2696 *Inorg. Chem.* **1987**, *26*, 2696-2699

Contribution from the Department of Chemistry,
Queen's University, Kingston, Ontario, Canada K7L 3N6

Axial-Ligand Substitution Reactions of Dirhodium(II) Tetraacetate with Phosphines and Phosphites in Acetonitrile

Manuel A. S. Aquino and Donal H. Macartney*

Received November 13, 1986

The kinetic and thermodynamic parameters for the axial-ligand substitution reactions of the bis(acetonitrile) adduct of dirhodium(II) tetraacetate with a variety of phosphines and phosphites in acetonitrile have been measured. The rate-determining formation of the $Rh_2(O_2CCH_3)_4(CH_3CN)PR_3$ adduct occurs with a rate constant that is independent of the nature of the ligand: $k_1(25.0\ °C) = (1.05 \pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$, $\Delta H_1^* = 10.9 \pm 0.6$ kcal mol^{-1}, and $\Delta S_1^* = 1 \pm 2$ cal K^{-1} mol^{-1}. Slightly higher rate constants ($1.6 \times 10^5\ M^{-1}\ s^{-1}$ at 25.0 °C) were found for several diphosphines ($PPh_2(CH_2)_nPPh_2$, $n = 2-4$) and are attributed to the presence of two ligand coordination sites. A dissociative mechanism is proposed for substitution of the axially coordinated acetonitrile, and the rate parameters are compared with values reported for substitutions of oxygen-donor solvent molecules on the dirhodium(II) complex. The stability constants for the mono- and bisadducts have been measured at 25 °C with $K_1/K_2 \sim 20$. The dependence of K_1 and K_2 on the nature of the phosphine or phosphite correlates well with the σ-donor strength of the ligand, with π-acceptor strengths and steric effects being relatively insignificant.

Introduction

Dimeric rhodium(II) complexes,[1] notably those with bridging carboxylate ligands,[2] have been the subject of considerable study in the past two decades. Their interesting structural and spectroscopic properties, along with observed catalytic[3] and antitumor[4] activities, have led to numerous investigations of the rhodium-rhodium and rhodium-ligand interactions. These complexes contain a rhodium-rhodium single bond with four equatorial bridging carboxylate ions, which are inert to substitution (k_1(acetate) = $7.2 \times 10^{-4}\ s^{-1}$).[5] The two axial positions may be occupied by donor solvents that can undergo rapid ligand exchange to yield adducts with a variety of ligand species.[2] Much attention has recently been focused on the electronic configurations of various adduct complexes[6-12] and on the nature of the rhodium-ligand bonding interactions.[8,11,13-15] The electronic configurations of dirhodium(II) tetracarboxylates have been shown, by theoretical and experimental studies, to be dependent on the donor atom of the axial ligands. It is now generally agreed,[12] after much controversy, that the configuration for oxygen- and nitrogen-donor bisadducts is $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ and for phosphorus-donor adducts is $\pi^4\delta^2\pi^{*4}\delta^{*2}\sigma^2$. There has also been considerable debate as to the relative importance of σ-donating and π-back-bonding interactions between the dirhodium core and axially coordinated π-acids such as phosphines, phosphites, and carbon monoxide.[8,14,15]

While the stability constants of the mono- and bisadducts of dirhodium(II) tetracarboxylates are known for a variety of donor ligands,[2] the kinetic and activation parameters associated with their formation and axial substitution have been measured for only a few species.[16,17] Nitrogen- and oxygen-donor adducts of dirhodium(II) tetraacetate have rather weak visible spectra (ϵ = $(2-3) \times 10^2\ M^{-1}\ cm^{-1}$),[2] making kinetic measurements of the rapid adduct formations difficult. Phosphorus-donor adducts, on the other hand, display strong absorbance bands in the 300-400-nm region ($\epsilon = (2-4) \times 10^4\ M^{-1}\ cm^{-1}$),[18] allowing for kinetic studies of their formation using stopped-flow techniques. In this paper the results of kinetic and spectroscopic studies of the reactions of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with a variety of phosphines and phosphites in acetonitrile are reported. The dependences of the kinetic and equilibrium parameters on the nature of the phosphorus-donor ligand are discussed in terms of the mechanism of axial-ligand substitution and the contributions of σ-donor and π-acceptor abilities to the stabilization of the adducts.

Table I. UV-Visible Band Coefficients and Stability Constants for Substituted Dirhodium(II) Tetraacetate Complexes in Acetonitrile (0.10 M TBAP)

	$Rh_2(O_2CCH_3)_4(CH_3CN)L$			$Rh_2(O_2CCH_3)_4L_2$		
L	λ_{max}, nm	log ϵ	log K_1[a]	λ_{max}, nm	log ϵ	log K_2[a]
PPh_3	309	4.37	4.74 (0.02)	362	4.68	3.73 (0.02)
$P(CH_2CH_2CN)_3$	297	4.39	6.26 (0.06)	337	4.56	4.86 (0.07)
$P(OCH_3)_3$	291	4.32	4.88 (0.07)	325	4.49	3.44 (0.01)
$P(OPh)_3$	289	4.00	3.13 (0.06)	320	4.19	1.92 (0.01)
$Ph_2PCH_2PPh_2$	310	4.44	4.51 (0.09)	362	4.78	3.08 (0.02)
$Ph_2P(CH_2)_n$-PPh_2[b]	311			355		
$AsPh_3$	296[c]		1.97 (0.10)	339	4.40	1.87 (0.05)

[a] At 25 °C; uncertainty in log K given in parentheses. [b] $n = 2-4$; complications from dimer formations and insolubility prevented determinations of ϵ and K values for $Ph_2P(CH_2)_nPPh_2$ ($n > 1$) adducts. [c] Shoulder.

Experimental Section

Materials. Dirhodium(II) tetraacetate (Aldrich) was used as received. Concentrations of stock solution of the dimer in acetonitrile, $Rh_2(O_2CCH_3)_4(CH_3CN)_2$, were determined spectrophotometrically: λ_{max} = 437 (ϵ = 125 $M^{-1}\ cm^{-1}$) and 552 nm (ϵ = 235 $M^{-1}\ cm^{-1}$).[17] Triphenylphosphine (Fisher), tris(2-cyanoethyl)phosphine, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane (Strem), and triphenylarsine (Eastman Kodak) were used as received. Triphenyl phosphite and trimethyl phosphite were distilled prior to use. Acetonitrile (BDH OmniSolv) and tetrabutylammonium perchlorate (Kodak and Baker) were used as received. Tetraethylammonium perchlorate was prepared by the metathesis of the corresponding bromide salt with concentrated perchloric acid, recrystallized from water, and vacuum-dried.

Kinetic Measurements. The kinetic measurements were made by using a TDI Model IIA stopped-flow apparatus (Cantech Scientific) and data acquisition system described previously.[20] Pseudo-first-order conditions

---

(1) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73.
(2) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109 and references therein.
(3) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley-Interscience: New York, 1982; Chapter 7 and references therein.
(4) Howard, R. A.; Spring, T. G.; Bear, J. L. *Cancer Res.* **1976**, *36*, 4402.
(5) Bear, J. L.; Kitchens, J.; Willcott, M. R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3479.
(6) Richmond, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055.
(7) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.
(8) Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.
(9) Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayshida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 364.
(10) Nakatsuji, H.; Onishi, Y.; Ushio, J.; Yonezawa, T. *Inorg. Chem.* **1983**, *22*, 1623.
(11) Drago, R. S.; Cosmano, R.; Telser, J. *Inorg. Chem.* **1984**, *23*, 3120.
(12) Kawamura, T.; Katayama, H.; Yamabe, T. *Chem. Phys. Lett.* **1986**, *130*, 20.
(13) Drago, R. S. *Inorg. Chem.* **1982**, *21*, 1697.
(14) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920; **1982**, *21*, 2196.
(15) Bilgrien, C.; Drago, R. S.; Vogel, G. C.; Stahlbush, J. *Inorg. Chem.* **1986**, *25*, 2864.
(16) Das, K.; Simmons, E. L.; Bear, J. L. *Inorg. Chem.* **1977**, *16*, 1268.
(17) Bear, J. L.; Howard, R. A.; Korn, J. E. *Inorg. Chim. Acta* **1979**, *32*, 123.
(18) Sowa, T.; Kawamura, T.; Shida, T.; Yonezawa, T. *Inorg. Chem.* **1983**, *22*, 56.
(19) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960.

0020-1669/87/1326-2696$01.50/0 © 1987 American Chemical Society

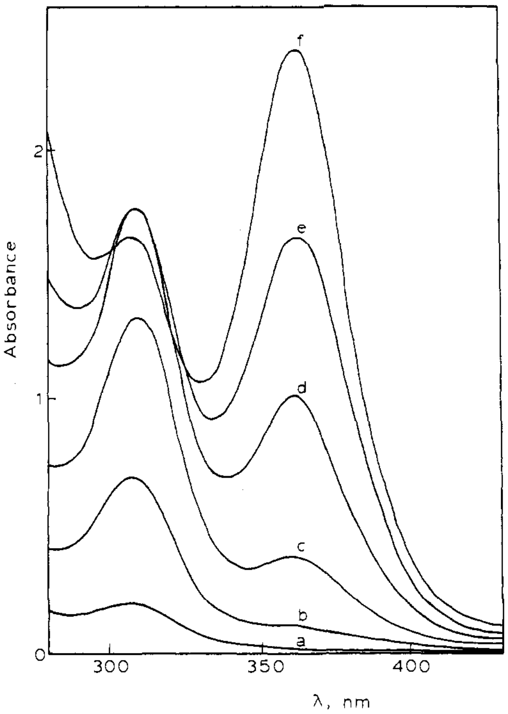


Figure 1. Spectrophotometric titration of 2.00 mL of 1.06 × 10^{-4} M $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with (a) 0.02, (b) 0.04, (c) 0.08, (d) 0.16, (e) 0.24, and (f) 0.40 mL of 1.91 × 10^{-3} M PPh_3 in acetonitrile. Spectra are not corrected for dilution.

of excess ligand ($[Rh_2] = 1.1 \times 10^{-6}$ M, $[L] = (1-4) \times 10^{-4}$ M) or excess dirhodium(II) tetraacetate concentrations ($[L] = 2.6 \times 10^{-6}$ M, $[Rh_2] = (2.5-5.0) \times 10^{-4}$ M) were employed, and plots of ln ($A_\infty - A_t$) against time were linear for at least 3 half-lives. The first-order rate constants were determined from the average of four to six replicate experiments. The reactions were conducted in acetonitrile containing 0.10 M tetrabutylammonium perchlorate (TBAP) and monitored at 315–325 nm for the monoadduct and 340–375 nm for the bisadduct formations. The reaction temperature was maintained to within 0.1 °C over the range of 5–35 °C by means of an external circulating water bath.

Equilibrium Studies. Spectrophotometric titrations of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with the phosphorus-donor ligands were carried out in acetonitrile (0.10 M TBAP) at 25 °C by using Bausch and Lomb 2000 and Perkin-Elmer 552 spectrophotometers. Solutions of the rhodium(II) complex (10^{-4} M) were titrated with 12–15 varied ligand concentrations (typically (0.2–8) × 10^{-4} M), and absorbances were measured at λ_{max} positions of the mono- and bisadducts in the 280–400-nm range. The adduct formation constants, K_1 and K_2, and the molar absorptivity coefficients at the two wavelengths were calculated by using a least-squares refinement procedure similar to that described elsewhere.[17]

Results

The dissolution of dirhodium(II) tetraacetate in acetonitrile yields a light purple species, $Rh_2(O_2CCH_3)_4(CH_3CN)_2$. The titration of this complex with tertiary phosphines or phosphites (PR_3) leads to the consecutive formation of mono- and bis(phosphine) adducts, with absorption maxima at 290–310 and 320–360 nm, respectively (Table I)

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)_2 + PR_3 \overset{K_1}{\rightleftharpoons} Rh_2(O_2CCH_3)_4(CH_3CN)PR_3 + CH_3CN} \quad (1)$$

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)PR_3 + PR_3 \overset{K_2}{\rightleftharpoons} Rh_2(O_2CCH_3)_4(PR_3)_2 + CH_3CN} \quad (2)$$

Similar λ_{max} values have been reported for the analogous dirhodium(II) tetrapropionate adducts with PPh_3, $P(OCH_3)_3$, and $P(OPh)_3$ in methylene chloride.[18] These rather intense bands (log $\epsilon > 4$) have been assigned to intermetallic $\sigma \rightarrow \sigma^*$ transitions. The distinctive peaks for these mono- and bisadducts allow for the calculation of their stability constants, K_1 and K_2, from spectrophotometric titrations. A least-squares treatment of the data yielded the stability constants and molar absorptivity coefficients (at λ_{max}) presented in Table I. The calculated absorbance values generally agreed with the experimental data to within 0.02 absorbance unit. Spectrophotometric titrations of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with the diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 2–4), did not give rise to absorbance data consistent with simple mono- and bisadduct formations. With these potential chelating or bridging ligands it appears that dimeric species may be formed at lower ligand to metal ratios. At higher ligand concentrations the adducts precipitated from the acetonitrile solution. This behavior does not apply to $Ph_2PCH_2PPh_2$, however, as it forms more soluble adducts analogous to those of the PR_3 ligands. The steric hindrance associated with interactions of the phenyl groups likely prevents this ligand from bridging two dirhodium(II) tetraacetate moieties.

Table II. Rate and Activation Parameters for the Substitution Reactions of Dirhodium(II) Tetraacetate with Phosphines and Phosphites in Acetonitrile (0.10 M TBAP)

ligand	$10^{-5}k_1$,[a] M^{-1} s^{-1}	ΔH_1^*, kcal mol^{-1}	ΔS_1^*, cal K^{-1} mol^{-1}
PPh_3	1.07 ± 0.02	11.6 ± 0.1	3.4 ± 0.4
$P(CH_2CH_2CN)_3$	1.08 ± 0.03	11.2 ± 0.6	2.2 ± 1.9
$P(OCH_3)_3$	1.10 ± 0.03	10.4 ± 0.8	−0.7 ± 2.3
$P(OPh)_3$	1.05 ± 0.03	10.5 ± 0.9	−0.5 ± 2.7
$Ph_2PCH_2PPh_2$	0.91 ± 0.17	11.0 ± 0.4	1.1 ± 1.2
$Ph_2P(CH_2)_2PPh_2$	1.60 ± 0.05	10.3 ± 0.1	−0.1 ± 0.3
$Ph_2P(CH_2)_3PPh_2$	1.63 ± 0.03	10.9 ± 0.3	1.7 ± 0.9
$Ph_2P(CH_2)_4PPh_2$	1.65 ± 0.05	11.5 ± 0.5	4.1 ± 1.5

[a] At 25.0 °C.

Kinetic Studies. The kinetics of the ligand substitution reactions of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with a series of tertiary phosphines and diphosphines have been studied in acetonitrile (0.10 M TBAP) by using stopped-flow techniques.

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)_2 + PR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh_2(O_2CCH_3)_4(CH_3CN)PR_3 + CH_3CN} \quad (3)$$

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)PR_3 + PR_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Rh_2(O_2CCH_3)_4(PR_3)_2 + CH_3CN} \quad (4)$$

The formation of $Rh_2(O_2CCH_3)_4(PR_3)_2$ was monitored at its λ_{max} (Table I) and, under pseudo-first-order conditions of excess phosphine concentrations, followed the rate expression in eq 5

$$d[\mathrm{Rh_2(O_2CCH_3)_4(PR_3)_2}]/dt = k_{obsd}[\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)_2}] \quad (5)$$

where $k_{obsd} = k_1[PR_3]$. Plots of k_{obsd} against phosphine concentration were linear for each ligand under study. The rate law in eq 5 implies that the formation of the monoadduct is the rate-determining step. This has been confirmed by a kinetic study of the reactions of PPh_3 and $P(CH_2CH_2CN)_3$ with pseudo-first-order excesses of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$, such that only the monoadduct is formed. A first-order dependence of k_{obsd} on the rhodium(II) tetraacetate concentrations was observed with the second-order rate constant agreeing with k_1 above.[21] An analogous mechanism has been proposed for the substitution reactions of the dirhodium(II) complex in aqueous solution with nitrogen-[16] and phosphorus-donor[23] ligands. The second-order rate constants

---

(20) Herbert, J. W.; Macartney, D. H. *Inorg. Chem.* **1985**, *24*, 4398.

(21) A reviewer has suggested that the consecutive formations of the mono- and bisadducts (Rh_2P and Rh_2P_2, respectively) may be a case of statistical kinetics.[22] In addition to situations where $k_1 \gg k_2$ or $k_2 \gg k_1$ (as suggested), adherence to pseudo-first-order behavior would also be seen where (a) $\epsilon(Rh_2P) = \epsilon(Rh_2P_2)$ and (b) $k_1/k_2 = \epsilon(Rh_2P_2)/\epsilon(Rh_2P)$, with $\epsilon(Rh_2) \simeq 0$. At the wavelength of observation $\epsilon(Rh_2P_2) \gg \epsilon(Rh_2P)$, such that (a) may be ruled out and (b) would imply $k_1 \gg k_2$.

(22) (a) Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630. (b) Chipperfield, J. R. *J. Organomet. Chem.* **1977**, *137*, 355.

and corresponding activation parameters are presented in Table II. The rate constants (at 25 °C) for the tertiary phosphines, $k_1 = (1.05 \pm 0.05) \times 10^5$ M^{-1} s^{-1}, are virtually identical with one another. For the diphosphines k_1 is also consistent (1.6×10^5 M^{-1} s^{-1}), with the exception of bis(diphenylphosphino)methane, for which a slightly lower rate constant (0.9×10^5 M^{-1} s^{-1}) was measured. The activation parameters for the phosphine ligands fall in a relatively narrow range; $\Delta H_1{}^{\ddagger} = 10.4$–$11.6$ kcal mol^{-1} and $\Delta S_1{}^{\ddagger} = -0.7$–$4.1$ cal K^{-1} mol^{-1}.

The kinetics of the substitution of axially coordinated PPh_3 by $P(CH_2CH_2CN)_3$ and $P(PCH_3)_3$ were investigated at 25 °C.

$$\mathrm{Rh_2(O_2CCH_3)_4(PPh_3)_2 + PR_3 \rightarrow Rh_2(O_2CCH_3)_4(PPh_3)(PR_3) + PPh_3} \quad (6)$$

$$\mathrm{Rh_2(O_2CCH_3)_4(PPh_3)(PR_3) + PR_3 \rightarrow Rh_2(O_2CCH_3)_4(PR_3)_2 + PPh_3} \quad (7)$$

A first-order dependence of the rate constant on the entering ligand concentration was observed with $k = 1.1 \times 10^5$ and 1.9×10^5 M^{-1} s^{-1} for $P(CH_2CH_2CN)_3$ and $P(OCH_3)_3$, respectively.

Discussion

The kinetic and activation parameters determined for the reactions of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with the phosphines and phosphite ligands in this study indicate that the rate-determining step is the formation of the monoadduct (eq 3), $Rh_2(O_2CCH_3)_4(CH_3CN)PR_3$, as a result of a dissociatively activated loss of a coordinated acetonitrile molecule. The highest occupied molecular orbitals of oxygen- and nitrogen-donor adducts of $Rh_2(O_2CCH_3)_4$ are the filled Rh–Rh π^* orbitals. The electron density located in these orbitals between the Rh–O(acetate) and Rh–L(axial) bond axes would hinder associative attack of an incoming ligand and promote a dissociative substitution process. The second-order rate constants for the overall formation of the bisadduct, $Rh_2(O_2CCH_3)_4(PR_3)_2$, in the presence of an excess of the ligand and for the monoadduct with an excess of dirhodium(II) are very similar, indicating that the second step (eq 4) likely proceeds much faster (10^7–10^9 M^{-1} s^{-1}) than the first step. The lack of a dependence of k_1 and the corresponding activation parameters (Table I) on the nature of the entering ligand is evidence in favor of a dissociative (D) mechanism of ligand substitution.

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)_2} \underset{k_{\mathrm{S}}}{\overset{k_{-\mathrm{S}}}{\rightleftharpoons}} \mathrm{Rh_2(O_2CCH_3)_4(CH_3CN) + CH_3CN} \quad (8)$$

$$\mathrm{Rh_2(O_2CCH_3)_4(CH_3CN) + PR_3} \xrightarrow{k_{\mathrm{P}}} \mathrm{Rh_2(O_2CCH_3)_4(CH_3CN)(PR_3)} \quad (9)$$

With solvent as the leaving ligand ($[CH_3CN] \gg [PR_3]$), $k_1 = k_{-S}k_P/k_S$. The invariance in k_1 indicates that k_P/k_S is independent of the nature of the phosphine or phosphite (both k_P and k_S are likely diffusion controlled).

The rate of axial-ligand substitution on dirhodium(II) tetraacetate complexes has also been measured in oxygen-donor solvent systems. Das et al.[16] have reported the rate constants for the formation of nitrogen-donor adducts from $Rh_2(O_2CCH_3)_4(H_2O)_2$ in aqueous solution. The values of k_1 (25 °C, $\mu = 0.10$ M) ranged from 4×10^5 M^{-1} s^{-1} (histidine) to 6.2×10^6 M^{-1} s^{-1} (imidazole), and the second step was estimated to be 10–100 times as fast. The order of magnitude range in k_1 suggests that the substitution of the coordinated water may not be a purely dissociative process but perhaps an interchange dissociative (I_d) mechanism. The presence of more than one donor atom (as in imidazole) and the possible variations in the outer-sphere association constants have been advanced as explanations for the ligand dependence of k_1.[16] The former suggestion is supported somewhat by the oservation in this study that the k_1 for the diphosphines, $PPh_2(CH_2)_nPPh_2$ ($n = 2$–4), is larger than for the monophosphines and phosphites. The formation of adducts with water-soluble phosphines occurs with rate constants of the same order of magnitude (e.g. $PPh_2(m\text{-}SO_3Ph)^-$; $k_1 = 6.5 \times 10^5$ M^{-1} s^{-1} ($\Delta H_1{}^{\ddagger} = 8.4$ kcal mol^{-1}, $\Delta S_1{}^{\ddagger} = -3.8$ cal K^{-1} mol^{-1}))[23] as for the N-donor ligands. The substitution of coordinated methanol in methanol is also rapid, with $k_1 = 2.3 \times 10^6$ M^{-1} s^{-1} ($\Delta H_1{}^{\ddagger} = 8.0$ kcal mol^{-1}, $\Delta S_1{}^{\ddagger} = -2.4$ cal K^{-1} mol^{-1}) for the reaction of $Rh_2(O_2CCH_3)_4(CH_3OH)_2$ with the $P(CH_2CH_2CN)_3$ ligand.[23]

Table III. Dependences of Substitution Rate Constants (25 °C) on Leaving Ligands X and Trans Ligands Y in Dirhodium(II) Tetraacetate Complexes $X{-}Rh(\mu\text{-}O_2CCH_3)_4Rh{-}Y$

leaving ligand	trans ligand	k, M^{-1} s^{-1}	ref
H_2O	H_2O	10^5–10^7	*b*, *c*
CH_3OH	CH_3OH	2×10^6	*c*
CH_3CN	CH_3CN	1.1×10^5	*d*
PPh_3	PPh_3	1.5×10^5	*d*
CH_3CN	PR_3	10^7–10^9	*d*
N-donor	H_2O	10^2–10^3 [a]	*b*
PR_3	CH_3CN	10^{-1}–10^2 [a]	*d*

[a] Units are s^{-1}. [b] Reference 16. [c] Reference 23. [d] This work.

While the rate of axial substitution on dirhodium(II) tetraacetate is observed to be independent of the nature of the entering ligand, it is dependent on the nature of the leaving ligand and to a smaller extent on the molecule coordinated in the other axial position across the Rh–Rh bond. Table III presents rate constants for axial substitution on dirhodium(II) tetraacetate adducts with a variety of leaving and trans-axial ligands. In the present system the rate constant k_2 would be expected to be larger than k_1 if the trans-axial phosphorus-donor ligand labilizes the coordinated CH_3CN. In the first step (eq 1) the leaving CH_3CN ligand is trans to another CH_3CN, while in the second step (eq 2) it is trans to a phosphine or phosphite. The phosphine ligands appear higher than acetonitrile in the trans-influence series for dirhodium(II) tetraacetate adducts.[24] The observation that $K_1 > K_2$ and the postulation that $k_1 \ll k_2$ implies that $k_{-2} \gg k_{-1}$. This rate comparison is also reasonable, as the rate of substitution of a PR_3 ligand trans to another PR_3 ($k_{-2} \simeq 10^5$ M^{-1} s^{-1}; eq 6 or 7) would be expected to be greater than the rate of substitution of a PR_3 ligand trans to a CH_3CN ligand ($k_{-1} = k_1/K_1 = 10^{-1}$–$10^2$ M^{-1} s^{-1}). The Rh–P bond, relatively strong in the presence of a poor trans-labilizing ligand such as water or acetonitrile, is weakened substantially upon coordination of a second phosphine. The influence of trans ligation in dirhodium(II) tetracarboxylate adducts has also been observed in (a) the unusually long Rh–L bond length in PPh_3,[25] $P(OPh)_3$,[25] and $AsPh_3$[26] adducts of dirhodium(II) tetraacetate, (b) the correlation of ^{31}P chemical shifts and ^2J(Rh–P) coupling constants in the ^{31}P NMR spectra of $Rh_2(O_2CCH_3)_4(P(OCH_3)_3)L$ complexes,[24] and (c) the inductive influence of trans base (B) coordination on ν_{CO} in $Rh_2(O_2C(CF_2)_2CF_3)_4(CO)B$ complexes.[15]

The ratio K_1/K_2 for the phosphine and phosphite ligands in this study ranges from 10 to 30. Similar ratios have been measured for a variety of nitrogen- and oxygen-donor adducts of $Rh_2(O_2CR)_4$ in aqueous and nonaqueous solution.[1,2] The ratios are higher than predicted by a statistical factor ($K_1/K_2 = 4$) alone. The coordination of the first phosphine ligand may weaken the interaction of the second phosphine with rhodium by σ-donation into the empty Rh–Rh σ^* orbital or perhaps by π-acceptance of electron density from the filled Rh–Rh π^* orbitals.

With the similarity in k_1 values for the dissociative substitution reactions, the magnitude of K_1 ($=k_1/k_{-1}$) for the phosphine adducts is a measure of the Rh–P bond strength. The observed trend in the stability constant K_1 for the phosphorus- and arsenic-donor ligands in this study (Table I) is consistent with their relative σ-donor strengths. With much weaker σ-donors the stability of the adducts with dirhodium(II) tetraacetate in acetonitrile is

---

[23] Aquino, M. A. S.; Macartney, D. H., unpublished results.

[24] Boyar, E. B.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1985**, 629.

[25] Christoph, G. G.; Halpern, J.; Khare, G. P.; Koh, Y. B.; Romanowski, C. *Inorg. Chem.* **1981**, *20*, 3029.

[26] Clark, R. J. H.; Hempleman, A. J.; Dawes, H. M.; Hursthouse, M. B.; Flint, C. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1775.

greatly reduced (e.g. dimethyl sulfoxide ($\log K_1 = 1.04$)[27] or carbon monoxide (no reaction observed)).[28] The relatively low equilibrium constants observed for good π-acceptor ligands such as $P(OPh)_3$ and CO indicate that the contribution of π-back-bonding interactions to the stability of the Rh–L bond is relatively insignificant. These findings are consistent with theoretical and experimental indications of a lack of π-stabilization in dirhodium(II) tetraacetate complexes.[24-26] Drago and co-workers, however, have observed that the properties of dirhodium(II) butyrate[14] and perfluorobutyrate[15] complexes with axial π-acceptor ligands cannot be interpreted on the basis of σ contributions alone and must include some metal-to-ligand π-back-bonding interactions. The presence of π interactions has also been observed to a certain extent in dirhodium(II) complexes in which the bridging acetates have been replaced by more electron-donating ligands such as the acetamide anion.[27,28] For the complexes in this study there appear to be no significant steric effects on the stability of the phosphine adducts or on the rates of their formation. The trend in the cone angles,[29] PPh_3 (150°) > $AsPh_3$ (147°) > $P(CH_2CH_2CN)_3$ (137°) > $P(OPh)_3$ (133°) > $P(OCH_3)_3$ (112°), is not reflected in the orders of k_1 or K_1.

The results of the present study indicated that axial-ligand substitution on $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ proceeds by a dissociative (D) mechanism. The relative stability constants of the phosphine and phosphite adducts may be rationalized on the basis of their σ-donor abilities, with π-back-bonding of only minor importance. The kinetics of the axial-solvent substitution in aqueous media suggest that the process may involve an interchange dissociative (I_d) mechanism, and further studies on the kinetics of axial substitution by water-soluble phosphines are in progress to clarify the mechanism.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada is acknowledged. We thank Queen's University for a graduate scholarship to M.A.S.A. and for a grant to D.H.M. from its Advisory Research Committee.

---

(27) Chavan, M. Y.; Lin, X. Q.; Ahsan, M. Q.; Bernal, I.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 1281.

(28) Chavan, M. Y.; Ahsan, M. Q.; Lifsey, R. S.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 3218.

(29) Imyanitov, N. S. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1986**, *11*, 663.

Contribution from the Department of Chemistry, Harbor Campus,
University of Massachusetts at Boston, Boston, Massachusetts 02125

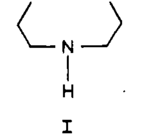
Equilibrium and Thermodynamic Study of the Aqueous Complexation of 1,4,7-Triazacyclononane-*N*,*N*′,*N*″-triacetic Acid with Protons, Alkaline-Earth-Metal Cations, and Copper(II)

Anthony Bevilacqua, Robert I. Gelb,* William B. Hebard, and Leverett J. Zompa*

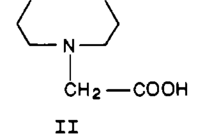
Received July 17, 1986

pH potentiometric titrations are employed to estimate temperature-dependent equilibrium constants for reactions of the amino acid 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid (H_3T) with H^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. Additionally, reactions of H_3T with Cu^{2+} are studied by both pH potentiometry and spectrophotometry. The equilibrium constant data serve to calculate $\Delta H°$ and $\Delta S°$ for the various reactions via a van't Hoff analysis. Interpretation of the thermodynamic data leads to several conclusions: (1) First and second protonation reactions of T^{3-} seem localized to nitrogen sites while addition of a third and fourth proton involve carboxylate groups. (2) Mg^{2+} complexation of T^{3-} is distinct from that of the other alkaline-earth-metal ions studied. It appears that T^{3-} forms only four or five bonds with Mg^{2+} whereas the congener ions likely form six bonds. MgT^- is however the most stable of the group IIA (group 2[23]) metal complexes apparently because of the formation of fewer but stronger metal to ligand bonds. (3) Cu^{2+} forms an unusually stable 1:1 complex with T^{3-}. The protonated form of the complex is dominant in the pH range from 0 to 2.7. The stability and properties of alkaline-earth-metal and Cu^{2+} complexes with T^{3-} are discussed and compared to those of other polyamino polycarboxylic acids in the light of the available thermodynamic, spectroscopic, and X-ray crystallographic data.

Complexation reactions of metal ions with macrocyclic polyamine ligands have been subjects of numerous investigations in recent years. These complexes have unusual stability, structural, spectroscopic, and magnetic properties. Additionally, some of the macrocycles are found to form kinetically inert complexes compared with their noncyclic analogues. As an example a number of unusual complexation properties of 1,4,7-triazacyclononane (I), abbreviated as [9]aneN_3, have been reported by several workers.[1-4]



I



II

The synthesis of a triacetic acid derivative of [9]aneN_3, 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid, was first reported by Takamoto and coworkers in 1973.[5] This compound (II), abbreviated here by the symbol H_3T, appears to share some of the macrocyclic complexing properties of the parent compound.[6] In particular, complexes with divalent metal ions have unusual stability in spite of a highly strained coordination geometry.[7,8]

---

(1) (a) Arishima, T.; Hamada, K.; Takamoto, S. *Nippon Kaqaku Kaishi*, **1973**, 1119. (b) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1977**, 1473. (c) Nonoyama, M. *Transition Met. Chem.* (*Weinheim, Ger.*) **1976**, *1*, 70.

(2) (a) DeRonde, M.; Driscoll, D.; Yang, R.; Zompa, L. J. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 521. (b) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499. (c) Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531.

(3) (a) Wieghardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650. (b) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659. (c) Buttafava, A.; Fabbrizzi, L.; Poggi, A.; Poli, G.; Seghi, B. *Inorg. Chem.* **1986**, *25*, 1456.

(4) (a) Boeyens, J.; Forbes, A.; Hancock, R. D.; Wieghardt, K.; *Inorg. Chem.* **1985**, *24*, 2926. (b) Boeyens, J.; Dobson, S. M.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3073.

(5) Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413.

(6) van der Merwe, M. J.; Boeyens, J.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3490.