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Oxidative Addition of α-Bromo Esters to Tetrakis(isocyanide) Rhodium(I) Complexes. Evidence for a Chain Mechanism

Sei Otsuka and Kikuo Ataka

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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The oxidative additions of chiral alkyl halides, (*S*)-(−)-ethyl α-bromopropionate $[\alpha]_D$ −18.9° (*c* 3.3, $CHCl_3$) and (*S*)-(+)-ethyl α-phenylbromoacetate $[\alpha]_D$ +56.4° (*c* 1.6, C_2H_5OH) to $[Rh(R'NC)_4]^+$ (R′=*t*-Bu, *p*-$CH_3C_6H_4$) produced the corresponding adducts, *trans*-$[RhBr(R)(R'NC)_4]^+$ (R=CH_3CHCO_2Et, $PhCHCO_2Et$), which were well characterized by elemental analysis, IR and ^1H NMR spectra. These adducts were found optically inactive, a fact which precludes a concerted mechanism. The reaction of $C_6H_5CHBrCO_2C_2H_5$ with $[Rh(t\text{-}BuNC)_4]^+$ commenced immediately in the absence of light. Taking this system as a typical example, the rate was studied by the stopped-flow method to find a rate equation, $R=k[Rh(I)]^2[RX]$. The relative rate of addition of *p*-$XC_6H_4CHBrCO_2C_2H_5$ to $[Rh(t\text{-}BuNC)_4]^+$ decreases in an order of Cl>H>CH_3 for X. The addition of $C_6H_5CHBrCO_2C_2H_5$ to $[Rh(p\text{-}CH_3C_6H_4NC)_4]^+$ in the dark proceeds only slowly, but rapidly under a low energy photo-irradiation (440 nm) with a large quantum yield (Φ 4.8). The addition of $CH_3CHBrCO_2C_2H_5$ requires photo-initiation. The optical activity of (*S*)-(−)-$CH_3CHBrCO_2C_2H_5$ was completely lost before the oxidative addition commenced. The rate of decrease in optical activity of the system (*S*)-(−)-$C_6H_5CHBrCO_2C_2H_5$/$[Rh(t\text{-}BuNC)_4]^+$ exhibited approximate second order kinetic behavior, and quantitative racemization took place prior to the completion of the oxidative addition. A chain mechanism appears to be consistent with all these results. Alternate mechanisms are also discussed in the light of the present results.

So called oxidative additions have received widespread interest in recent years from the stand point of their novelty as a new class of transition metal reactions and of their significance in homogeneous catalytic reactions.$^{1)}$ A number of papers have reported mechanistic studies on the alkyl halide addition reaction yielding divergent conclusions. Halpern's group$^{2)}$ and others$^{3,4)}$ proposed a linear dipolar transition state $M^+\cdots R\cdots X^-$ similar to that involved in the Menschutkin reaction. Ugo$^{5)}$ *et al.* have invented a somewhat sophisticated version of a multi-center mechanism, *i.e.* a non-concerted polar three center S_N2 attack. In contrast to these views is the radical mechanism proposed by Osborn.$^{6-9)}$ Lappert's$^{10)}$ group has detected a radical in the system, MeI/*t*-BuNO/Pt(O). Recently Stille$^{11,12)}$ *et al.* reported the stereospecific oxidative addition of chiral C_6H_5CHDCl to Pd(O) complexes. Kinetic studies on the addition of alkyl halides to Ir(I)$^{5,13,14)}$ or Rh(I)$^{15-17)}$ complexes gave a general impression in favor of the polar mechanism. Doubtless the mechanisms will depend on the electronic and steric characteristics of reactants involved and also on the nature of solvent.

The stereochemical course of addition should be related to the structure of the transition state and to the timing of bond-forming and bond-breaking processes. Our previous study$^{18)}$ on the addition of an optically active *s*-alkyl bromide, $CH_3CHBrCO_2C_2H_5$ or $C_6H_5CHBrCO_2C_2H_5$, to a strong nucleophile, "Pd(*t*-BuNC)$_2$", indicates loss of the stereochemical integrity at the chiral carbon. Pearson *et al.*$^{19)}$ reported that addition of $CH_3CHBrCO_2C_2H_5$ to Ir(I) was stereospecific, but Osborn$^{7)}$ *et al.* reexamined this reaction to show that the adduct has no optical activity. We were able to isolate the oxidative adducts from the reaction of two chiral *s*-alkyl halides, (*S*)-(−)-$CH_3CHBrCO_2C_2H_5$ and (*S*)-(+)-$C_6H_5CHBrCO_2C_2H_5$ with $[Rh(R'NC)_4]^+$ (R′=*t*-Bu, *p*-$CH_3C_6H_4$). The adducts, however, showed no optical activity. Various other experimental facts were then collected to elucidate the reaction mechanism. The study has led to a discovery of a dramatic effect of low-energy photo-irradiation in the alkyl halide addition, a fact intelligible in terms of a chain reaction. In this paper we also describe a few other interesting observations consistent with the chain mechanism.

Experimental

IR spectra were measured with a Hitachi-Perkin Elmer 225, UV spectra with a Hitachi EPS-3T, ^1H NMR spectra with a Jeol JNM-4H-100 or JNM-C60-HL, ESR spectra with a JES-ME-2X and optical rotation with a JASCO DIP-SL equipped with an automatic recorder using a 0.5 dm, 5ϕ mm cell incorporating a three way stop cock allowing measurements to be carried out in an inert atmosphere. Solvents were dried and distilled under nitrogen. All reactions and manipulations were carried out under a pure nitrogen atmosphere.

Preparation of Starting Materials. "Pd(*t*-BuNC)$_2$",$^{20)}$ $[Rh(t\text{-}BuNC)_4]BPh_4$$^{21)}$ and $[Rh(p\text{-}CH_3C_6H_4NC)_4]BPh_4$$^{21)}$ were prepared by known methods. (*S*)-(−)-Ethyl α-bromopropionate, $[\alpha]_D$ −18.9° (*c* 3.3; $CHCl_3$), was prepared from L-alanin according to the conventional method.$^{22)}$ The optical purity was estimated to be about 38%. (*S*)-(+)-Ethyl phenylbromoacetate, [α] +56.4° (*c* 1.75; C_2H_5OH), was prepared from (−)-ethyl mandelate by bromination with PBr_3.$^{23)}$ The rotation was about 70% of the highest literature value.$^{23)}$ Methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate was prepared by the reaction of methyl α-bromoacrylate with diazodiphenylmethane.$^{24)}$ *d*-3-*endo*-Bromocamphor was a commercial product of which stereochemical purity was found by ^1H NMR to be 95%. *d*-3-*endo*-Iodocamphor was prepared by known method from *d*-3-*endo*-bromocamphor.$^{25)}$

Kinetic Experiments. The initial rates were measured in CH_2Cl_2 with a stopped-flow spectrophotometer (Union RA-1100) by following the intensity of the 440 nm absorption band (ε=358) of $[Rh(t\text{-}BuNC)_4]^+$ at 25±0.5 °C.

The initial concentration of $C_6H_5CHBrCO_2C_2H_5$ being kept at 0.16 M, the concentration of $[Rh(t\text{-}BuNC)_4]^+$ was varied over a range of 3.2—11×10^{-3} M. Similarly, with an initial concentration of 0.16×10^{-2} M for $[Rh(t\text{-}BuNC)_4]^+$, the concentration of $C_6H_5CHBrCO_2C_2H_5$ was varied from 7.8×10^{-2} M to 2.7×10^{-1} M. Generally a short induction period (3—20 s) was observed. It was found in case of the addition of $CH_3CHBrCO_2C_2H_5$ to [Rh(*t*-BuNC)$_4$]$^+$ that the light (440 nm) used to monitor the reaction initiates the addition with some induction periods. After the commencement of the reaction, the spectrum showed a diffusion controlled process preventing determination of the kinetic orders (see Text).

The rates of decrease in optical rotation during slow addition of α-bromoesters were followed by the polarimetric measurement of the $[\alpha]_D$ values. A dichloromethane solution of a mixture of [Rh(*t*-BuNC)$_4$]$^+$ and the α-bromoesters was prepared and an aliquot was immediately transferred to the cell. The rotation was measure at 20 °C using the following two solutions; one containing 1.9×10^{-2} M of [Rh(*t*-BuNC)$_4$]$^+$ plus 2.0×10^{-2} M of $C_6H_5CHBrCO_2C_2H_5$ and other containing 0.10 M of [Rh(*t*-BuNC)$_4$]$^+$ plus 0.98 M of $CH_3CHBrCO_2C_2H_5$. The initial rates could not be measured accurately because a few minutes were required to secure a stable response on the polarimeters.

Addition of (S)-(−)-*Ethyl α-Bromopropionate to* [*Rh*(t-*BuNC*)$_4$]-*BPh*$_4$. (*S*)-(−)-Ethyl α-bromopropionate (44 mg, 0.22 mmol) was added to a solution of [Rh(*t*-BuNC)$_4$]BPh$_4$ (150 mg, 0.2 mmol) in 2 ml of CH_2Cl_2 at room temperature. When the reaction mixture was stirred under diffused sun light, the yellow color rapidly (within a few min) faded yielding a colorless solution. After stirring was continued for 2 h, the mixture was concentrated. Treatment of the concentrate with a few ml of hexane allowed isolation of *trans*-[RhBr(CH$_3$CHCO$_2$C$_2$H$_5$)(*t*-BuNC)$_4$]BPh$_4$ (**1**), as colorless powder (130 mg, 70%), which showed no optical activity in $CHCl_3$ at 24°. Recrystallization from methanol gave an analytically pure sample, mp 110—111° dec. The mother liquor from the above concentrate contains approximately equimolar amounts of ethyl acrylate and ethyl propionate as detected by GLC.

Addition of (S)-(+)-*Ethyl Bromophenylacetate to* [*Rh*(t-*BuNC*)$_4$]-*BPh*$_4$. To a suspension of [Rh(*t*-BuNC)$_4$]BPh$_4$ (160 mg, 0.21 mmol) in ethanol (5 ml) was added (*S*)-(+)-ethyl phenylbromoacetate (60 mg, 0.25 mmol) at room temperature. The reaction appears to occur immediately even in dark. After stirring for a few hours, the reaction mixture yielded the adduct, *trans*-[RhBr(PhCHCO$_2$C$_2$H$_5$)(*t*-BuNC)$_4$]BPh$_4$ (**2**) as a pale yellow precipitate (190 mg, 90%) which was separated, washed with hexane, and dried *in vacuo*. The optical activity was totally lost. Recrystallization from methanol gave an analytically pure sample, mp 118—119° dec.

Addition of (S)-(−)-*Ethyl α-Bromopropionate to* [*Rh*(p-*CH*$_3$*C*$_6$*H*$_4$*NC*)$_4$]*BPh*$_4$. Similar to the above, reaction of [Rh(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$ (251 mg, 0.28 mmol) with an excess of ethyl α-bromopropionate (0.21 ml, 1.6 mmol) was carried out under irradiation of tungsten lamp (500 W) in CH_2Cl_2 solution at room temperature for 2 h. The product obtained was optically inactive *trans*-[RhBr(CH$_3$CHCO$_2$C$_2$H$_5$)(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$ (**3**), colorless crystals, recrystallized from a methanol-ethanol system, mp 140—145° dec (115 mg, 36% yield). The reaction does not take place in the absence of light.

Addition of (S)-(−)-*Ethyl Phenylbromoacetate to* [*Rh*(p-*CH*$_3$*C*$_6$*H*$_4$*NC*)$_4$]*BPh*$_4$. The reaction of [Rh(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$ (144 mg, 0.16 mmol) with ethyl phenylbromoacetate (150 mg, 0.6 mmol) in CH_2Cl_2 occurs rapidly under irradiation with decoloration producing the adduct, *trans*-[RhBr(C$_6$H$_5$CHCO$_2$C$_2$H$_5$)(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$. (**4**), as pale yellow crystals, recrystallized from ethanol (80 mg, 45% yield).

Reaction of d-*3*-endo-*Bromocamphor with "Pd*(t-*BuNC*)$_2$". To a suspension of "Pd(*t*-BuNC)$_2$" (530 mg, 1.9 mmol) in ether (40 ml) was added at −70 °C *d*-3-*endo*-bromocamphor (460 mg, 2 mmol). The temperature was allowed to rise to 0 °C and stirring was continued for 4 h at 0 °C to give a slurry. The slurry was filtered and the solid was washed with cold ether (50 ml). The combined ether solution was concentrated to give ,on cooling to −20°, an adduct as almost colorless crystals (520 mg, 53%), mp. 114° (dec). ^{1}H NMH (CDCl$_3$): a double doublet peak at τ 6.5 (M–CH).

Found: C, 46.6; H, 6.50; N, 5.64%. Calcd for $C_{20}H_{25}N_2OBrPd$: C, 47.7; H, 6.60; N, 5.56%.

Rection of d-*3*-endo-*Iodocamphor with* [*Rh*(p-*CH*$_3$*C*$_6$*H*$_4$*NC*)$_4$]-*BPh*$_4$. A mixture of the Rh(I) compound (670 mg, 0.75 mmol) and iodocamphor (230 mg, 0.75 mmol) in ethanol-dichloromethane (2 : 1, 10 ml) was stirred overnight to give a yellow brown slurry. Filtration gave the adduct as pale yellow crystals (430 mg, 49%) mp 140—143° (dec).

Found: C, 67.7; H, 5.38; N, 4.71%. Calcd for $C_{66}H_{63}N_4BIORh$: C, 67.8; H, 5.43; N, 4.79%.

Quantum yield for the Reaction of [*Rh*(p-*CH*$_3$*C*$_6$*H*$_5$*NC*)$_4$]*BPh*$_4$ *with C*$_6$*H*$_5$*CHBrCO*$_2$*C*$_2$*H*$_5$. Noyes's method was essentially followed.[26] The photo-reaction was carried out using the following optical system; a 150 W Xenon lamp, a slit, a lens for paralleling the beam, a filter cutting off ultraviolet light shorter than 350 nm, and a square window of *ca.* 2 cm^2. Two 1 cm quartz cells, one for the reaction mixture and another for the actiometer, were placed so as to successively receive the incident light. A mixture of 40 ml of K$_3$[Fe(C$_2$O$_4$)$_3$] (5.2×10^{-2} M) in 1/2 M sulfuric acid and 10 ml of a buffer solution containing acetic acid (1 M) and sodium acetate (1 M) was used as the actinometer solution.[27] The quantity of Fe^{2+} ion formed by irradiation was measured colorimetrically as the 1,10-phenanthroline complex (λ_{max} 510 nm). Irradiating the solution containing [Rh(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$ (1.8×10^{-3} M) and $C_6H_5CHBrCO_2C_2H_5$ (1.1×10^{-2} M) in dichloromethane for 180 s, the concentration of the unreacted Rh(I) complex was determined by measuring the absorption at 462 nm. Correction was made by measuring the difference in concentration of the Rh(I) complex between the irradiated sample and the unirradiated one as the blank. The quantum yield (Φ) was calculated by the equation, $\Phi = A/I\cdot F$, where A is the number of the Rh(III) molecules formed by the photo-reaction, I the number of photons entering the reaction cell, and F the fraction of photons absorbed by the reaction mixture.[26]

Spin Trap Experiment. ESR samples, *e.g.*, a mixture of [Rh(*t*-BuNC)$_4$]BPh$_4$, RBr (R=C$_6$H$_5$CHCO$_2$C$_2$H$_5$, CH$_3$CHCO$_2$C$_2$H$_5$) and *t*-BuNO in CH_2Cl_2, was prepared in a 50 ml flask in the dark under pure nitrogen. The solutions (1.3—1.5×10^{-3} M for each component) were transferred to the 2 mm ESR tubes by syringe, and the measurement was carried out for a temperature range 77—300 K.

ESR Measurement. A sample solution was prepared by mixing two dichloromethane solutions of [Rh(*p*-CH$_3$C$_6$H$_4$NC)$_4$]BPh$_4$ (1.1×10^{-2} M) and $C_6H_5CHBrCO_2C_2H_5$ (4.4×10^{-2} M) of equal volume at room temperature. After standing for a few minutes under diffuse sunlight, the mixture was chilled to 195 K. ESR measurements (X band) were carried out at 77, 200, 240 K, and room temperature. Signals were difficult to detect at 77 K. Broad signals of weak intensities centered at $g=2.14$ were observed above 200 K, the hyperfine structure being unresolved.

Results

Product Characterization. The reaction of the cationic square planar complexes [Rh(R′NC)$_4$]$^+$(R′=

TABLE 1. PROPERTIES AND ANALYTICAL DATA OF $[RhBr(R)L_4]BPh_4$

	Compound	Color	Mp °C[a]	Found %				Calcd %			
				C	H	N	Br	C	H	N	Br
1	$[RhBr(CH_3CHCO_2C_2H_5)$-$(t$-$BuNC)_4]BPh_4$	colorless	110—111	62.60	7.01	6.08	8.32	62.89	7.00	5.99	8.31
2	$[RhBr(C_6H_5CHCO_2C_2H_5)$-$(t$-$BuNC)_4]BPh_4$	colorless	118—119	65.03	6.83	5.64	8.33	65.00	6.77	5.62	8.01
3	$[RhBr(CH_3CHCO_2C_2H_5)$-$(p$-$CH_3C_6H_4NC)_4]BPh_4$[b]	pale yellow	140—145	66.85	5.31	5.11	—	66.20	5.24	5.02	—
4	$[RhBr(C_6H_5CHCO_2C_2H_5)$-$(p$-$CH_3C_6H_4NC)_4]BPh_4$	pale yellow	120	70.25	5.16	5.00	7.65	69.91	5.24	4.94	7.05

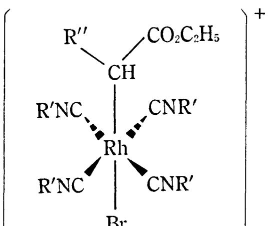
a) All compounds decompose without melting at the temperature. b) Containing crystallization solvent (1/2 CH_2Cl_2).

TABLE 2. SPECTRAL DATA OF $[RhBr(R)L_4]BPh_4$

Compound	IR, cm^{-1} a)		NMR, τ b)				
	$\nu_{N\equiv C}$	$\nu_{C=O}$	t-Bu,	$C\underline{H}_3C_6H_4$,	M-C$\underline{H}$,	C$\underline{H}_3$-CH	$^2J_{Rh-H}$, Hz
1	2240	1710	8.45(s)		5.7(m)	8.60(d)	c)
2	2210	1715	8.55(s)		5.68(d)		3.0
3	2220	1703		7.60(s)	5.90(q,d)	8.39(d)[d]	2.7
4	2220	1713		7.59(s)	5.05(d)		2.8

a) Measured in Nujol mull. b) Measured in $CDCl_3$. TMS as internal reference. Multiplicity is indicated in parentheses. c) Not fully resolved. d) This CH_3 peak appears as doublet-doublet pattern presumably due to $^3J_{Rh-H} \approx 1.5$ Hz.

t-Bu, *p*-$CH_3C_6H_4$) with $CH_3CHBrCO_2C_2H_5$ or C_6H_5-$CHBrCO_2C_2H_5$ in CH_2Cl_2 produces the corresponding thermally unstable adducts, *trans*-$[RhBr(CHR''CO_2C_2H_5)(R'NC)_4]^+(R''=CH_3,\ C_6H_5)$ as characterized by the elemental analysis, and IR and ^1H NMR spectra (Tables 1, 2). The *trans* geometry is deduced from the IR spectra which contain only one N≡C stretching absorption. Consistently the ^1H NMR spectra show one singlet signal for the *t*-butyl or *p*-methyl protons of the four isocyanide ligands. The NC stretching frequencies of the adducts **1**—**4** are higher than those of the corresponding starting complex $[Rh(t\text{-}BuNC)_4]^+$ (2170 cm^{-1}) or $[Rh(p\text{-}CH_3C_6H_4NC)_4]^+$ (2190 cm^{-1}) reflecting the oxidation state, Rh(III). The CO stretching vibration of the carboxylate group in the adducts shifts to the lower frequency region compared to that of free ester (1740 cm^{-1} for $CH_3CHBrCO_2C_2H_5$ or 1750 cm^{-1} for $C_6H_5CHBrCO_2C_2H_5$). Thermal decomposition of **1** or **3** takes place at 80 °C during a few hours yielding ethyl propionate and ethyl acryate indicating β-hydrogen elimination. The optical rotation of adducts **1**—**4**, measured immediately after the solution make-up below 20 °C, was still zero.



1 $R'=t$-Bu, $R''=CH_3$
2 $R'=t$-Bu, $R''=C_6H_5$
3 $R'=p$-$CH_3C_6H_4$, $R''=CH_3$
4 $R'=p$-$CH_3C_6H_4$, $R''=C_6H_5$

Methyl 1-bromo-2, 2-diphenylcyclopropanecarboxylate does not react with $[Rh(t\text{-}BuNC)_4]^+$ or with a stronger nucleophile, "$Pd(t\text{-}BuNC)_2$". Other halocycloalkanes, *e. g.* 3-*endo*-halocamphor, react with the low valent metal complexes. Thus, *d*-3-*endo*-bromocamphor reacts with "$Pd(t\text{-}BuNC)_2$" to give an adduct $[PdBr\text{-}(\eta^1\text{-}3\text{-}camphor)(t\text{-}BuNC)_2]$ which retains the *endo* form. The conformation can be readily established by the ^1H NMR of the methine signal at the 3-position which shows a double doublet pattern ($^3J_{HH}=4$ Hz, $^4J_{HH}=1.3$ Hz). It has been established[28] that the *exo* proton at the 3-position couples with the methine proton at the 4-position and the *exo* proton at the 5-position, but the *endo* proton does not couple with the proton at the 4-position, because of the bond angle of nearly 90 °C. $[Rh(t\text{-}BuNC)_4]^+$ reacts with 3-*endo*-iodocamphor at ambient temperature to give an adduct whose conformation could not be determined from the key ^1H NMR signal due to the complexity induced by the coupling with ^{103}Rh. Interestingly, it fails to react with 3-*endo*-bromocampher under diffused light. *erythro*-1-Bromo-3,3-dimethyl-1,2-didueteriobutane does not react with $[Rh(t\text{-}BuNC)_4]^+$ or "$Pd(t\text{-}BuNC)_2$".

Photochemical Effects. Unexpectedly, the addition reaction of $CH_3CHBrCO_2C_2H_5$ to $[Rh(RNC)_4]^+$ ($R'=t$-Bu, *p*-$CH_3C_6H_4$) does not take place in the absence of light, as indicated by the IR NC stretching absorption which shows no change over a day or two at room temperature, reflecting the retention of the oxidation state Rh(I). There is, however, some indication in the ^1H NMR spectrum for complexation of the bromo ester as will be described later. On exposure to light the addition occurred with an induction period ranging from a few minutes to half an hour, depending on the intensity of light. Remarkably, this irradiation effect was observed even with a low-energy light beam

(440 nm) used for monitoring the concentration of the species $[Rh(t\text{-}BuNC)_4]^+$. Generally, the induction period is followed by a very rapid addition reaction which prevents an accurate kinetic measurement and intelligible analysis. A photo-initiation was required for the reaction of $[Rh(p\text{-}CH_3C_6H_4NC)_4]BPh_4$ with both of the α-bromo esters; under irradiation with a 500 W tungsten lamp the reaction of $C_6H_5CHBrCO_2C_2H_5$ is complete within a few minutes and that of $CH_3CHBrCO_2C_2H_5$ within one hour. The quantum yield of the photo-reaction of the former system was estimated to be 4.8, implying a chain mechanism. Since the addition of $CH_3CHBrCO_2C_2H_5$ to $[Rh(R'NC)_4]BPh_4$ ($R'=t\text{-}Bu$, $p\text{-}CH_3C_6H_4$) exhibits an induction period even under photo-irradiation, it was impossible to obtain the quantum yield.

Mechanistic Features. The reaction of $C_6H_5CHBrCO_2C_2H_5$ with $[Rh(t\text{-}BuNC)_4]^+$ does not require photo-initiation. However, the oxidative addition shows an induction period ranging from a few seconds to half a minute depending on the concentration of substrates. The intensity of the absorption at 440 nm of the reaction mixture increased slightly during the induction period. After the induction period, the rate was found, by differential analysis, to be first order with respect to the alkyl halide, while it approximated an order of 1.5 with respect to Rh(I). Integral analyses of a few typical runs using a large excess of the alkyl halide (*e. g.* $[Rh(I)]=1.6\times10^{-2}$ M, $[RBr]=0.22$ M) revealed pseudo second-order dependence on [Rh(I)]. Thus the overall rate roughly follows the following rate equation:

$$R = k[Rh(I)]^2[RX].$$

Perhaps the accuracy of the differential analysis suffers from the occurrence of the induction period. Addition of 1—3 mol of free *t*-BuNC to system $RX/[Rh(t\text{-}BuNC)_4]^+$ does not affect the rate appreciably.

The relative rate of addition of $p\text{-}XC_6H_4CHBrCO_2C_2H_5$ to $[Rh(t\text{-}BuNC)_4]^+$ was measured at 20 °C. The rate decrease in a sequence of $Cl>H>CH_3$ for X, *i.e.*, *t* 1/2 (min) at 20 °C: Cl, 2.8; H, 6.0; CH_3, 9.6, a trend suggestive of nucleophilic character of the metal species. The relative rate, however, deviates from the Hammett plots. In contrast to $C_6H_5CHBrCO_2C_2H_5$ the oxidative addition of the corresponding chloride does not occur.

Attempting to study solvent effect, we found that the addition of $C_6H_5CHBrCO_2C_2H_5$ to $[Rh(t\text{-}BuNC)_4]^+$ in acetone and CH_3CN also exhibits a complex kinetic feature thus preventing a reasonable analysis. Qualitatively the reaction rate does not vary appreciably among the solvents, acetone, CH_3CN, and CH_2Cl_2. A peculiar phenomenon was observed for the reaction in acetone; the time-conversion curve obtained by recording the intensity of the absorption at 440 nm on an ordinary spectrometer exhibited oscillations of small amplitudes suggesting a diffusion-controlled process. In addition to the 440 nm absorption the acetone solution shows two absorption maxima at 524 ($\varepsilon=692$) and 670 nm ($\varepsilon=365$) and the acetonitrile solution one maximum at 566 nm ($\varepsilon=1420$), indicating strong solvation in both solvents.

The rates of decrease in optical activity of the alkyl halide upon interaction with metal nucleophiles deserve investigation. The decrease in optical rotation of the system $C_6H_5CHBrCO_2C_2H_5/[Rh(t\text{-}BuNC)_4]^+$ was fairly fast at 20 °C in CH_2Cl_2. Apart from the initial peroid (2—3 min), we were able to follow the polarimetric rate for a certain limited initial concentration (1.0×10^{-2}M), and found approximate second order kinetics with a rate constant, k_2, of 0.6 $M^{-1}s^{-1}$. As the addition of $CH_3CHBrCO_2C_2H_5$ to $[Rh(t\text{-}BuNC)_4]^+$ takes place neither in the dark nor under irradiation of Na-D light beam (589 nm), the rate of optical loss can be followed by the polarimeter in the absence of concurrent oxidative addition. Surprisingly, the optical activity of a mixture of $CH_3CHBrCO_2C_2H_5$ (4.4×10^{-2} M) and $[Rh(t\text{-}BuNC)_4]^+$ (0.92×10^{-2} M) decreases rapidly even in the dark. The initial rate could not be measured accurately because of the experimental difficulty due to the low $[\alpha]_D$ value of the bromo ester and to the strong color of $[Rh(t\text{-}BuNC)_4]^+$, which prevents use of high concentrations. The rotation of a mixture containing 4.4×10^{-2} M of $CH_3CHBrCO_2C_2H_5$ and 0.92×10^{-2} M of $[Rh(t\text{-}BuNC)_4]^+$ in CH_2Cl_2 kept at 20 °C decreased after 2 hr from a calculated value of 0.167 to 0.116° which corresponds to a value of a solution containing 3.4×10^{-2} M of the chiral propinate. Hence the amount (1.0×10^{-2} M) of the propionate which has lost the chirality is quite close to that (0.93×10^{-2} M) of $[Rh(t\text{-}BuNC)_4]^+$ initially present in the system. Beyond this stoichiometric point, the rate of decrease in optical rotation became extremely slow. The starting complex, $[Rh(t\text{-}BuNC)_4]^+$ was recovered almost completely from the sample solution upon precipitation by adding ethanol. The racemization of chiral $CH_3CHBrCO_2C_2H_5$ in the presence of $[Rh(t\text{-}BuNC)_4]^+$ in methanol, which is faster than in CH_2Cl_2, was completed within a few hours at 80 °C. In the absence of the metal complex no racemization took place under the comparable conditions. The rate of decrease in optical rotation of the system $C_6H_5CHBrCO_2C_2H_5/[Rh(t\text{-}BuNC)_4]^+$ was faster than the system $CH_3CHBrCO_2C_2H_5/[Rh(t\text{-}BuNC)_4]^+$, and the rapid rate prevented accurate measurements.

Since the racemization suggests a possibility of complexation of the bromo esters to the metal, the IR and ^1H NMR spectra were examined. Electronic absorption spectroscopy cannot be employed here, as light of wavelength shorter than 440 nm initiates the addition reactions. An equimolar mixture of $CH_3CHBrCO_2C_2H_5$ and $[Rh(t\text{-}BuNC)_4]^+$ in CH_2Cl_2 shows a slight bathochromic shift (10 cm^{-1}) in the IR CO stretching band as compared to the free bromoester. The sharp single absorption of NC stretching remains unchanged. The free bromo ester exhibits six peaks (1 : 2 : 4 : 5 : 4 : 2) for the methine and methylene protons derived from overlap of two quartet signals ($^3J_{HH}=6.2$ Hz). The equimolar mixture of the bromo ester and $[Rh(t\text{-}BuNC)_4]^+$ in $CDCl_3$ gives a complex pattern for the protons, in which at least fourteen peaks are discernible. Although the complete assignment was impossible, these spectral data point to the presence of the complexed bromo ester. This is consistent with the slight intensity increase at 440 nm observed during the induction period.

An ESR measurement was carried out during the oxidative addition of the bromo ester to $[Rh(t\text{-}BuNC)_4]^+$, using t-BuNO as a spin trap as applied to a system of $CH_3I/Pt(PPh_3)_3$.[10)] The ESR signals of a radical, $t\text{-}Bu(R)NO\cdot(R{=}CH_3CHCO_2C_2H_5,\ C_6H_5CHCO_2C_2H_5)$ were observed as three doublets with hyperfine coupling constants (Gauss): $A_0(N)=14.5$, $A_0(H)=3.0$ for $R=CH_3CHCO_2C_2H_5$; $A_0(N)=15.5$, $A_0(H)=4.5$ for $R=C_6H_5CHCO_2C_2H_5$. The ESR signals were more intense in the case of bromo phenylacetate than that of the bromo propionate. An irradiation of a few minutes duration of both systems with a low pressure mercury lamp does not cause any essential change in the ESR signals. The ESR signals was observed for system $[RhBr(C_6H_5CHCO_2C_2H_5)(t\text{-}BuNC)_4]^+/t\text{-}BuNO$, but not for the alkyl halides/t-BuNO or $[Rh(t\text{-}BuNC)_4]^+/t\text{-}BuNO$ system.

A radical scavenger, duroquinone, was not effective in inhibiting the reaction. Because of the facile reaction of reactive radical scavengers like galvinoxyl with Rh(I) species itself, the use as a diagnostic probe was not attempted.

Discussion

Here we focus our discussion on the mechanism of the oxidative addition of s-alkyl halides, α-bromo esters, to $[Rh(R'NC)_4]^+(R'=t\text{-}Bu, p\text{-}CH_3C_6H_4)$. Other alkyl halides were also studied as the substrate and "$Pd(t\text{-}BuNC)_2$" was used as the acceptor to argue the above results. The oxidative addition of RX to $[Rh(t\text{-}BuNC)_4]^+$, producing *trans*-octahedral Rh(III) complexes **1**—**4**, may be viewed as a substitution reaction at the saturated carbon atom. Any proposal on the mechanism must accommodate various experimental observation: (i) the *trans* geometry of the Rh(III) complexes formed, (ii) the absence of the dihalide complex, alkene, and alkane in the products, (iii) the effect of leaving group X, (iv) the electronic effect and structural effect of the alkyl moiety, (v) the racemization of the chiral bromoesters prior to the oxidative addition, (vi) the observed kinetic behaviors involving an induction period, (vii) the low-energy photo-initiation and the large quantum yield, and (viii) the results of spin-trap experiments. These results, *inter alia* vi and vii strongly suggest a chain mechanism. While non-radical chain mechanisms cannot be excluded conclusively we favor a radical chain as will be discussed later.

The following simple scheme is sufficient to describe the radical chain reaction ($[Rh(RNC)_4]^+=M$).

Scheme 1.

initiation:

$$M + RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\cdots X\cdots R \qquad (1)$$

$$M\cdots X\cdots R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M{-}X + R\cdot \qquad (2)$$

chain:

$$M^*\cdots X\cdots R + M\text{-}X \xrightarrow{k_3} M^*\text{-}X + RMX \qquad (3)$$

termination:

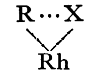
$$M\text{-}X + R\cdot \xrightarrow{k_t} RMX \qquad (4)$$

Note: Star was added to distinguish the metal identity in the product R-M-X from that involved the reagent M-X.

Step (1) is a reversible formation of an intermediate from RX and $[Rh(R'NC)_4]^+$. Although the instability prevents isolation and characterization, the existence in system $CH_3CHBrCO_2C_2H_5/[Rh(t\text{-}BuNC)_4]^+$ is supported by the IR, ^1H NMR, and electronic spectra. Three possible modes may be distinguished for the interaction between the alkyl halide and the metal species; a) an essentially linear complex with a metal-carbon interaction, $(R'NC)_4Rh\cdots R\cdots X$, similar to a Menshutkin-type intermediate, b) a three-centered cyclic structure, and c) an essentially linear complex with a metal-halogen interaction, $(R'NC)_4Rh\cdots X\cdots R$.

Rh···R···X

(a)



(b)

Rh···X···R

(c)

The former, (a), corresponds to a transition state of an S_N2 type attack of the metal species at the alkyl carbon. The *para*-substituent effect on the rate of oxidative addition of $p\text{-}XC_6H_4CHBrCO_2C_2H_5$ shows the feeble nucleophilic character of $[Rh(R'NC_4]^+$. If the interaction of type (a) leads to the final adduct, then the stereochemical course should be inversion. Although Stille[11,12,29)] has observed the inversion of configuration the oxidative addition of PhCHDCl to $Pd(PPh_3)_4$, the racemization observed for the present system renders the transition state structure untenable. The addition of 3-*endo*-iodocamphor, to which an *exo*-attack by a bulky nucleophile is prohibited, would not occur through the S_N2 type complex.

A cyclic intermdieate (b) is evidently incompatible with the observed loss of stereochemical integrity at the carbon atom. Ugo *et al.*[5)] proposed a polar asymmetric three center transition state in which the iridium-carbon interaction takes place prior to the carbon-halogen bond breaking. The mechanism alleged would still imply retention of the carbon atom configuration since the incipient metal-alkyl bond formation prohibits configurational change at the carbon atom. Both claims of retention[19)] and inversion[30)] for an oxidative addition of a chiral s-alkyl halide to Ir(I) complexes were found erroneous. The cyclic transition state would lead to stereospecific *cis*-addition of alkyl halides to the metal. The possibility of *cis*-addition in a kinetically-controlled process followed by a rapid isomerization to the *trans*-adduct is unlikely in the present case where even trace of the *cis*-product was not detected. This was confirmed by monitoring the IR NC stretching band region (2200 cm^{-1}) which showed no indication for appearance of absorptions other than the bands due to the starting materials and the *trans*-adduct.

The third intermediate (c) appears to be the most likely species whose incipient formation must be assumed in order to account for the racemization preceding the addition. Complexation of the corresponding chloride is not detected spectroscopically for the system $C_6H_5CHClCO_2C_2H_5/[Rh(t\text{-}BuNC)_4]^+$, and the system shows neither racemization nor oxidative addition. Thus, the racemization of the chiral α-bromoesters may be associated with step (1) and/or (2). The racemization of (*S*)-(+)-$CH_3CHBrCO_2C_2H_5$ in CH_2Cl_2 became extremely slow after the amount of the racemate reached a stoichiometric amount, equivalent to that of the complex present, while it proceeds catalytically in methanol. Practically, no oxidative addition takes place during the racemization in both solvents. The result in CH_2Cl_2 can then be accounted for by the large formation constant, $K_1=(k_1/k_{-1})$, coupled with a small value of k_2. Thus, the reversible step (1) appears to be responsible for the racemization. This constitutes, in turn, strong evidence for complexation of the *s*-alkyl halides forming (c). The observation of an increase in absorption intensity around 440 nm delineates the formation of an intermediate complex. This intermediate complex, albeit not isolable, must be fairly substitution stable since the catalytic racemization occurs slowly.

A radical or an ionic character could emerge in the alkyl moiety in intermediate, $L_4Rh\cdots X\cdots R$. If the alkyl group is held in the vicinity of the metal through, *e. g.*, a weak interaction of the carbonyl group with metal, the intermediate resembles a radical pair or an ion pair. Some cage reactions of chiral radical pairs have been shown to lead to racemization before diffusing apart with a rate depending on solvents.[31] Thus the observed solvent effect for the racemization does not necessarily imply an ionic intermediate.

The step (2) is the formation of the chain carrier. The failure of $CH_3CHBrCO_2C_2H_5$ to initiate the reaction in the dark and the contrasting smooth initiation of $C_6H_5CHBrCO_2C_2H_5$ reflect the relative ease of the halide abstraction. The primary importance of the C–Br bond cleavage for the initiation is evident. The facile addition of $CH_3CHBrCO_2C_2H_5$ to "Pd-(t-Bu)$_2$" in the dark suggests that the nucleophilicity of the metal species affects the initiation. There is no indication for disproportionation or coupling of the radicals. The acrylate and propionate detected in small amounts during isolation of adduct $[Rh(CH_3CHCO_2C_2H_5)(R'NC)_4]^+$ are presumably produced due to the thermal decomposition of the adduct once formed. CIDNP was not observed. The system RX/PtL_3 ($L=P(C_2H_5)_3$) showed CIDNP due to the alkane or alkene derived from diffused encounter of the alkyl radical only when PtX_2L_2 was formed.[9] Consistently the present system does not produce $[RhX_2(RNC)_4]$.$^+$ Spin-trap experiments using *t*-BuNO showed formation of a radical *t*-BuN(R)O. This again does not prove the presence of a free alkyl radical in the reaction mixture, since *t*-BuNO could react with both the alkyl halide complex $(R'NC)_4Rh\cdots X\cdots R$ and the final product, $[(R'NC)_4RhX(R)]$.$^+$

$$(R'NC)_4Rh^+\cdots X\cdots R \text{ or } [(R'NC)_4RhX(R)]^+ + t\text{-BuNO} \longrightarrow [(R'NC)_4Rh^{II}X(R)]^+ + t\text{-BuN(R)O}\cdot \quad (5)$$

The ineffectiveness of radical scavengers, *e.g.* 1,2,4,5-tetramethyl-*p*-benzoquinone, was observed. These results, however, fail to exclude conclusively the formation of organic radicals (in fact, the formation in a small amount is implied in Eq. 2). A mechanism involving short lived radicals or caged radical pairs is perfectly consistent with the available data.

Both possibilities, radical and ionic chains, must then be examined for step (3) which is rate-determining. The relative rates of $[Rh(p\text{-}CH_3C_6H_4NC)_4]^+$ and $[Rh(t\text{-}BuNC)_4]^+$ suggest that the nucleophilicity of the metal species affects the rate-determining step too. Although this trend is in accord with the observed electronic effect for the addition of $p\text{-}XC_6H_4CHBrCO_2C_2H_5$, the chain cannot be described in terms of a simple S_N2 type scheme as is evident from the molecularity of the step and the deviation from the Hammett rule. Since a low-energy photo-exitation of a similar Ir(I) compound is known,[32] let us examine an ionic chain mechanism such as Scheme II, which assumes a dissociative process (Eq. 6) to be photochemically induceable.

Scheme 2.

$$RhL_3^+ \rightleftharpoons RhL_3^+ + L \quad (6)$$

$$RhL_3^+ + RX \longrightarrow \{RhL_3X + R^+\} \rightarrow RhL_3X(R)^+ \quad (7)$$

$$RhL_3X(R)^+ + RhL_4^+ \longrightarrow RhL_4S(R)^+ + RhL_3^+ \quad (8)$$

$$RhL_3X(R)^+ + L \longrightarrow RhL_4X(R)^+ \quad (9)$$

Irradiation effect for the addition or substitution reaction of $[Rh(t\text{-}BuNC)_4]^+$ with neutral ligand such as CO, PR_3 or RNC was examined to find no effect. Further, an addition of free *t*-BuNC (1—3 mol) caused practically no effect on the rate of oxidative addition of the bromo ester to $[Rh(t\text{-}BuNC)_4]^+$.

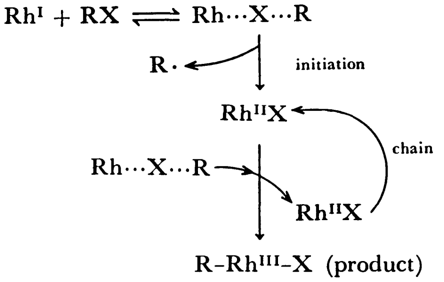
Thus the dissociative process (Eq. 6) appears not to be important.

Alternative mechanisms involving carbonium ions may be possible. However, participation of carbonium ions in the rate-determining step is incompatible with the observed relative rate, *i. e.*, $C_6H_5CHBrCO_2C_2H_5 > CH_3CHBrCO_2C_2H_5$. Therefore we favor Scheme 1. Experimental tools are not available to kinetically discern the photochemical effect for the addition of $C_6H_5CHBrCO_2C_2H_5$, which occurs rapidly without irradiation. The information, even if available, would not affect our conclusion.

The low-energy of light (440 nm) used for initiating the reaction of $CH_3CHBrCO_2C_2H_5$ is insufficient to cause fission of the RX bond. The photochemical effect can only be expected for the complexed RX, but not for the free RX. The possibility of an alkyl radical as the chain carrier is excluded on the basis of the quantum yield ($\Phi=4.8$ for $C_6H_5CHBrCO_2C_2H_5$). It is most unlikely for a reactive alkyl radical (or carbonium ion) in solution to achieve such a high quantum yield.[33] Tentatively RhL_4X^+ species is assigned as the carrier.

It is rather surprising to find the inability of 1-bromo-2,2-diphenyl-cyclopropanecarboxylate to undergo the oxidative addition to $[Rh(R'NC)_4]$.$^+$ At first sight, this seems to support an ionic, solvolysis mechanism, because the formation of an S_N2-type transition state would be hindered sterically. The steric hindrance, however, could also be influential for the bimolecular reaction step (3). The observed addition of 3-*endo*-iodo campher to $[Rh(R'NC)_4]^+$ is apparently incompatible with an S_N2-type transition state. The failure of the bromocyclopropane toward the addition may then be accounted for by the high activation energy required for a substituted cyclopropane to form the cyclopropyl radical.[35] The inertness of a primary alkyl bromide, *erythro*-1-bromo-3,3-dimethyl-1,2-dideuteriobutane, to $[Rh(t\text{-}BuNC)_4]^+$ can be accounted for by the steric effect primarily operating in step (3). The steric congestion around the carbon atom carrying the bromine atom is apparently more enhanced in step (3) than in the preceding steps (1)—(2).

The reverse reaction of the initiation constitutes the terimination (4). A similar situation has been found for halogen radical chain reactions.[34] Another termination could be dimerization of the Rh(II) species[36] forming $[RhX(t\text{-}BuNC)_4]_2^{2+}$. The formation, however, could not be detected, a result expected from the high yield of the oxidative addition. The whole sequence may be depicted as shown.



Although the addition of α-bromopropionate showed complicated kinetic features, it seems reasonable to assume a similar radical chain mechanism involving a rate-determining initiation. Once the initiation has started photochemically, the reaction apparently proceeds through the same sequence as for $C_6H_5CHBrCO_2C_2H_5$.

In summary, various facts described above appear to be mostly consistent with a radical chain mechanism. Osborn[9] has suggested such a mechanism for a similar addition reaction to a stronger metal nucleophile PtL_3 without direct experimental evidence. The present results clearly exclude an intermediacy of an alkylrhodium species[37] such as $[Rh^{III}(R)L_4]^{2+}$. We do not claim that this radical chain mechanism is valid for the addition of different types of alkyl halides to the metal system. However, a similar radical mechanism should be valid for the addition of these α-bromo esters to Pd(0) systems which also show complete loss of stereochemical integrity at the carbon atom.[18]

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