Bull. Chem. Soc. Jpn., 53, 118—120 (1980) [Vol. 53, No. 1

Halogenotriphenyltin(IV) Adducts of Tetrakis(t-butyl isocyanide)-rhodium(I) Perchlorate. Preparation and Kinetics

Ryosho KUWAE and Toshio TANAKA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received July 3, 1979)

[Rh(t-BuNC)$_4$]ClO$_4$ undergoes oxidative addition reactions with Ph$_3$SnX (X=Cl, Br) to give *cis*-[Rh(Ph$_3$Sn)X(t-BuNC)$_4$]ClO$_4$. The adducts partly dissociate in solution to exist as an equilibrium mixture with the Rh(I) substrate and the addendum. Kinetics of the equilibrium reactions in three different organic solvents were studied spectrophotometrically under pseudo-first-order conditions with excess Ph$_3$SnX. Rate constants for the forward reaction (k_f) are strongly dependent on the solvent polarity; k_f increases in the order of 1,2-dichloroethane<acetone<acetonitrile, whereas those for the backward reaction are little dependent on the solvents. Activation parameters also were obtained for the X=Cl system in acetonitrile; ΔS^* for the forward reaction is $-99.2\ \mathrm{J\ mol^{-1}\ K^{-1}}$, while that for the backward reaction is $+24.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$. These results indicate that the addition reactions proceed *via* a three-center transition state formed by the nucleophilic attack of the Rh(I) ion to the tin atom.

Low-valent square planar rhodium(I) and iridium(I) complexes are known to undergo oxidative addition reactions with alkyl, aryl, and metal halides to afford octahedral rhodium(III) and iridium(III) complexes.[1—4] Some of these reactions have been studied kinetically.[5—11] As the results, the oxidative addition reactions may be classified mechanistically into the following three types; (i) a mechanism similar to the Menschutkin type reaction,[5—7] (ii) radical mechanisms,[8,9] and (iii) the mechanism involving a three-center transition state.[10] These reactions kinetically studied so far, however, were all irreversible. The present work was undertaken to study some reversible oxidative addition reactions, which will give more clear insight into transition states of the reactions.

This paper reports the preparation and configuration of chloro- and bromotriphenyltin(IV) adducts with tetrakis(t-butyl isocyanide)rhodium(I) perchlorate, and the kinetic study on the adduct formation

Experimental

Materials. [Rh(t-BuNC)$_4$]ClO$_4$ was prepared as described elsewhere.[12] Chloro- and bromotriphenyltin(IV) were prepared and purified according to the literature methods, mp 105—106 °C (lit,[13] 104—106 °C) and 122—123 °C (lit,[14] 120—121 °C), respectively. Acetonitrile and acetone used as the solvents for kinetic measurements were dried over P$_2$O$_5$ and CaSO$_4$, respectively, followed by distillation. 1,2-Dichloroethane used for the same purpose was purified by the usual method.[15]

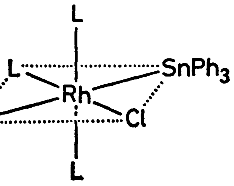
Isolation of [Rh(Ph$_3$Sn)X(t-BuNC)$_4$]ClO$_4$ (X=Cl, Br). An acetone (7 cm^3) solution containing [Rh(t-BuNC)$_4$]ClO$_4$ (0.75 mmol) and Ph$_3$SnCl (2.3 mmol) was stirred for 4 h at room temperature, followed by the addition of ligroin (*ca.* 15 cm^3). The solution was allowed to stand for 2 d in a refrigerator to afford white plates of [Rh(Ph$_3$Sn)Cl(t-BuNC)$_4$]ClO$_4$, which were collected by filtration and dried *in vacuo*. From the filtrate, the adduct was further obtained by the addition of ligroin (*ca.* 15 cm^3), followed by the same procedure, 60% yield as a whole. ν(Rh–Cl), 301 cm^{-1}. Found: C, 49.47; H, 5.60; N, 6.08%. Calcd for C$_{38}$H$_{51}$Cl$_2$N$_4$O$_4$RhSn: C, 49.59; H, 5.59; N, 6.09%. The Ph$_3$SnBr adduct, [Rh(Ph$_3$Sn)Br(t-BuNC)$_4$]ClO$_4$, was similarly obtained as white needles in a 65% yield by the reaction of [Rh(t-BuNC)$_4$]ClO$_4$ with Ph$_3$SnBr at the mole ratio of 1:3. Found: C, 47.13; H, 5.36; N, 5.82%. Calcd for C$_{38}$H$_{51}$BrClN$_4$O$_4$RhSn: C, 47.31; H, 5.33; N, 5.81%.

Kinetic and Other Measurements. Kinetic measurements were performed using a Union Giken SM-401 spectrophotometer and a 10 mm quartz cell equipped with a Union Giken MX-7 mixing apparatus thermostated to ±0.2 °C. Two reactant solutions were rapidly introduced into the cell by the mixing apparatus. The initial concentration of the Rh(I) substrate was 8.0×10^{-5} mol dm^{-3}. All the reactions were carried out under pseudo-first-order conditions, using at least twenty-fold excess of Ph$_3$SnX. The rate of reaction was determined by following the decay of absorbances at 381 nm (absorption maximum of the Rh(I) substrate in acetonitrile) or at 383 nm (absorption maxima in acetone and in 1,2-dichloroethane) with time.

Infrared and ^{1}H NMR spectra were recorded as described elsewhere.[12]

Results and Discussion

Configuration of the Adducts. The infrared spectrum of [Rh(Ph$_3$Sn)Cl(t-BuNC)$_4$]ClO$_4$ in acetone (2.0×10^{-2} mol dm^{-3}) showed three ν(N≡C) bands at 2156, 2202, and 2230 cm^{-1}. The same spectrum was observed in an equimolar mixture (2.0×10^{-2} mol dm^{-3}) of [Rh(t-BuNC)$_4$]ClO$_4$ with Ph$_3$SnCl in acetone. The 2156 cm^{-1} band was assigned to the Rh(I) substrate with a square planar configuration, on the basis of its coincidence with the ν(N≡C) frequency observed in an acetone solution containing [Rh(t-BuNC)$_4$]ClO$_4$ alone. On the other hand, the 2202 and 2230 cm^{-1} bands are due to the adduct, because of their proximity in positions to the ν(N≡C) bands exhibited by the adduct in Nujol mulls(2205 and 2238 cm^{-1}). When one more equivalent Ph$_3$SnCl was added to the equimolar solution, the two high frequency bands were intensified at the expense of the low frequency one. It is therefore suggested that the adduct] partly dissociates in acetone to exist as an equilibrium mixture with the Rh(I) substrate and the addendum. The appearance of the two ν(N≡C) bands assignable to the adduct indicates its *cis* configuration in an octahedral geometry around the rhodium ion, as shown in **1**. This configuration was confirmed also by ^{1}H NMR spectra. A chloroform-d_1 solution of [Rh(t-BuNC)$_4$]ClO$_4$ (5.0×10^{-2} mol dm^{-3}) exhibited a triplet signal due to the t-BuNC protons at δ 1.58 (J(H–^{14}N)=2 Hz). Upon addition of excess Ph$_3$SnCl (5.0×10^{-1}



1: L=*t*-BuNC

mol dm^{-3}) to the solution, the triplet signal disappeared, instead three singlets[16] occurred at δ 1.27, 1.55, and 1.67 with the relative intensities of 2:1:1, which is compatible with the *cis* configuration of the adduct involving four *t*-BuNC placed in three magnetically different environments from one another. The same configuration is suggested also for the Ph_3SnBr adduct from its infrared and ^1H NMR spectra in acetone. Thus, the stoichiometry of the adduct formation is expressed as follow,

$$[Rh(t\text{-}BuNC)_4]^+ + Ph_3SnX \rightleftharpoons [Rh(Ph_3Sn)X(t\text{-}BuNC)_4]^+. \quad (1)$$

Kinetics and Mechanism. Figure 1 depicts the decay of the 381 nm band after mixing the Rh(I) substrate with Ph_3SnCl in acetonitrile. Plots of ln($A_t - A_\infty$) *vs.* time, where A_t and A_∞ are absorbances at a time *t* and at the end of reaction respectively, showed a good linearity. Pseudo-first-order rate constants, k_{obsd}, were calculated by the least squares method. As shown in Fig. 2, plots of k_{obsd} *vs.* the concentration of Ph_3SnCl at each temperature give a straight line with non-zero intercept which is characteristic of reversible reactions. In the presence of excess Ph_3SnCl, k_{obsd} is expressed as,[17]

$$k_{obsd} = k_f[Ph_3SnCl] + k_b \quad (2)$$

where k_f and k_b stand for the rate constants of forward and backward reactions of Eq. 1, respectively. The k_f and k_b values were obtained from the slope and intercept of the straight lines, respectively (Fig. 2). The rate constants for the $[Ph(t\text{-}BuNC)_4]ClO_4$–$Ph_3SnCl$ system in acetone and 1,2-dichloroethane and for the $[Ph(t\text{-}BuNC)_4]ClO_4$–$Ph_3SnBr$ system in three different solvents were similarly obtained. The results are listed in Table 1, which contains also equilibrium constants $K(=k_f/k_b)$. The ClO_4^- anion may not participate in the reactions, because the rate of reactions was little influenced by the presence of excess ClO_4^-. The reaction rate was hardly altered also by changing the slit width of the spectrophotometer. Thus, the light intensity has no appreciable effect upon the reaction rate, confirming that radical mechanisms may be ruled out for the present reactions.

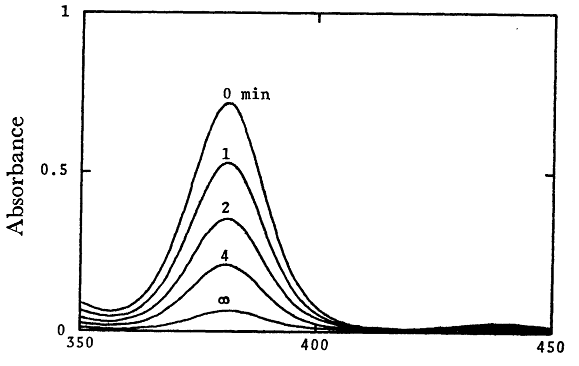


Fig. 1. Decay of the absorbance with time after mixing $[Rh(t\text{-}BuNC)_4]ClO_4$ (8.0×10^{-5} mol dm^{-3}) with Ph_3SnCl (4.8×10^{-3} mol dm^{-3}) in acetonitrile at 25 °C, cell length = 10 mm.

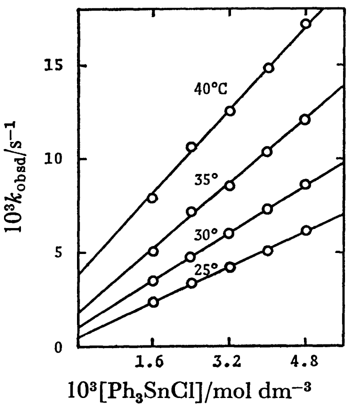


Fig. 2. Plots of k_{obsd} *vs.* $[Ph_3SnCl]$ for the reactions of $[Rh(t\text{-}BuNC)_4]ClO_4$ (8.0×10^{-5} mol dm^{-3}) with Ph_3SnCl in acetonitrile at various temperatures.

The rate constant of forward reactions is strongly dependent on the solvent; k_f increases in the order 1,2-dichloroethane<acetone<acetonitrile in the two reaction systems. On the contrary, the rate constant of backward reactions is little dependent on solvent

TABLE 1. RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTIONS OF $[Rh(t\text{-}BuNC)_4]ClO_4$ WITH Ph_3SnX

X	Solvent	Temp °C	k_f[a)] dm^3 mol^{-1} s^{-1}	$10^3 k_b$[a)] s^{-1}	K dm^3 mol^{-1}
Cl	Acetonitrile	25	1.18 ±0.01	0.502±0.014	2350± 70
		30	1.57 ±0.01	1.02 ±0.01	1540± 10
		35	2.16 ±0.04	1.78 ±0.14	1220±100
		40	2.80 ±0.06	3.68 ±0.19	762± 43
	Acetone	35	0.416±0.012	1.70 ±0.04	245± 9
	1,2-Dichloroethane	35	0.275±0.004	1.39 ±0.01	198± 3
Br	Acetonitrile	35	1.39 ±0.02	1.03 ±0.06	1340± 80
	Acetone	35	0.297±0.006	0.855±0.018	348± 10
	1,2-Dichloroethane	35	0.134±0.003	0.724±0.009	185± 5

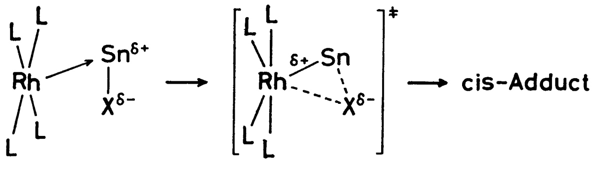
a) k_f and k_b stand for rate constants of the forward and backward reactions, respectively.

Table 2. Activation and thermodynamic parameters for the reaction of $[Rh(t\text{-}BuNC)_4]ClO_4$ with Ph_3SnCl in acetonitrile at 25 °C

Reaction	E_a / kJ mol^{-1}	ΔH^* or ΔH° / kJ mol^{-1}	ΔS^* or ΔS° / J mol^{-1} K^{-1}	ΔG^* or ΔG° / kJ mol^{-1}
Forward	45.8±0.8	43.3±0.8	−99.2± 2.6	72.9± 2.3
Backward	102 ±3	99.5±2.5	24.9± 8.1	92.1±30.0
Equilibrium	—	−56.2±3.7	−124 ±12	−19.2± 2.2

polarity (Table 1). Accordingly, the equilibrium constant, K, undergoes the solvent effect to the same extent as k_f. This result suggests that an activated complex in the transition state has virtually the same polarity as the final product.

Table 2 lists activation and thermodynamic parameters for the $[Rh(t\text{-}BuNC)_4]ClO_4$–$Ph_3SnCl$ system in acetonitrile at 25 °C. The entropy of activation, ΔS^*, for the forward reaction is large negative value, which implies that the activated complex is subjected to stereochemical restriction in the transition state. On the other hand, the ΔS^* value for the backward reaction is small, suggesting the activated complex may assume a structure which resembles that of the adduct. It is well known that low-valent transition metal complexes function as nucleophiles.[2] In the present reaction the Rh(I) ion of $[Rh(t\text{-}BuNC)_4]ClO_4$ may initially attack the tin atom which is an electron deficient part of the addendum. In the Menschutkin-type oxidative addition reactions which have been suggested to proceed *via* a linear transition state $M^{\delta+}\cdots R\cdots X^{\delta-}$ (M=metal complex, RX=alkyl halide), the rate constant of the reaction for X=Br has been reported to be several hundred times larger than that for X=Cl.[6] In contrast to this, the k_f value in the present reactions is larger in Ph_3SnCl than in Ph_3SnBr in any solvents (Table 1), suggesting that the transition state may be different from that of the Menschutkin-type reactions. Thus, the oxidative addition of Ph_3SnX toward $[Rh(t\text{-}BuNC)_4]ClO_4$ may proceed *via* a three-center (asymmetric) transition state which may involve deformation of the $[Rh(t\text{-}BuNC)_4]^+$ moiety from a square planar configuration to some extent as follow.



L=t-BuNC

Similar transition states have been proposed for the reactions of $IrCl(CO)(PR_3)_2$ (R=alkyl, aryl) with MeI and $PhCH_2X$ (X=Cl, Br).[10]

The authors are grateful to the Ministry of Education for support of this work through Grant-in-Aid for Scientific Research, No. 147074.

References

1) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 53 (1968).

2) D. F. Shriver, *Acc. Chem. Res.*, **3**, 231 (1970).

3) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970).

4) J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, **1973**, 2046.

5) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

6) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **10**, 1653 (1971).

7) M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195 (1973).

8) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Am. Chem. Soc.*, **94**, 4043 (1972).

9) S. Otsuka and K. Ataka, *Bull. Chem. Soc. Jpn.*, **50**, 1118 (1977).

10) R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Am. Chem. Soc.*, **94**, 7364 (1972).

11) W. H. Thompson and C. T. Sears, Jr., *Inorg. Chem.*, **16**, 769 (1977).

12) R. Kuwae and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **52**, 1067 (1979).

13) H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **74**, 5580 (1952).

14) J. B. Pedley and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 544 (1959).

15) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Interscience, New York (1955), Vol. 7, p. 415.

16) Spin-spin couplings of the isocyanide-protons with the ^{14}N nucleus in some isocyanide metal complexes are often not observed; T. Sawai and R. J. Angelici, *J. Organomet. Chem.*, **80**, 91 (1974).

17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York (1961), p. 186.