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Barrier to the Intramolecular Rearrangement of Tetrakis(isocyano)(tetracyanoethylene)cobalt(I) and -rhodium(I) Complexes

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The $[M(RNC)_4(TCNE)]X$ type complexes ($M = Co(I), Rh(I)$; $R = t\text{-}C_4H_9, CH_3, 4\text{-}CH_3OC_6H_4$; $X = ClO_4, PF_6, BPh_4$; TCNE = tetracyanoethylene; but not all combinations) undergo TCNE rotation coupled with the Berry pseudorotation. The activation parameters of the intramolecular rearrangement, which causes the exchange of the isocyanide protons between two nonequivalent sites, were determined by the line-shape analysis of the ^1H NMR spectra recorded in both dichloromethane and benzonitrile in the −20 to +70 °C range. The activation energy and entropy, E_a and $\Delta S^\ddagger$, range from 54 to 87 kJ/mol and from −59 to +51 J/(deg mol), respectively. The E_a values obtained for $[Co(RNC)_4(TCNE)]ClO_4$ (54 and 52 kJ/mol when $R = t\text{-}C_4H_9$ and $4\text{-}CH_3OC_6H_4$, respectively) were fairly larger than the apparently very low values of $[Co(RNC)_5]ClO_4$ which undergo the Berry pseudorotation alone. This is indicative of the significant contribution of the TCNE rotation to the rearrangement barrier of the $[M(RNC)_4(TCNE)]X$ type complexes. The E_a and $\Delta S^\ddagger$ values are almost independent of the steric and/or electronic effects of the isocyanides but dependent on the counteranion. The dependence of these values on the anion observed in dichloromethane is interpreted by the presence of appreciable amounts of ion pairs. Thus, the E_a value increases in the order $ClO_4 < PF_6 < BPh_4$ in dichloromethane, which is consistent with the bulkiness of the anion.

Introduction

It is well-known that cyano olefins react with most low-valent transition-metal complexes containing tertiary phosphines and/or carbon monoxide to form rigid adducts.[1] Recently, we prepared the $[Rh(RNC)_4(TCNE)]ClO_4$ type complexes (R = organic group, TCNE = tetracyanoethylene) whose ^1H NMR spectra show two nonequivalent isocyanide signals with equal intensity at low temperatures, while they coalesce at elevated temperatures.[2] This result has been interpreted in terms of TCNE rotation around the coordination bond coupled with the Berry pseudorotation as shown in Figure 1.[2] It is of interest to compare quantitatively the barrier of this rearrangement with those of the complexes exhibiting the Berry pseudorotation alone. This paper reports activation parameters of the rearrangement of the $[M(RNC)_4(TCNE)]X$ type complexes ($M = Co(I), Rh(I)$; $R = t\text{-}C_4H_9, CH_3, 4\text{-}CH_3OC_6H_4$; $X = ClO_4, PF_6, BPh_4$; but not all combinations) on the basis of the line-shape analysis of ^1H NMR spectra.

Experimental Section

Materials. Dichloromethane and benzonitrile used as solvents were purified by the standard methods.[3] Chloroform-d_1 was used as supplied. The $[Co(RNC)_4(TCNE)]X$ complexes ($R = t\text{-}C_4H_9$, $X = ClO_4, PF_6, BPh_4$; $R = 4\text{-}CH_3OC_6H_4$, $X = ClO_4$) were prepared by equimolar reaction of TCNE with the appropriate $[Co(RNC)_5]X$.[4] The $[Rh(RNC)_4(TCNE)]X$ complexes ($R = t\text{-}C_4H_9$, $X = ClO_4, PF_6, BPh_4$; $R = CH_3$, $X = BPh_4$; $R = 4\text{-}CH_3OC_6H_4$, $X = ClO_4$) were synthesized as described previously.[2] However, $[Rh(RNC)_4]X$ as the starting complex was prepared by the stoichiometric reaction of the appropriate isocyanide with di-μ-chloro-bis(1,5-cyclooctadiene)dirhodium(I), $[RhCl(COD)]_2$,[5] followed by the metathesis with $NaClO_4 \cdot H_2O$, NH_4PF_6, or $NaBPh_4$. Analytically pure samples were used for the NMR measurements.

Measurements. Electric conductivities and molecular weights were measured as described previously.[2]

NMR Spectra and Line-Shape Analysis. ^1H NMR spectra in CH_2Cl_2 or C_6H_5CN were recorded on a JEOL-PS-100 spectrometer equipped with a JNM-VT-3B variable-temperature controller in the −20 to +70 °C range and ^{13}C NMR spectra in $CDCl_3$ on JEOL FX-60 and FX-100 spectrometers at 27 °C. Tetramethylsilane was used as the internal standard in both cases. The sample solutions were degassed and sealed before measurements. They were allowed to stand with spinning in the NMR probe at least for 10 min before each measurement to ensure temperature equilibration. To maintain temperature stability, little adjustments in gas-flow and spinning rates were made. The sample temperature was determined from the chemical shift of methanol (low temperatures)[6] or 1,3-propanediol (high temperatures) on the basis of the calibration chart supplied from JEOL. Theoretical spectra were calculated on a NEAC 2200 Model N-700 and drawn by a NUMERICON System 7000. Rate constants of the rearrangement were determined by visual comparison of the experimental and theoretical spectra. Line widths at half-height, $H_{1/2}$, and chemical shift separations, $\Delta\nu$, in the region of broadening of the spectra were determined by linear interpolation of the plot $H_{1/2}$ vs. $1/T$ and by linear extrapolation of the plot $\Delta\nu$ vs. $1/T$ in the low-temperature region, respectively.

Results and Discussion

Figures 2a and 3a depict variable-temperature $t\text{-}C_4H_9$ and 2,6 ring proton spectra of two representative complexes: $[Rh(RNC)_4(TCNE)]ClO_4$ where $R = t\text{-}C_4H_9$ and $4\text{-}CH_3OC_6H_4$, in CH_2Cl_2, respectively. The $t\text{-}C_4H_9$ complex exhibits a simple coalescing doublet. Similar spectra were observed for five other $t\text{-}C_4H_9$ analogues and one CH_3 analogue in CH_2Cl_2 and/or C_6H_5CN. The 2,6 ring proton signals of the $4\text{-}CH_3OC_6H_4$ complex are considered as a superimposition of two coalescing doublets, each of which corresponds to the low-field components of AB-type quartets. Similar spectra were found for the analogous Co(I) complex. Thus, all nine $[M(RNC)_4(TCNE)]X$ type complexes examined exhibit dynamic ^1H NMR spectra in CH_2Cl_2 and C_6H_5CN in the 0–70 °C range; the limiting spectra were observed in the −20 to +17 °C range depending on the metal, isocyanide, etc. These spectra may be explained by the intramolecular rearrangement involving TCNE rotation coupled with the Berry pseudorotation (Figure 1), as described previously.[2] A similar rearrangement mode has been proposed for the $Fe(CO)_4$(olefin) type complexes.[7,8]

The ^{13}C NMR spectrum of $[Rh(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$ in $CDCl_3$ (0.15 M) containing $Cr(acac)_3$ (0.05 M) as a relaxation reagent[9,10] at 27 °C showed doublet signals due to the olefinic and isocyanide carbons at δ 13.7 ($J(^{103}Rh\text{-}^{13}C) = 12.5$ Hz) and δ 119.8 ($J(^{103}Rh\text{-}^{13}C) = 49.4$ Hz), respectively. This may rule out the possibility for the dissociative exchange both of the TCNE and of the isocyanide ligands in solution on the NMR time scale. For the analogous Co(I) complex, little dissociation of ligands is suggested from the fact that its charge-transfer band at 417 nm observed in CH_2Cl_2 at 25 °C obeys the Lambert–Beer law over the concentration range of $(0.29\text{–}3.27) \times 10^{-3}$ M.[4]

The rate constants for the rearrangement (k) were determined by the Gutowsky–Holm total line shape equation.[11] Computer-simulated line shapes were calculated by using Nakagawa's formulation[12] for the $t\text{-}C_4H_9$ and CH_3 complexes. Those of the $4\text{-}CH_3OC_6H_4$ complexes were calculated by the method of superimposition of two coalescing doublets.[13] Examples of the best fits between the observed and calculated spectra are illustrated in Figures 2 and 3. The plots of ln (k/T)

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Table I. Activation Parameters of the Intramolecular Rearrangement of $[M(RNC)_4(TCNE)]X$

expt	M	R	X	solvent	E_a(298 K), kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(deg mol)	$\Delta G^{\ddagger}$(298 K), kJ/mol
1	Co	t-C_4H_9	ClO_4	CH_2Cl_2	54.4 ± 0.8	51.9 ± 0.8	−53.1 ± 1.3	67.8 ± 1.3
2			PF_6		67.8 ± 1.7	65.3 ± 1.7	−21.3 ± 5.4	72.0 ± 2.5
3			BPh_4		77.4 ± 2.5	74.9 ± 2.5	4.2 ± 7.9	73.6 ± 3.3
4		4-$CH_3OC_6H_4$	ClO_4		52.3 ± 0.8	49.8 ± 0.8	−59.0 ± 2.9	67.4 ± 1.3
5	Rh	t-C_4H_9	ClO_4		66.1 ± 0.8	63.6 ± 0.8	−5.9 ± 2.9	65.3 ± 1.3
6			PF_6		71.5 ± 1.3	69.0 ± 1.3	11.7 ± 4.6	65.7 ± 2.1
7			BPh_4		74.1 ± 2.1	71.5 ± 2.0	31.8 ± 7.6	62.3 ± 2.9
8		4-$CH_3OC_6H_4$	ClO_4		68.2 ± 2.1	65.7 ± 2.0	−3.8 ± 6.7	66.5 ± 2.9
9	Co	t-C_4H_9	PF_6	C_6H_5CN	67.4 ± 0.8	64.9 ± 0.8	−18.4 ± 3.3	67.8 ± 1.3
10			BPh_4		57.3 ± 0.8	54.8 ± 0.8	−49.0 ± 2.5	69.5 ± 1.3
11	Rh	t-C_4H_9	PF_6		71.1 ± 1.7	68.6 ± 1.7	11.3 ± 5.9	65.3 ± 2.5
12			BPh_4		82.0 ± 1.3	79.5 ± 1.3	50.2 ± 3.8	64.4 ± 1.7
13		CH_3	BPh_4		87.0 ± 2.1	84.5 ± 2.1	51.0 ± 6.7	69.0 ± 2.9

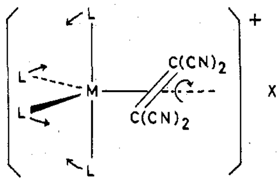

Figure 1. Possible mode of the intramolecular rearrangement of the $[ML_4(TCNE)]X$ type complexes (M = Co(I), Rh(I); L = isocyanide; TCNE = tetracyanoethylene; X = ClO_4, PF_6, BPh_4).

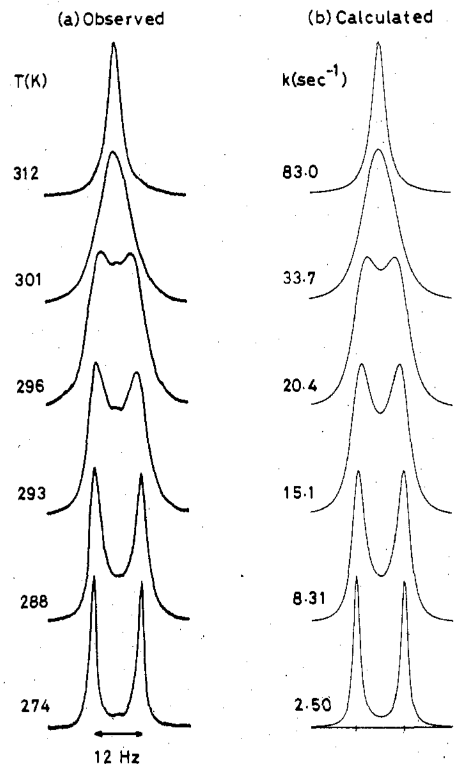

Figure 2. Observed and calculated spectra for the *tert*-butyl protons of $[Rh(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$ in CH_2Cl_2 (0.06 M).

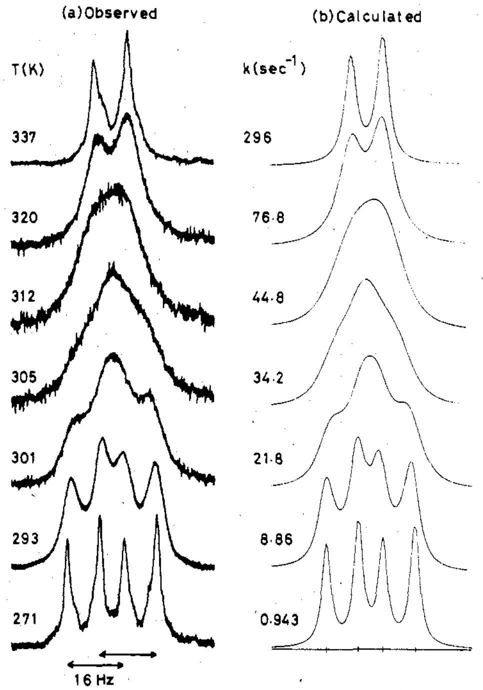

Figure 3. Observed and calculated spectra for the 2,6 ring protons of $[Rh(4\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$ in CH_2Cl_2 (0.06 M).

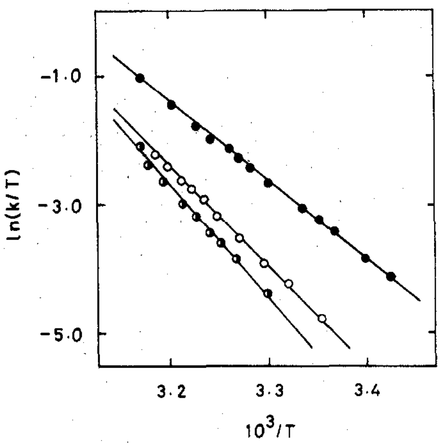

Figure 4. Eyring plots for exchange of the *tert*-butyl protons in $[Co(t\text{-}C_4H_9NC)_4(TCNE)]X$ in CH_2Cl_2 (0.06 M): X = ClO_4 (●), PF_6 (○), BPh_4 (◐).

against $1/T$ are displayed in Figure 4, from which the activation enthalpy and entropy, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained by the least-squares analyses. The results together with the activation energy and the Gibbs energy of activation, E_a ($=\Delta H^{\ddagger} + RT$) and $\Delta G^{\ddagger}$ ($=\Delta H^{\ddagger} - T\Delta S^{\ddagger}$), are collected in Table I.

The E_a values obtained for $[Co(RNC)_4(TCNE)]ClO_4$ in CH_2Cl_2 (54 kJ/mol when R = t-C_4H_9 and 52 kJ/mol when R = 4-$CH_3OC_6H_4$) are much larger than those of the corresponding $[Co(RNC)_5]ClO_4$, which should be very small because the ^1H NMR spectra have shown no evidence of restriction of the Berry pseudorotation in CH_2Cl_2 down to −96 °C.[14] The E_a values of the $[M(RNC)_4(TCNE)]X$ type complexes may, therefore, have significant contributions from the TCNE rotation. This is further supported by comparing the E_a values obtained for the present complexes (52–87 kJ/mol) with those of many pentakis(phosphite) complexes

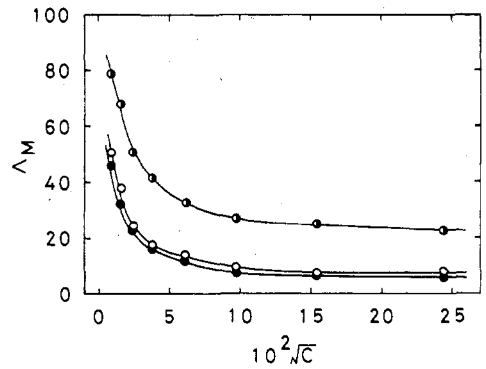

Figure 5. Molar conductance, Λ_M, of $[Co(t\text{-}C_4H_9NC)_4(TCNE)]X$ in CH_2Cl_2 at various concentrations, C, at 25 °C: X = ClO_4 (●), PF_6 (○), BPh_4 (◑).

Table II. Proportions, α, of the Ion Pair $[M(t\text{-}C_4H_9NC)_4(TCNE)]^+X^-$ in CH_2Cl_2 (0.06 M) at 25 °C

M	X	mol wt		α
		obsd	calcd	
Co	ClO_4	523	619	0.82
	PF_6	574	664	0.82
	BPh_4	666	838	0.74
Rh	ClO_4	609	663	0.91
	PF_6	680	709	0.96
	BPh_4	732	883	0.79

of d^8 transition metals (28–52 kJ/mol) which undergo the Berry pseudorotation alone.[15] A similar contribution of the olefin rotation to the E_a value has been proposed for the $Fe(CO)_4$(olefin) type complexes, whose E_a values (46–60 kJ/mol[7,8]) were larger than that of $Fe(CO)_5$ ($E_a < 20$ kJ/mol[16]).

It is to be noted that the E_a and $\Delta S^\ddagger$ values obtained for $[M(RNC)_4(TCNE)]X$ in CH_2Cl_2 increase in the order X = ClO_4 < PF_6 < BPh_4 (experiments 1–3 and 5–7 in Table I). The dependence of E_a values on X is rationalized in terms of the bulkiness of X; the counteranion seems to sterically restrict the intramolecular rearrangement of the $[M(RNC)_4(TCNE)]^+$ moieties, although it has been reported that the E_a values for $[Rh(P(OCH_3)_3)_5]X$ (X = noncoordinating anions) are not influenced by counteranions.[16] If one can neglect the solvent effect of CH_2Cl_2 as the first approximation, the dependence may be ascribed to the existence of ion pairs in solution. In fact, an appreciable amount of ion pairs is suggested to exist at the ^1H NMR concentration (0.06 M) from the electric conductivity measurements of $[Co(t\text{-}C_4H_9NC)_4(TCNE)]X$ (X = ClO_4, PF_6, BPh_4) (Figure 5) and from the molecular weight determinations of $[M(t\text{-}C_4H_9NC)_4(TCNE)]X$ (M = Co(I), Rh(I); X = ClO_4, PF_6, BPh_4) in CH_2Cl_2 (Table II). It should be noted that the variations of $\Delta S^\ddagger$ values from complex to complex exceed systematic errors. Such variations in $\Delta S^\ddagger$ may be consistent with the existence of ion pairs (in CH_2Cl_2), which will loosen more in transition states of the rearrangement in proportion to the bulkiness of X.

Comparison of experiments 1–3 with 5–7 (Table I) shows that the effect of counteranions on the activation parameters is more important in the Co complexes than in the Rh analogues. This is compatible with the smaller covalent radius of the Co atom (1.16 Å[17]) than that of the Rh atom (1.25 Å[17]). On the other hand, activation parameters are almost independent of the steric and/or electronic effects of the isocyanides (compare experiments 1 with 4, 5 with 8, and 12 with 13). The absolute values of $\Delta S^\ddagger$ obtained for all the complexes are not so large. Moreover, the rate constants (k) for the rearrangement of $[M(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$ (M = Co(I) and Rh(I)) are little dependent on the concentration at a given temperature below and above the coalescence temperature (Table III). These results are consistent with the intramolecular nature of the rearrangement of the $[M(RNC)_4(TCNE)]X$ type complexes.

Table III. Rate Constants (k) for the Rearrangement of $[M(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$ at Two Different Concentrations in CH_2Cl_2

M	T, K	k, s^{-1}	
		0.06 M	0.18 M
Co	304	11.5 ± 0.3	10.5 ± 0.3
	319	28.5 ± 1.0	26.9 ± 1.0
	333	90.5 ± 2.8	91.8 ± 3.2
Rh	288	8.29 ± 0.15	8.32 ± 0.30
	309	51.2 ± 2.7	49.6 ± 1.7
	318	112 ± 4	110 ± 5

Thus, it may be concluded that the barrier to the intramolecular rearrangement of the present complexes is mainly due to (i) the Berry pseudorotation, (ii) TCNE rotation around the coördination bond, and (iii) the formation of the ion pairs, although each contribution has not been estimated quantitatively in the present work. It seems, however, to be difficult to rationalize the activation parameters of $[Co(t\text{-}C_4H_9NC)_4(TCNE)]X$ (X = PF_6, BPh_4) in C_6H_5CN in terms of the effect of the counteranion. This may partly be due to a polar nature of the solvent, whose solvation of the complex may be an additional contribution to the intramolecular rearrangement.

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Registry No. $[Co(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$, 69653-29-8; $[Co(t\text{-}C_4H_9NC)_4(TCNE)]PF_6$, 69653-30-1; $[Co(t\text{-}C_4H_9NC)_4(TCNE)]BPh_4$, 69668-74-2; $[Co(4\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$, 69653-32-3; $[Rh(t\text{-}C_4H_9NC)_4(TCNE)]ClO_4$, 69653-34-5; $[Rh(t\text{-}C_4H_9NC)_4(TCNE)]PF_6$, 69653-35-6; $[Rh(t\text{-}C_4H_9NC)_4(TCNE)]BPh_4$, 69653-36-7; $[Rh(4\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$, 36682-31-2; $[Rh(CH_3NC)_4(TCNE)]BPh_4$, 51567-54-5.

References and Notes

(1) J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971).
(2) T. Kaneshima, K. Kawakami, and T. Tanaka, *Inorg. Chem.*, **13**, 2198 (1974).
(3) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry", Vol. VII, Interscience, New York, 1955.
(4) K. Kawakami and M. Okajima, submitted for publication.
(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(6) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968); **42**, 679 (1970).
(7) L. Kruczynski, L. K. K. LiShingMan, and J. Takats, *J. Am. Chem. Soc.*, **96**, 4006 (1974).
(8) S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 4038 (1974).
(9) E. L. Muetterties, *Inorg. Chem.*, **13**, 495 (1974).
(10) F. A. Cotton, K. Kanegynski, B. L. Sapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, **94**, 6191 (1972).
(11) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
(12) T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **39**, 1006 (1966).
(13) T. H. Siddall, III, W. E. Stewart, and F. D. Knight, *J. Phys. Chem.*, **74**, 3580 (1970).
(14) It was reported that there is no evidence (from ^{13}C and ^1H NMR spectra) of ligand inequivalence in $[Co(t\text{-}C_4H_9NC)_5]^+$ down to −160 °C, although the counteranion and solvent were not specified: E. L. Muetterties, *J. Chem. Soc., Chem. Commun.*, 221 (1973).
(15) J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5760 (1974).
(16) P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 7272 (1973), and references cited therein.
(17) J. A. Dean, Ed., "Lange's Handbook of Chemistry", 11th ed., McGraw-Hill, New York, 1973, pp 3–118.