

The chloride salt was converted to the yellow BPh_4^- salt by methathesis with $NaBPh_4$ in CH_3OH. The purple-red PF_6^- and ClO_4^- salts were prepared by methathesis with NH_4PF_6 and $NaClO_4$, respectively.

$[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$. IR (KBr): 2160 cm^{-1} (N≡C). Anal. Calcd for $C_{80}H_{80}N_8B_2Rh_2$: C, 69.58; H, 5.84; N, 8.11. Found: C, 69.00; H, 6.21; N, 8.23.

$[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2\cdot H_2O$. IR (KBr): 2167 cm^{-1} (N≡C). $\Lambda = 53$ S cm^2 mol^{-1}. Anal. Calcd for $C_{32}H_{42}N_8OP_2F_{12}Rh_2$: C, 36.59; H, 4.03; N, 10.67. Found: C, 36.33; H, 4.21; N, 10.59.

$[Rh_2(1S,2S\text{-ICH})_4](ClO_4)_2\cdot 5H_2O$. IR (KBr): 2162 cm^{-1} (N≡C). Anal. Calcd for $C_{32}H_{50}N_8O_{13}Cl_2Rh_2$: C, 37.26; H, 4.89; N, 10.86. Found: C, 37.08; H, 4.32; N, 10.86.

$[Rh_2(1R,2R\text{-ICH})_4](BPh_4)_2\cdot 2H_2O$. IR (KBr): 2161 cm^{-1} (N≡C). Anal. Calcd for $C_{80}H_{84}N_8O_2B_2Rh_2$: C, 67.81; H, 5.97; N, 7.91. Found: C, 67.53; H, 6.07; N, 8.11.

$Rh(S\text{-PEI})_4Cl$. IR(KBr): 2153 cm^{-1} (N≡C). Anal. Calcd for $C_{36}H_{36}N_4ClRh$: C, 65.21; H, 5.47; N, 8.45. Found: C, 65.00; H, 5.59; N, 8.31.

$Rh(R\text{-PEI})_4Cl$. IR (KBR): 2153 cm^{-1} (N≡C). Anal. Found for $C_{36}H_{36}N_4ClRh$: C, 64.89; H, 5.81; N, 8.22.

Determination of Equilibrium Constant. The spectra were measured in the concentration range 10^{-4} M < [Rh] < 3×10^{-3} M. The equilibrium constant was determined from eq 1, described in the

$$\frac{[Rh]}{A_2^{1/2}} = \frac{1}{(\epsilon K_1)^{1/2}} + \frac{2A_2^{1/2}}{\epsilon_2} + \frac{3K_2A_2}{\epsilon_2(\epsilon_2K_1)^{1/2}} \quad (1)$$

literature,[2a] where [Rh] is the total Rh concentration in terms of monomer, A_2 is the absorbance due to dimers, and ϵ_2 is the corresponding molar extinction coefficient. The third term in eq 1 is neglected.

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Registry No. $[Rh_2(1S,2S\text{-ICH})_4]Cl_2$, 80387-85-5; $[Rh_2(1S,2S\text{-ICH})_4](BPh_4)_2$, 80433-09-6; $[Rh_2(1S,2S\text{-ICH})_4](PF_6)_2$, 80433-08-5; $[Rh_2(1S,2S\text{-ICH})_4](ClO_4)_2$, 80433-10-9; $[Rh_2(1R,2R\text{-ICH})_4](BPh_4)_2$, 80433-76-7; $Rh(S\text{-PEI})_4Cl$, 80398-81-8; $Rh(R\text{-PEI})_4Cl$, 80433-77-8; $[Rh(COD)Cl]_2$, 12092-47-6.

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