# A Rate Study on the Oxidative Addition Reactions of Iodine toward Tetrakis(2,4,6-trimethylphenyl and *t*-butyl isocyanide)-rhodium(I) Perchlorates

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The reaction of $[RhL_4]ClO_4$ (L=2,4,6-$Me_3C_6H_2NC$ and *t*-BuNC) with an equimolar amount of iodine yields a *trans* adduct, $[RhI_2L_4]ClO_4$. The rate of this reaction in acetonitrile was measured employing a stopped-flow technique under pseudo-first-order conditions with excess iodine. The result indicates that the reaction proceeds *via* an intermediate which is presumably assigned to *cis*-$[RhI_2L_4]ClO_4$, followed by intramolecular isomerization to the *trans* adduct.

Kinetics of oxidative addition reactions of various molecules such as hydrogen[1,2] and olefins[2-4] to rhodium(I) substrates have been reported by several research groups. The rate of addition reaction of halogen to rhodium(I) complexes has, however, been little measured, although a number of halogen adducts with Rh(I) are known.[5-7] Our recent kinetic study[8] has shown that the addition of iodine to $Rh(S_2CNMe_2)$-(2,4,6-$Me_3C_6H_2NC)_2$ proceeds *via* a charge transfer complex formed between the sulfur atom of the $S_2CNMe_2$ ligand (donor) and iodine (acceptor), which is rearranged to *cis*-$RhI_2(S_2CNMe_2)$(2,4,6-$Me_3C_6H_2NC)_2$, followed by isomerization to the *trans* adduct with respect to the iodide anions. It is of interest to examine whether the formation of a *cis* adduct in advance of a *trans* one is general in the addition reaction of iodine to Rh(I) substrates.

This paper reports the rate study on the reactions of tetrakis(2,4,6-trimethylphenyl and *t*-butyl isocyanide)-rhodium(I) perchlorates, $[RhL_4]ClO_4$, with iodine giving *trans*-$[RhI_2L_4]ClO_4$.

## Experimental

*Materials and Spectra.* Iodine was sublimed three times. Acetonitrile and acetone were dried over phosphorus pentaoxide and Drierite, respectively. Dichloromethane was purified by the usual method.[9] $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]$-$ClO_4$ was prepared as follows; a methanol (10 ml) solution of 2,4,6-$Me_3C_6H_2NC$ (4 mmol) was added dropwise to a suspension of $[RhCl(1,5\text{-}C_8H_{12})]_2$ (0.5 mmol) in methanol (5 ml). The mixture was stirred for 2 h, followed by the addition of a methanol (10 ml) solution of sodium perchlorate monohydrate (2 mmol). The resulting precipitate was recrystallized from a mixture of dichloromethane with ligroin to give yellowish orange plates in a 73% yield. $\nu$(NC) 2142 $cm^{-1}$. $\lambda_{max}$ 402 nm ($\varepsilon$ 7500), 339 nm ($\varepsilon$ 56300), and 252 nm ($\varepsilon$ 66200). Found: C, 61.44; H, 5.74; N, 7.40%. Calcd for $C_{40}H_{44}ClN_4O_4Rh$: C, 61.35; H, 5.66; N, 7.15%. $[Rh(t\text{-}BuNC)_4]ClO_4$ was similarly prepared by the use of *t*-BuNC for 2,4,6-$Me_3C_6H_2NC$, 74% yield. $\nu$(NC) 2156 $cm^{-1}$. $\lambda_{max}$ 381 nm ($\varepsilon$ 9600) and 309 nm ($\varepsilon$ 27900). Found: C, 45.10; H, 6.83; N, 10.37%. Calcd for $C_{20}H_{36}ClN_4O_4Rh$: C, 44.91; H, 6.78; N, 10.47%.

Infrared and electronic spectra were measured with Hitachi-Perkin Elmer 225 and Hitachi 124 spectrophotometers, respectively. $^1H$ NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer.

*Equimolar Reaction of $[RhL_4]ClO_4$ (L=2,4,6-$Me_3C_6H_2NC$ and t-BuNC) with Iodine.* An acetonitrile (10 ml) solution of $I_2$ (0.5 mmol) was added to $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ (0.5 mmol) in acetonitrile (20 ml). After stirred for 1 h, the solution was evaporated to dryness under reduced pressure. The resulting product was recrystallized from dichloromethane–petroleum ether to give orange plates of $[RhI_2$-$(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ in an 87% yield. $\nu$(NC) 2216 $cm^{-1}$. $\lambda_{max}$ 391 nm ($\varepsilon$ 9500) and 256 nm ($\varepsilon$ 86000). Found: C, 46.44; H, 4.39; N, 5.19%. Calcd for $C_{40}H_{44}ClI_2N_4O_4Rh$: C, 46.33; H, 4.28; N, 5.40%.

$[RhI_2(t\text{-}BuNC)_4]ClO_4$ was similarly obtained by reaction of $[Rh(t\text{-}BuNC)_4]ClO_4$ with an equimolar amount of $I_2$ in acetonitrile, 68% yield. $\nu$(NC) 2231 $cm^{-1}$. $\lambda_{max}$ 384 nm ($\varepsilon$ 10000) and 277 nm ($\varepsilon$ 42000). Found: C, 30.85; H, 4.70; N, 6.99%. Calcd for $C_{20}H_{36}ClI_2N_4O_4Rh$: C, 30.46; H, 4.60; N, 7.10%.

*Reaction of $[RhL_4]ClO_4$ with Excess Iodine.* To an acetonitrile (10 ml) solution of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ (0.3 mmol) was added excess $I_2$ (3 mmol) in acetonitrile (25 ml). After stirred for 15 h, the solution was evaporated to dryness under reduced pressure. The product obtained was washed with diethyl ether to remove unreacted $I_2$, followed by recrystallization from dichloromethane–ligroin to give brown plates of $RhI_5(2,4,6\text{-}Me_3C_6H_2NC)_4$ in a 64% yield. $\nu$(NC) 2214 $cm^{-1}$. Found: C, 36.48; H, 3.28; N, 4.24%. Calcd for $C_{40}H_{44}I_5N_4Rh$: C, 36.45; H, 3.36; N, 4.25%.

$RhI_5(t\text{-}BuNC)_4$ was similarly obtained by reaction of $[Rh$-$(t\text{-}BuNC)_4]ClO_4$ with excess $I_2$ in acetonitrile, 66% yield. $\nu$(NC) 2227 $cm^{-1}$. Found: C, 22.43; H, 3.35; N, 5.28%. Calcd for $C_{20}H_{36}I_5N_4Rh$: C, 22.45; H, 3.29; N, 5.24%.

These complexes were also obtained by reaction of $[RhI_2L_4]$-$ClO_4$ with excess $I_2$.

*Kinetic Measurements.* Kinetic runs were carried out under pseudo-first-order conditions by mixing an acetonitrile solution of $[RhL_4]ClO_4$ ($2.0\times10^{-4}$ M) with excess $I_2$ in acetonitrile ($2.0-10.0\times10^{-3}$ M). The reaction rate was followed by measuring absorbances of the reaction mixture, using a Union RA-413 stopped flow-rapid scanning spectrophotometer equipped with a 0.2 cm quartz cell in a cell holder thermostated to $\pm0.2$ °C. At least five reaction curves were accumulated by a Union System-71 kinetic data processor and an average curve was recorded on a National VP-6421A X-Y recorder.

## Results and Discussion

*Characterization of the Iodine Adducts.* The four iodine adducts, $[RhI_2L_4]ClO_4$ and $RhI_5L_4$ (L=2,4,6-$Me_3C_6H_2NC$ and *t*-BuNC), exhibit only a $\nu$(N≡C) band, whose frequency is higher than that of the corresponding

Rh(I) substrate. This confirms the occurrence of oxidative addition reactions[8] of $I_2$ to Rh(I) with retention of $D_{4h}$ symmetry of the four isocyanide ligands centered at the metal. Thus, $[RhI_2L_4]ClO_4$ (L=2,4,6-$Me_3C_6H_2NC$, *t*-BuNC) assumes an octahedral geometry, in which the two iodide ligands are in mutual *trans* positions. A similar *trans* configuration was reported for $[RhI_2(t\text{-}BuNC)_4]PF_6$.[10] Complexes of the $RhI_5L_4$ type behave as electrolytes in acetonitrile; molar conductivities are 151 (L=2,4,6-$Me_3C_6H_2NC$, $1.0\times10^{-4}$ M) and 176 $cm^2\,ohm^{-1}\,mol^{-1}$ (L=*t*-BuNC, $1.0\times10^{-4}$ M). These complexes may be formulated as *trans*-$[RhI_2L_4]I_3$ since their $\nu$(NC) frequencies were essentially identical with those of the corresponding perchlorate salts and their electronic spectra in acetonitrile appeared as a superposition of the spectrum of the $I_3^-$ anion on that of the *trans*-$[RhI_2L_4]^+$ cation.

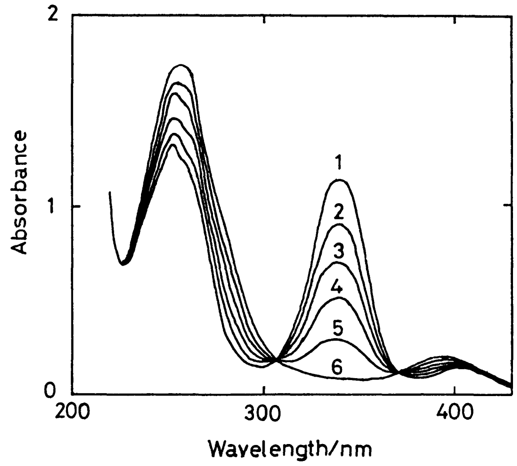
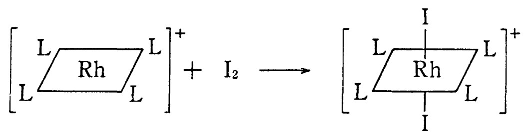



Fig. 1. Electronic spectra of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ ($2.0\times10^{-4}$ M) in acetonitrile containing varying amounts of iodine; (**1**) 0, (**2**) $0.4\times10^{-4}$ M, (**3**) $0.8\times10^{-4}$ M, (**4**) $1.2\times10^{-4}$ M, (**5**) $1.6\times10^{-4}$ M, (**6**) $2.0\times10^{-4}$ M; cell length=0.1 cm.

*Stoichiometry.* The electronic spectra of $[RhL_4]ClO_4$ in acetonitrile obeyed the Lambert-Beer law over the concentration range from $3\times10^{-6}$ to $4\times10^{-4}$ M. Self-association of these square-planar Rh(I) cations is, therefore, negligible in this range, though such phenomenon has been reported to occur in some Rh(I) complexes at relatively high concentrations.[11] Electronic spectra of acetonitrile solutions containing $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ and varying amounts of $I_2$ are shown in Fig. 1. The spectrum of a solution containing equimolar amounts of the Rh(I) substrate and $I_2$ (**6** in Fig. 1) was essentially same as that of an acetonitrile solution of the *trans*-$[RhI_2(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ adduct. In addition, there was seen no appreciable change in the spectrum even in a solution containing the Rh(I) substrate and $I_2$ with the mole ratio of 1:2. As shown in Fig. 2, the mole ratio method using the absorbances at 339 and 256 nm indicates the composition of the adduct to be 1:1. The same result was obtained in the $[Rh(t\text{-}BuNC)_4]ClO_4$–$I_2$ system. Thus, the stoichiometry for equimolar reaction of $I_2$ with the Rh(I) substrate is expressed by



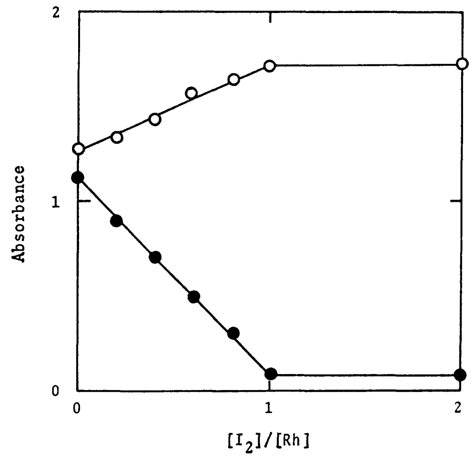



Fig. 2. A plot of the absorbances at 339 (●) and 256 nm (○) *vs.* the mole ratio $[I_2]/[\mathbf{Rh}]$ in acetonitrile; $[\mathbf{Rh}]=2.0\times10^{-4}$ M ($\mathbf{Rh}=[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$).

*Kinetics and Mechanism.* Rapid scanning spectra of the solution after mixing $[Rh(t\text{-}BuNC)_4]ClO_4$ ($2.0\times10^{-4}$ M) with excess $I_2$ ($2.0\times10^{-3}$ M) in acetonitrile is illustrated in Fig. 3, which shows decay of the absorption maxima at 282 and 376 nm both with half-lives of about 1 s. The spectrum finally obtained shows the absorption maxima at 277 and 384 nm due to *trans*-$[RhI_2(t\text{-}BuNC)_4]ClO_4$. As $[Rh(t\text{-}BuNC)_4]ClO_4$ and $I_2$ exhibit no band maximum at 282 and 376 nm, the bands observed at these wavelengths may be associated with a reaction intermediate which is formed during the dead time of the instrument. Similarly, an intermediate

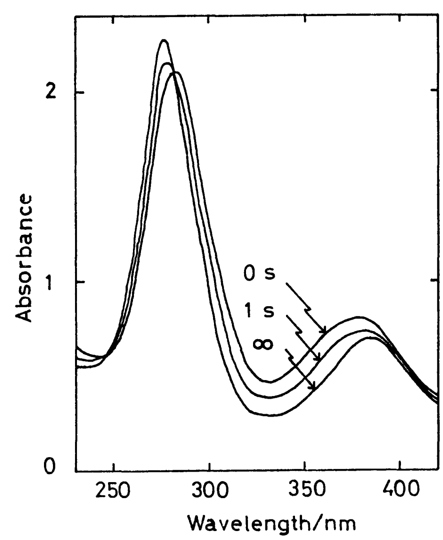
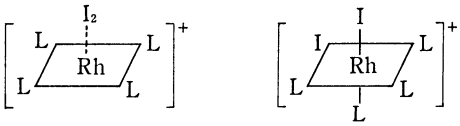



Fig. 3. Rapid scanning spectra after mixing $[Rh(t\text{-}BuNC)_4]ClO_4$ ($2.0\times10^{-4}$ M) with excess $I_2$ ($2.0\times10^{-3}$ M) in acetonitrile at 25.0 °C, cell length=0.2 cm.


Fig. 4. The $^1$H NMR spectrum of an equimolar mixture ($5.0\times10^{-2}$ M) of $[Rh(t\text{-}BuNC)_4]ClO_4$ and $I_2$ in acetonitrile-$d_3$ at $-40$ °C; the solution was prepared at this temperature.

with absorption maxima at 256 and 375 nm was observed in the reaction of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ with $I_2$. The discordant wavelengths of the short-lived absorptions observed in the two reaction systems imply that the intermediates are not a common species such as the $I_3^-$ anion.

In order to obtain some knowledge of the intermediate, $^1$H NMR and infrared spectra were measured for solutions of the mixture of reactants at low temperatures because the intermediate might be stabilized at low temperatures. Figure 4 shows the $^1$H NMR spectrum of an acetonitrile-$d_3$ solution containing equimolar amounts ($5.0\times10^{-2}$ M) of $[Rh(t\text{-}BuNC)_4]ClO_4$ and $I_2$ immediately after preparing at $-40$ °C. There appear two methyl signals, of which the upfield one is ascribed to the intermediate because this signal decreases in intensity with ascending temperature and disappears at $-10$ °C completely, while the downfield signal assignable to *trans*-$[RhI_2(t\text{-}BuNC)_4]ClO_4$ remains unchanged even at room temperature. Figure 5 shows the infrared spectra in the $\nu$(N≡C) region for two acetone solutions both containing equimolar quantities ($2.5\times10^{-2}$ M) of $[Rh(t\text{-}BuNC)_4]ClO_4$ and $I_2$; one was prepared by rapid introduction of the reactant solutions into a cell at $-60$ °C (solution **a**), and the other was prepared at room temperature, followed by cooling down to $-60$ °C (solution **b**). The 2231 cm$^{-1}$ band observed in **b** is attributable to *trans*-$[RhI_2(t\text{-}BuNC)_4]ClO_4$ because of its coincidence in position with the band of this compound in acetone at room temperature. The same assignment is given to the high frequency band (2231 cm$^{-1}$) found in **a**. On the other hand, the low frequency band (2217 cm$^{-1}$) may be due to the intermediate since it disappeared after solution **a** was allowed to stand at room temperature for more than 20 min and recooled to $-60$ °C. It is to be noted that the position of the 2217 cm$^{-1}$ band is 61 cm$^{-1}$ higher than that of $\nu$(N≡C) of the starting complex $[Rh(t\text{-}BuNC)_4]ClO_4$ (2156 cm$^{-1}$). The magnitude of this high frequency shift is larger than that observed in one electron oxidation (35—50 cm$^{-1}$) of some Rh(I)–isocyanide complexes, and is close to that in the two electron oxidation (65—80 cm$^{-1}$).[12] This indicates that the rhodium metal of the intermediate is oxidized with $I_2$. Thus, two possible configurations, **A** and **B**, are proposed for the intermediate, though the oxidation number of the rhodium metal in **A** is ambiguous. A configuration with metal–iodine interaction like **A** has been suggested as an intermediate in the reactions of $I_2$ with $Pt(acac)_2$[13] and $Me_3SnCr(CO)_3(\eta\text{-}C_5H_5)$,[14] although no direct spectral evidence for the existence of such an intermediate has been obtained, probably because of its low stability. On the other hand, the half-life of the intermediate (about 1 s) in the present reaction is compared with that of *cis*-$[Cr(CO)_2(Ph_2PCH_2PPh_2)_2]^+$ (about 0.6 s) which isomerizes to a *trans* cation.[15] In addition, the electronic spectrum of the present intermediate resembles that of the *trans* adduct (Fig. 3), suggesting that they are at least structurally similar to each other. This is supported from the similarity between the spectra of *cis*- and *trans*-$RuCl_2(4\text{-}MeC_6H_4NC)_2(PPh_3)_2$ prepared by the literature method,[16] as shown in Fig. 6. In view of these facts, the intermediate is presumably assigned to the *cis* adduct **B** in the present reactions.




**A**  **B**

Unsatisfactory solubility of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ in polar solvents such as acetonitrile and acetone at low temperatures has prevented $^1$H NMR and infrared spectral measurements, as described above, for the $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$–$I_2$ system.

The rate of reaction of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$ with $I_2$ was followed by measuring the decay of absorb-

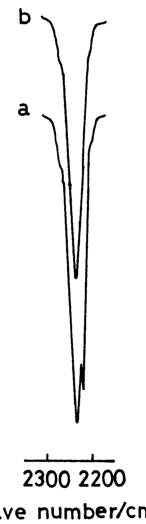



Fig. 5. Infrared spectra of acetone solutions containing equimolar quantities ($2.5\times10^{-2}$ M) of $[Rh(t\text{-}BuNC)_4]ClO_4$ and $I_2$ at low temperatures; **a** and **b** are the solutions prepared at $-60$ °C and at room temperature, respectively.

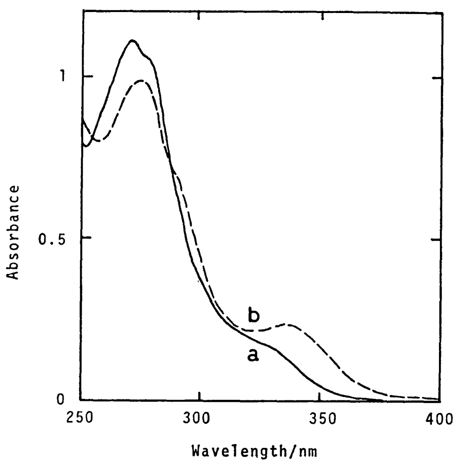



Fig. 6. Electronic spectra of acetonitrile solutions ($2.5\times10^{-5}$ M) of *cis*- (**a**) and *trans*-$RuCl_2(4\text{-}MeC_6H_4NC)_2(PPh_3)_2$ (**b**), cell length=1.0 cm.

TABLE 1. OBSERVED RATE CONSTANTS FOR THE REACTIONS OF $[RhL_4]ClO_4$ ($2.0\times10^{-4}$ M) WITH EXCESS $I_2$ IN ACETONITRILE[a)] AT VARIOUS TEMPERATURES

| Temp °C | $[I_2]$ $10^{-3}$ M | $k_{obsd}/s^{-1}$ L=2,4,6-$Me_3C_6H_2NC$ 360 nm | 300 nm | L=*t*-BuNC 290 nm |
|---|---|---|---|---|
| 15.0 | 2.0 | 0.193 | 0.196 | 0.206 |
| | 4.0 | 0.191 | 0.202 | 0.182 |
| | 6.0 | 0.189 | 0.201 | 0.172 |
| | 8.0 | 0.193 | 0.194 | 0.170 |
| | 10.0 | 0.208 | 0.210 | 0.196 |
| | Mean | $0.198\pm0.005$ | | $0.185\pm0.011$ |
| 19.9 | 2.0 | 0.360 | 0.327 | 0.336 |
| | 4.0 | 0.322 | 0.357 | 0.331 |
| | 6.0 | 0.343 | 0.360 | 0.313 |
| | 8.0 | 0.329 | 0.379 | 0.316 |
| | 10.0 | 0.336 | 0.347 | 0.325 |
| | Mean | $0.346\pm0.012$ | | $0.324\pm0.007$ |
| 25.0 | 2.0 | 0.604 | 0.564 | 0.555 |
| | 4.0 | 0.582 | 0.641 | 0.561 |
| | 6.0 | 0.602 | 0.638 | 0.549 |
| | 8.0 | 0.581 | 0.605 | 0.516 |
| | 10.0 | 0.579 | 0.606 | 0.558 |
| | Mean | $0.600\pm0.017$ | | $0.548\pm0.012$ |
| 30.1 | 2.0 | 0.954 | 0.980 | 0.916 |
| | 4.0 | 1.001 | 0.924 | 0.897 |
| | 6.0 | 0.991 | 0.988 | 0.843 |
| | 8.0 | 0.967 | 0.982 | 0.873 |
| | 10.0 | 0.926 | 0.942 | 0.900 |
| | Mean | $0.966\pm0.019$ | | $0.886\pm0.019$ |

a) In dichloromethane, $k_{obsd}$ values for the reactions of $[RhL_4]ClO_4$ ($2.0\times10^{-4}$ M) with $I_2$ ($2.0\times10^{-3}$ M) are 2.98 $s^{-1}$ (L=2,4,6-$Me_3C_6H_2NC$) and 7.08 $s^{-1}$ (L=*t*-BuNC) at 25.0 °C.

ances at both 360 and 300 nm after mixing their acetonitrile solutions. With $[Rh(t\text{-}BuNC)_4]ClO_4$, the reaction was monitored by the absorbance at 290 nm. Plots of $\ln(A_t-A_\infty)$ *vs.* time were found to be linear, where $A_t$ and $A_\infty$ are absorbances at the time "*t*" and at the end of reaction. Pseudo-first-order rate constants, $k_{obsd}$, were obtained by the least-squares method. The results are shown in Table 1. The $k_{obsd}$ value in each reaction is essentially independent of the concentration of $I_2$ at a given temperature. This is consistent with the assumption that the reaction of $[RhL_4]ClO_4$ with $I_2$ proceeds *via* the *cis* adduct. Furthermore, the formation of the *cis* adduct as an intermediate is compatible with the result that the $k_{obsd}$ value is considerably larger in dichloromethane than in acetonitrile (see the footnote of Table 1), owing to destabilization of the *cis* adduct more polar than the *trans* one in less polar solvent dichloromethane. Thus, the present reaction may be expressed by Eq. 1 which involves *cis-trans* isomerization.

$$[RhL_4]ClO_4 + I_2 \xrightarrow{k} cis\text{-}[RhI_2L_4]ClO_4 \xrightarrow{k'} trans\text{-}[RhI_2L_4]ClO_4 \quad (1)$$

As the first step, though it has not been clarified mechanistically in the present study, is much faster than the second one, $k_{obsd}$ is equal to $k'$.

The Arrhenius plots gave activation parameters for the *cis-trans* isomerization: $\Delta H^{\ne}_{298}=74.0\pm1.3$ kJ mol$^{-1}$, $\Delta S^{\ne}_{298}=-1.3\pm4.2$ J mol$^{-1}$ K$^{-1}$ for the $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]ClO_4$–$I_2$ system, and $\Delta H^{\ne}_{298}=73.6\pm1.6$ kJ mol$^{-1}$, $\Delta S^{\ne}_{298}=-3.2\pm5.4$ J mol$^{-1}$ K$^{-1}$ for the $[Rh(t\text{-}BuNC)_4]ClO_4$–$I_2$ system. The small negative values of $\Delta S^{\ne}_{298}$ in both reactions suggest the isomerization to proceed intramolecularly, probably *via* a twist mechanism. Moreover, the $\Delta H^{\ne}_{298}$ values obtained are compared with that of the *cis-trans* isomerization of $RhI_2(S_2CNMe_2)(2,4,6\text{-}Me_3C_6H_2NC)_2$(75.5 kJ mol$^{-1}$),[8)] reinforcing the assignment of the intermediate as *cis*-$[RhI_2L_4]ClO_4$.

Finally, it should be mentioned that the formation of *trans*-$[RhI_2L_4]ClO_4$ was followed by a much slower reaction which takes about 8 h to completion at 28 °C, giving *trans*-$[RhI_2L_4]I_3$. This reaction, however, has not been kinetically analyzed because we have been interested in the addition reaction.

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