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Ligand substitution reactions of dirhodium(II) tetraacetate with water-soluble phosphines

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of this observation requires further investigation and is forthcoming.

The trigonal-prismatic structure of $V(DDDT)_3^-$ was not unexpected. Gray et al.²¹ attribute the stability of trigonal-prismatic coordination to two π -bonding interactions. First, the overlap of the π_h orbitals of the sulfurs with the d_{z^2} orbital of the metal gives rise to the $2a_1'$ bonding orbital, which is always filled, and the $3a_1'$ antibonding orbital. Second, the interaction between the π_v ligand orbitals and the metal $d_{x^2-y^2}$ and d_{xy} forms $4e'$ and $5e'$, which are bonding and antibonding, respectively. The crossover point for TP to octahedral coordination is not well-defined but balances on the occupation of the bonding and antibonding orbitals. The vanadium dianions have one electron in $3a_1'$ and a filled $2a_2'$. Although $Re(S_2C_2Ph_2)_3$ is isoelectronic with these dianions and exhibits TP geometry, the destabilization of the vanadium species to a distorted octahedral structure is attributed to the small size of the metal and the occupation of the nonbonding orbital resulting in weakening of the π overlap. The neutral and monoanion have one and two electrons in $3a_1'$, respectively, and an empty $2a_2'$ due to the inversion of these levels. The π -bonding interactions outweigh the effect of one or two electrons in the $3a_1'$ antibonding level, and TP coordination results. On the basis of these arguments, $V(DDDT)_3^{2-}$ is predicted to have a distorted octahedral structure. However, recent reports^{29,30} of

two Mo dithiolene structures indicate that there are factors other than the occupation of the bonding and antibonding levels contributing to the coordination. The authors suggest the substituents attached to the dithiolene carbons play a role. Therefore, a full explanation of the coordination preference must be obtained by examining tris complexes of the same ligand, and several structural studies of complexes with the $DDDT^{2-}$ ligand are in progress.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank the National Science Foundation for funds toward upgrading our diffractometer (Grant CHE-8307022), John Cooper for assistance in collection of UV/vis/near-IR spectra, and Jack Trexler for assistance with computer software.

Registry No. $[(C_2H_5)_4N][V(DDDT)_3]$, 115244-54-7; $[(C_4H_9)_4N][V(DDDT)_3]$, 115269-49-3; $[(C_2H_5)_4N]_2[V(DDDT)_3]$, 115244-56-9; $V(DDDT)_3$, 115269-50-6; $V(DDDT)_3^{2-}$, 115244-57-0.

Supplementary Material Available: Cyclic voltammogram of $[(C_2H_5)_4N][V(S_4C_4H_4)_3]$, solution ESR spectrum of $[(C_2H_5)_4N]_2[V(S_4C_4H_4)_3]$, stereoview of the molecular packing for $[(C_4H_9)_4N][V(S_4C_4H_4)_3]$, a table of bond lengths and bond angles, and listings of hydrogen coordinates and anisotropic temperature factors (9 pages); a listing of calculated and observed structure factors (34 pages). Ordering information is given on any current masthead page.

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Ligand Substitution Reactions of Dirhodium(II) Tetraacetate with Water-Soluble Phosphines

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The kinetics of the axial ligand substitution reactions of the diaqua adduct of dirhodium(II) tetraacetate, $Rh_2(O_2CCH_3)_4(H_2O)_2$, with a series of water-soluble alkyl- and arylphosphines (PR_3^{n+}) of various charges have been investigated. The rate-determining formation of the $Rh_2(O_2CCH_3)_4(H_2O)PR_3^{n+}$ adducts occurs with rate constants (25.0 °C, $I = 0.10$ M) in the range of $(1.3-8.9) \times 10^5$ M⁻¹ s⁻¹ ($\Delta H^\ddagger = 8.0-10.3$ kcal mol⁻¹, $\Delta S^\ddagger = -5$ to 0 cal K⁻¹ mol⁻¹), with the rate constant decreasing with an increase in the absolute charge on the ligand. A dissociative mechanism is proposed for the substitution of the axially coordinated water molecules, and the rate parameters are compared with values reported for substitutions by nitrogen heterocyclic ligands. The acid dissociation constants of the protonated phosphonium ligands and the stability constants of the phosphine mono and bis adducts have been measured at 25 °C.

Introduction

Dirhodium(II) tetrakis(μ -carboxylate) complexes have been the subject of numerous investigations in recent years.^{1,2} Their interesting structural and spectroscopic properties, together with the observed catalytic³ and antitumor activities,⁴ have prompted studies of the rhodium-rhodium and rhodium-ligand interactions. These complexes contain a rhodium-rhodium single bond with four equatorial bridging carboxylate ions that are inert to substitution ($k_1(\text{acetate}) = 7.2 \times 10^{-4}$ s⁻¹ at 38 °C).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 We have recently reported the rate and activation parameters for the formation of phosphine and phosphite adducts of dirhodium(II)

tetrakis(μ -acetate) in acetonitrile.⁶ The kinetic behavior is consistent with the rate-determining formation of the mono adduct by a dissociative ligand substitution mechanism. The rate constant for the formation of the mono adduct was found to be independent of the nature of the phosphine ligand, with $k_1(25^\circ\text{C}) = (1.05 \pm 0.05) \times 10^5$ M⁻¹ s⁻¹, $\Delta H^\ddagger = 10.9 \pm 0.6$ kcal mol⁻¹ and $\Delta S^\ddagger = 1 \pm 2$ cal K⁻¹ mol⁻¹. Bear and co-workers⁷⁻¹⁰ have determined the kinetic and thermodynamic parameters associated with the formation of mono and bis adducts of dirhodium(II) tetrakis(μ -carboxylate) complexes with nitrogen heterocyclic ligands in aqueous solution. The rate constants (k_1 , 25 °C, $I = 0.10$ M) for the formation of the mono adducts, measured by temperature-jump techniques, ranged from 4×10^5 M⁻¹ s⁻¹ (histidine) to 6.2×10^6 M⁻¹ s⁻¹ (imidazole), with the formation of the bis

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Table I. UV-Visible Spectral Data and Formation Constants^a for Phosphine Adducts of Dirhodium(II) Tetraacetate

ligand	λ_1 , nm	$\log \epsilon_1$	$\log K_1^b$	λ_2 , nm	$\log \epsilon_2$	$\log K_2^b$
$\text{Ph}_2\text{P}(m\text{-SO}_3\text{Ph})^-$	314	4.29	7.20 (0.06)	385	4.68	5.38 (0.37)
$\text{P}(\text{CH}_2\text{CH}_2\text{COO})_3^{3-}$	303	4.39	7.04 (0.07)	350	4.61	4.60 (0.10)
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NH}(\text{CH}_3)_2^+$	308	4.33	6.40 (0.10)	356	4.70	4.46 (0.08)
$\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2^+$	306	4.42	6.72 (0.02)	352	4.65	5.06 (0.02)
$\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{COO})^-$	312	4.48	6.60 (0.07)	362	4.69	5.26 (0.12)

^a At 25.0 °C, $I = 0.10$ M, pH 6.8, unless otherwise indicated. ^b Uncertainties given in parentheses. ^c pH 10.4.

adducts estimated to be 10–100 times as rapid.

The variations in the formation rate constants suggest a possible change in the substitution mechanism in aqueous solution and prompted us to further investigate the kinetics of ligand substitution reactions of dirhodium(II) tetrakis(μ -acetate) with other ligand systems. The strong absorbance bands of the phosphorus donor adducts in the 300–400-nm region ($\epsilon = (2\text{--}4) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) allows for kinetic studies of their formation by using stopped-flow techniques.^{6,11} Tertiary alkyl- or arylphosphines may be rendered water soluble by the introduction of $-\text{SO}_3^-$, $-\text{COO}^-$, and $-\text{NR}_3^+$ substituents, and a number of these compounds have been synthesized for use as metal complexing agents^{12–15} and in two-phase (aqueous/organic solvent) catalytic systems.¹⁶ In this paper we report the results of spectroscopic and kinetic studies of the axial ligand substitution reactions of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ with a series of water-soluble phosphines bearing charges from -2 to $+3$. The dependences of the kinetic and equilibrium parameters on the nature of the phosphine ligands are compared with the values for the nitrogen donor ligands and discussed in terms of the mechanism of axial ligand substitution.

Experimental Section

Materials. Dirhodium(II) tetraacetate, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ (Aldrich), was used as received or prepared by literature methods.¹⁷ The rhodium dimer concentrations were determined by measurements on Perkin-Elmer 552 or Hewlett-Packard 8452A spectrophotometers; $\lambda_{\text{max}} = 585$ nm ($\epsilon = 241 \text{ M}^{-1} \text{ cm}^{-1}$) and 443 nm ($\epsilon = 110 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸ Sodium (diphenylphosphino)benzene-*m*-sulfonate dihydrate, $\text{Na}[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{SO}_3)] \cdot 2\text{H}_2\text{O}$, was prepared from triphenylphosphine (Fisher) according to the procedure of Ahrlund et al.¹² (mp = 145–147 °C, lit. mp = 146–148 °C). Tris(2-carboxyethyl)phosphine hydrochloride, $[\text{HP}(\text{CH}_2\text{CH}_2\text{COOH})_3]\text{Cl}$, was prepared from tris(2-cyanoethyl)phosphine (Strem) by the method of Rauhut et al.¹⁹ (mp 176–178 °C, lit. mp 175–177 °C). Diphenylphosphine-3-propionic acid, $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{COOH})$, was prepared by hydrolysis of the corresponding ethyl ester (Strem) using a procedure reported by Podlahova.¹⁴ (mp 129–130 °C (lit. mp 127–128 °C)²⁰) ¹H NMR (CDCl_3 , δ (ppm) vs TMS): C_6H_5 , 7.37 m, (10 H); CH_2 , 2.3–2.5 m (4 H); COOH , 11.07 s (1 H). The ligand (2-diphenylphosphinoethyl)dimethylammonium chloride, $[\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_3)_2)]\text{Cl}$, was prepared by the procedure of Taylor and co-workers.²¹ The ¹H NMR spectrum (CDCl_3 , δ vs TMS): C_6H_5 , 7.43 m (10 H); N-CH_2 , 3.15 m (2 H); CH_3 , 2.74 m (6 H), P-CH_2 , 2.58 m (2 H)) is in agreement with the literature data. The (3-phenylphosphino)bis(propylammonium) ion, $[\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2]^{2+}$, was generated in solution by the protonation of bis(3-aminopropyl)phenylphosphine (Strem).

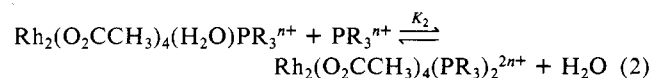
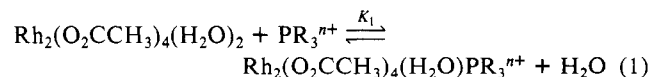
Kinetic Measurements. The kinetic studies were made by using a TDI Model IIA stopped-flow apparatus (Cantech Scientific) and data acquisition system as described previously.²² All measurements were made under pseudo-first-order conditions of excess ligand concentrations and plots of $\ln(A_\infty - A_t)$ against time were linear for at least 3 half-lives. The reported first-order rate constants represent the average of six to eight replicate experiments, monitored at 350–400 nm. The reactions were studied in aqueous media with the ionic strength maintained with added lithium perchlorate. The pH of the reaction solution was controlled by the use of acetate, phosphate, borate, and carbonate buffers or the appropriate amounts of perchloric acid at low pH.

Spectroscopic Measurements. The ligand acid dissociation constants and the adduct stability constants were determined by UV-visible spectrophotometric titrations at 25.0 °C ($I = 0.10$ M (LiClO_4)) using Bausch and Lomb 2000 and Hewlett-Packard 8452A spectrophotometers. Solutions of the rhodium(II) complex (10^{-4} M) were titrated with 12–15 varied phosphine ligand concentrations (typically $(0.2\text{--}8) \times 10^{-4}$ M), and absorbances were measured at the λ_{max} positions of the mono and bis adducts in the 300–400-nm range. The adduct formation constants, K_1 and K_2 , and molar absorptivity coefficients at the two wavelengths were calculated by using a least-squares refinement procedure similar to that described elsewhere.¹⁰ The ¹H NMR spectra of the phosphine ligands were recorded on Bruker HX-60 and AM-400 spectrometers.

Results

Acid Dissociation Constants of Phosphine Ligands. The phosphine ligands employed in this study are involved in proton equilibria involving protonation at the phosphorus atom and in some instances at the ionic functional groups (e.g. $-\text{COO}^-$). The acid dissociation constants of the protonated phosphonium ions were determined for several of the ligands at 25 °C from spectrophotometric pH titrations. The unprotonated phosphines invariably display an absorption maxima in the 245–255-nm range ($\epsilon \approx 4000 \text{ M}^{-1} \text{ cm}^{-1}$) while protonation at phosphorus results in a diminution of this peak and the appearance of a group of three peaks at 261 (sh), 268 ($\epsilon \approx 1200 \text{ M}^{-1} \text{ cm}^{-1}$), and 275 (sh) nm. Similar spectra have been reported previously for the acid/base forms of a number of other water-soluble mixed aryl/alkylphosphines.^{13,15,23} Using the pH/absorbance data at the appropriate maxima of the unprotonated phosphine, we obtained the following pK_a values at 25.0 °C: for (H)PPh₂-(CH₂CH₂COOH)⁺, $\text{pK}_a = 2.11 \pm 0.05$ ($I = 0.10$ M); for (H)-PPh(CH₂CH₂CH₂NH₃)₂³⁺, $\text{pK}_a = 2.84 \pm 0.05$ ($I = 0.10$ M); for (H)PPh₂(CH₂CH₂NH(CH₃)₂)₂²⁺, $\text{pK}_a = 0.66 \pm 0.08$ ($I = 1.0$ M). Acid dissociation constants have been reported previously for (H)PPh₂(*m*-SO₃Ph), $\text{pK}_a = 0.18$ (estimated for $I = 0.10$ M at 25 °C),²³ and for (H)P(CH₂CH₂COO)₃²⁻, $\text{pK}_a = 7.66 \pm 0.04$ ($I = 0.10$ M, 25 °C).¹⁴

Adduct Equilibrium Constants. The spectrophotometric titrations of the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ complex with a series of the water-soluble phosphines (PR_3^{n+}) lead to the consecutive formations of axial mono and bis adducts, with absorption maxima in the ranges of 300–320 and 340–390 nm, respectively.



Similar spectra have been reported for the phosphine adducts of

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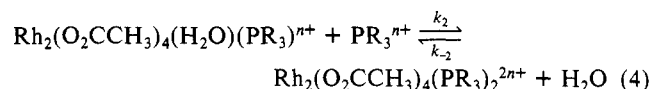
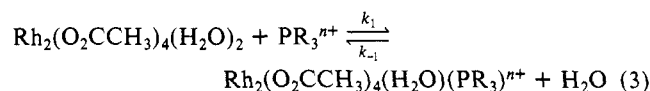
Table II. Rate and Activation Parameters for the Axial Ligand Substitution Reactions of Dirhodium(II) Tetraacetate in Aqueous Media

ligand	$10^{-5}k_1$, ^a M ⁻¹ s ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal K ⁻¹ mol ⁻¹	ref
P(CH ₂ CH ₂ CN) ₃	8.85 ± 0.14	8.6 ± 0.7	-2.5 ± 2.0	b
Ph ₂ P(CH ₂ CH ₂ COOH)	7.40 ± 0.10			b
Ph ₂ P(<i>m</i> -SO ₃ Ph) ⁻	6.48 ± 0.22	8.4 ± 0.3	-3.8 ± 0.9	b
Ph ₂ P(CH ₂ CH ₂ COO) ⁻	4.41 ± 0.06	9.5 ± 0.2	-0.8 ± 0.6	b
P(CH ₂ CH ₂ COO) ₃ ³⁻	1.32 ± 0.03	10.3 ± 0.4	-0.7 ± 1.2	b
Ph ₂ P(CH ₂ CH ₂ NH(CH ₃) ₂) ⁺	5.83 ± 0.05	8.0 ± 0.3	-5.2 ± 1.0	b
PhP(CH ₂ CH ₂ CH ₂ NH ₃) ₂ ²⁺	3.01 ± 0.06	9.9 ± 0.2	-0.2 ± 0.6	b
imidazole	71 ± 12			9
L-histidine	3.6 ± 0.4			9
5'-AMP	29 ± 4			9
isonicotinic acid	10 ± 2			10
nicotinic acid	8 ± 2			10

^a At 25.0 °C, *I* = 0.10 M. ^b This work.

dirhodium(II) tetracarboxylates in methylene chloride¹¹ and acetonitrile,⁶ and the intense bands have been assigned to inter-metallic $\sigma\text{-}\sigma^*$ transitions. A least-squares treatment of the data yielded the stability constants and molar absorptivity coefficients (at λ_{max}) presented in Table I. The agreement between the calculated and experimental absorbance values was generally to within 0.02 absorbance units.

Kinetic Studies. The kinetics of the axial ligand substitution reactions of Rh₂(O₂CCH₃)₄(H₂O)₂ with the series of water-soluble phosphines (PR₃^{*n*+}) have been studied in aqueous solution at an ionic strength of 0.10 M (LiClO₄), by monitoring the formation of the Rh₂(O₂CCH₃)₄(PR₃)₂^{2*n*+} complex at its λ_{max} (Table I).



In the pH range where pH \gg pK_a((H)PR₃^{*n*+}) and under pseudo-first-order conditions of excess phosphine concentrations, the rate expression in eq 5, where $k_{\text{obsd}} = k_1[\text{PR}_3^{n+}]$, was followed.

$$d[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PR}_3)_2^{2n+}]/dt = k_{\text{obsd}}[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2] \quad (5)$$

Plots of k_{obsd} against phosphine ligand concentration were linear for each ligand, as shown in Figure 1. The second-order rate constants, k_1 (25.0 °C and *I* = 0.10 M), and the corresponding activation parameters for the substitution reactions are presented in Table II. It has been demonstrated^{6,9} in axial ligand substitution reactions of Rh₂(O₂CR)₄(S)₂ (S = solvent) that the formation of the mono adduct is the rate determining step. In the present study, the reaction of Rh₂(O₂CCH₃)₄(H₂O)₂ with the Ph₂P(*m*-SO₃Ph)⁻ ligand gave a similar second-order rate constant when the metal complex was present in a pseudo-first-order excess. The coordination of [PR₃]^{*n*+} to the dirhodium(II) complex results in a labilization of the second solvent molecule across the Rh-Rh bond. The rate constant for the formation of the bis adduct, k_2 , is estimated to be about 100 times greater than k_1 . For several of the ligands in this study (Ph₂P(*m*-SO₃Ph)⁻, Ph₂P-(CH₂CH₂NH(CH₃)₂)⁺, and PhP(CH₂CH₂CH₂NH₃)₂²⁺) the values of k_1 were also measured at 25.0 °C as a function of ionic strength. Over the range of *I* = 0.0 (no added electrolyte) to 1.0 M (LiClO₄) the values of k_1 were within 5% of that at *I* = 0.10 M for each ligand, with no discernible trend in either direction.

For the phosphinecarboxylate ligands, (Ph)_{*n*}P-(CH₂CH₂COOH)_{3-*n*} (*n* = 0 or 2), the pH dependence of the formation rate constants was investigated. The acid dissociation constants for tris(2-carboxyethyl)phosphine have been determined by Podlaha and Podlahova¹⁴ at 25 °C and an ionic strength of 0.10 M (NaClO₄). The pK_a values for the carboxylic acid groups are 2.99, 3.67, and 4.36, while the phosphonium hydrogen has a pK_a of 7.66. The dependence of the substitution rate constant

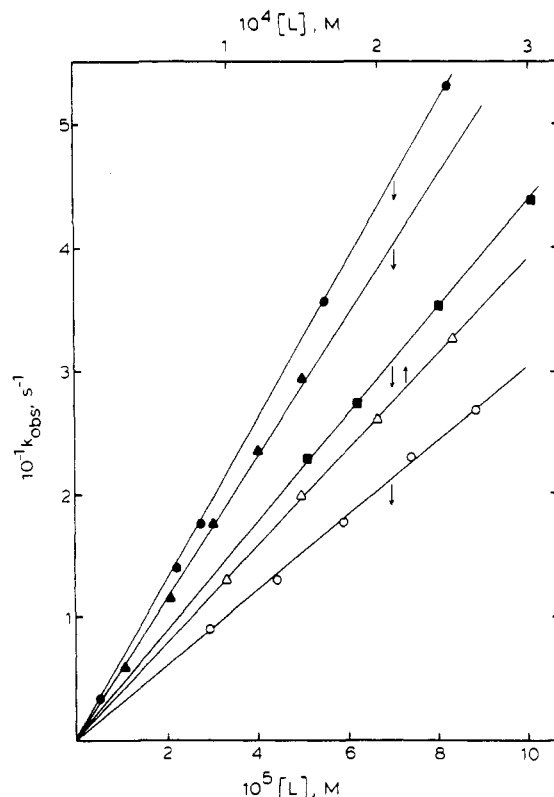
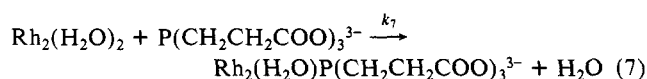
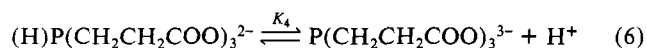


Figure 1. Dependence of k_{obsd} on ligand concentration for the axial ligand substitution reactions (at 25.0 °C, *I* = 0.10 M (LiClO₄)) of Rh₂(O₂CCH₃)₄(H₂O)₂ with Ph₂P(*m*-SO₃Ph)⁻ (pH 6.8) (●), P(CH₂CH₂COO)₃³⁻ (pH 9.8) (Δ), Ph₂P(CH₂CH₂NH(CH₃)₂)⁺ (pH 6.8) (▲), PhP-(CH₂CH₂CH₂NH₃)₂²⁺ (pH 6.8) (○), and Ph₂P(CH₂CH₂COO)⁻ (pH 7.8) (■).

on the pH of the solution (Figure 2) indicates that the dirhodium complex (Rh₂(H₂O)₂) reacts with the ligand species in which the phosphorus is deprotonated.



Over the pH range of 5–10.5 the dependence of the substitution rate constant on [H⁺] may be expressed by eq 8. A fit of the

$$k_1 = \frac{k_7 K_4 / [\text{H}^+]}{1 + K_4 / [\text{H}^+]} \quad (8)$$

experimental data to eq 8 yields $k_7 = 1.32 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and a pK₄ of 7.65, in excellent agreement with the reported value. Below pH 5 there is a small rise in the rate constants to a maximum at

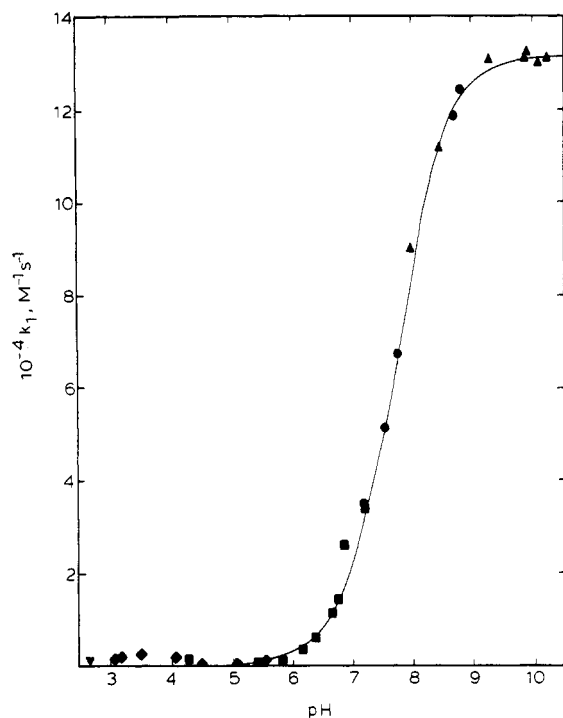
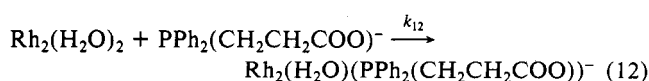
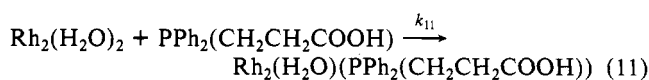
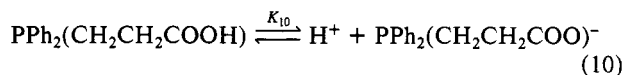
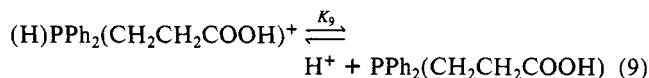


Figure 2. pH dependence of k_1 for the substitution reaction of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ with $\text{P}(\text{CH}_2\text{CH}_2\text{COO})_3^{3-}$ at 25.0°C ($I = 0.10\text{ M}$ (LiClO_4)). The pH was controlled by using HClO_4 (\blacktriangledown), acetate (\blacklozenge), phosphate (\blacksquare), borate (\bullet), and carbonate (\blacktriangle) buffers.

about pH 3.7 ($\approx 3 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$) followed by a decrease with decreasing pH. This feature may be due to small concentrations of $\text{P}(\text{CH}_2\text{CH}_2\text{COO})_n(\text{CH}_2\text{CH}_2\text{COOH})_{3-n}^{n-}$ ($n = 0, 1$) species present in equilibria with the respective $(\text{H})\text{P}(\text{CH}_2\text{CH}_2\text{COO})_{n+1}(\text{CH}_2\text{CH}_2\text{COOH})_{2-n}^{n-}$ ions. The determination of specific rate constants for these ligand species would require measurements of the appropriate microscopic equilibrium constants. From rate constants for other phosphines of the same charge type, in this study, it is estimated that the presence of the deprotonated phosphorus ions in roughly 1% quantities could account for the small increase at lower pH.

The acid dissociation constants for the (2-carboxyethyl)di-phenylphosphine ligand were determined by a spectrophotometric pH titration (described above) and from the pH profile of the substitution rate constants. The pH rate profile (Figure 3) shows an increase in the rate constant above pH 1 to a plateau at pH 4 followed by a decrease to a constant rate constant above pH 6. The experimental data were fit to the rate expression (eq 13) for the following mechanism:



$$k_1 = \frac{k_{11}K_9/[\text{H}^+] + k_{12}K_9K_{10}/[\text{H}^+]^2}{1 + K_9/[\text{H}^+] + K_9K_{10}/[\text{H}^+]^2} \quad (13)$$

A fit of the rate constants to eq 13 yielded $k_{11} = 7.40 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$ and $k_{12} = 4.41 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$, with $\text{p}K_9 = 2.19$ and $\text{p}K_{10} = 4.12$. The value of $\text{p}K_9$ is in agreement with the value from the spectrophotometric pH titration, while $\text{p}K_{10}$ is in the range ob-

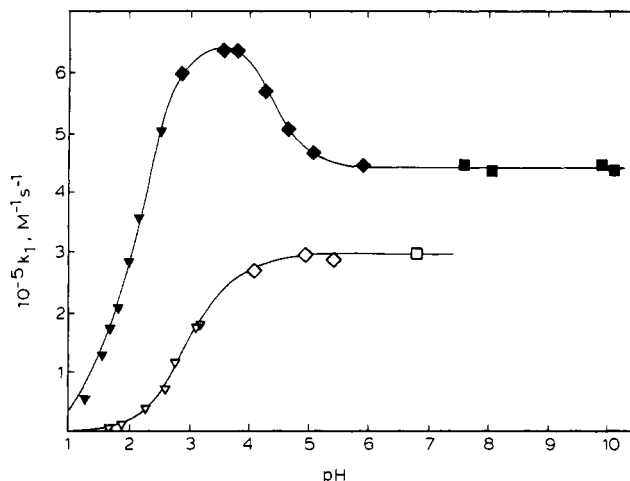


Figure 3. pH dependence of the substitution rate constants for the reactions of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ with $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{COO})^-$ (filled symbols) and $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2^{2+}$ (unfilled symbols) at 25.0°C ($I = 0.10\text{ M}$ (LiClO_4)). The pH was controlled by using HClO_4 (\blacktriangledown), acetate (\blacklozenge), and phosphate (\blacksquare) buffers.

served for related phosphine carboxylic acids.¹³⁻¹⁵

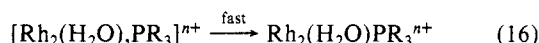
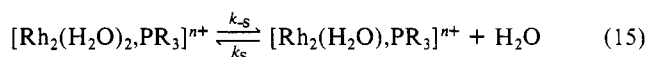
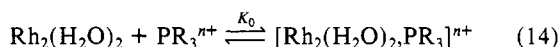
The pH rate profile of the substitution reaction with the $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2^{2+}$ ligand, shown in Figure 3, is a curve with an increase in rate constant with increasing pH. This relationship is also consistent with a mechanism involving the deprotonated phosphine as the reactive species, as seen above with the $\text{P}(\text{CH}_2\text{CH}_2\text{COO})_3^{3-}$ ligand. A fit of the kinetic data to a rate expression as in eq 8 yields a $\text{p}K_a$ value of 2.97 for $(\text{H})\text{PPh}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2^{3+}$, in good agreement with the value determined from the spectrophotometric titration.

Discussion

A previous kinetic study on the axial ligand substitution reactions of dirhodium(II) tetraacetate with phosphine ligands in acetonitrile⁶ indicated that the formation of the mono adduct is the rate-determining step, proceeding by a dissociative (D) mechanism. The formation of the mono adduct appears also to be the rate-determining step in the substitution reactions of dirhodium(II) tetraacetate with phosphines and N-heterocycles^{9,10} in aqueous solution. The substitution rate constants measured at 25.0°C for the phosphine ligands in this study fall in a relatively narrow range, from 1.3×10^5 to $8.9 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$. The corresponding activation parameters are also found to be similar to one another with $\Delta H^\ddagger = 8.0\text{--}10.3\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -5$ to $0\text{ cal K}^{-1}\text{ mol}^{-1}$. Within the range of rate constants for the phosphines, there appears to be some dependence of the rate constant on the charge of the incoming ligand. The higher the absolute charge on the ligand, the smaller the substitution rate constant. A large range of substitution rate constants (Table II) has been observed with a series of N-heterocyclic ligands.^{9,10} With the exception of imidazole, the rate constants for these ligands are similar to those obtained for the phosphines. The larger value of 5'-adenosine monophosphate may be related to the presence of three potential N-heterocyclic binding sites in the ligand. We have previously observed a dependence of the substitution rate constant on the number of binding sites in the reactions of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{C}_6\text{H}_5\text{CN})_2$ with phosphines: for PPh_3 ,⁵ $k_1 = 1.07 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$; for $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$,⁵ $k_1 = 1.60 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$; for $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$,²⁴ $k_1 = 2.0 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$. The small dependence of the substitution rate constants on the nature of the ligand suggests that while the process is dissociatively activated, there may be some interaction of the entering ligand with the dirhodium(II) complex (K_0) prior to dissociation of the axial water (k_{-5}). This interaction can be accommodated in either an ion-pair

(24) Macartney, D. H., unpublished results.

dissociative (D_{IP}) or an interchange dissociative (I_d) mechanism.



The former mechanism would seem to be unlikely in view of the overall neutrality of the dirhodium(II) complex and the lack of an ionic strength dependence of the substitution rate constants. The observed dependence of k_1 on the absolute charge of the entering ligand, however, suggests that the ligands may be involved in specifically oriented interactions with the charges distributed within the $Rh_2(O_2CCH_3)_4(H_2O)_2$ complex. The latter mechanism involves the partial formation of a Rh-P bond prior to complete dissociation of the Rh-OH₂ bond. The highest occupied molecular orbitals of $Rh_2(O_2CCH_3)_4(H_2O)_2$ complex are the filled Rh-Rh π^* orbitals²⁵ and the electron density located in these orbitals between the Rh-O(acetate) and Rh-OH₂ bond axes would discourage the associative attack of an entering phosphine. Further kinetic studies with a wider variety of ligand types may help to clarify the nature of the interactions between the metal complex and entering ligands prior to the dissociation of the coordinated solvent. The substitution of axially coordinated solvent molecules on dirhodium(II) tetraacetate by tris(2-cyanoethyl)phosphine has now been studied in water, methanol,⁶ and acetonitrile,⁶ with rate constants (25.0 °C, $I = 0.10$ M) of 8.5×10^5 , 2.6×10^6 , and 1.1×10^5 M⁻¹ s⁻¹, respectively, for the phosphine monoadduct formation. The rate constants reflect the relative σ -donor strengths of the three solvent ligands and are consistent with a dissociatively

activated substitution mechanism.

The stability constants for the formation of the mono and bis adducts (Table I) span several orders of magnitude for the ligands in this study. The ratios of K_1/K_2 for the phosphine ligands range from 7 to 275, which are higher than predicted by a statistical factor alone ($K_1/K_2 = 4$). The ratios generally increase with an increase in the magnitude of K_1 and reflect the degree of phosphine trans labilization of the axial ligand across the Rh-Rh bond. With the exception of $PhP(m-SO_3Ph)^-$, the values of $\log K_1$ follow the trend in the pK_a values of the protonated phosphonium species. These observations support the importance of the σ -donor strength of the phosphine ligand in the relative adduct stabilities, as seen previously.⁶

The rapid adduct formation reactions of $Rh_2(O_2CCH_3)_4(H_2O)_2$ with the water-soluble phosphines are followed by slower processes in which the strong absorption band in the 350-400-nm region is lost and new bands in the ultraviolet region (e.g. 270 nm for the tris(2-carboxyethyl)phosphine ligand) are formed following an induction period. The inability to regenerate the phosphine adduct upon further additions of ligand suggest that the $Rh_2-(O_2CCH_3)_4$ core has been altered, perhaps as a result of inter- or intramolecular electron transfer between the metals and the phosphine ligand. Further kinetic and spectroscopic studies on these secondary reactions are in progress.

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Registry No. $Rh_2(O_2CCH_3)_4(H_2O)_2$, 29998-99-0; $P(CH_2CH_2CN)_3$, 4023-53-4; $Ph_2P(CH_2CH_2COOH)$, 2848-01-3; $Ph_2P(m-SO_3Ph)^-$, 65355-51-3; $Ph_2P(CH_2CH_2COO)^-$, 115290-69-2; $P(CH_2CH_2COO)_3^{3-}$, 115290-70-5; $Ph_2P(CH_2CH_2NH(CH_3)_2)^+$, 115290-71-6; $PhP(CH_2CH_2CH_2NH_3)_2^{2+}$, 115305-74-3.

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Contribution from the Departments of Organic and Inorganic Chemistry, University of Sydney, Sydney, NSW, Australia 2006

Diamagnetic \rightleftharpoons Paramagnetic Equilibria in Solutions of Bis(dialkylphosphino)ethane Complexes of Iron

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The X-ray structures of two iron(II) chloride complexes, $Fe(DEPE)_2Cl_2$ (DEPE = 1,2-bis(diethylphosphino)ethane) and $Fe(DPrPE)_2Cl_2$ (DPrPE = 1,2-bis(di-*n*-propylphosphino)ethane), have been determined ($Fe(DEPE)_2Cl_2$, monoclinic, space group $P2_1/c$, $a = 10.179$ Å, $b = 13.506$ (2) Å, $c = 10.674$ (2) Å, $\beta = 108.69$ (1)°, $Z = 2$; $Fe(DPrPE)_2Cl_2$, monoclinic, space group $P2_1/c$, $a = 11.673$ (1) Å, $b = 11.029$ (1) Å, $c = 14.803$ (3) Å, $\beta = 106.21$ (1)°, $Z = 2$). There is a small but significant increase in the Fe-P bond length in progressing from DEPE to DPrPE ligands (2.260 to 2.268 Å), and the Fe-P bond length in both complexes is markedly greater than that in the closely related complex $Fe(DMPE)_2Cl_2$ (DMPE = 1,2-bis(dimethylphosphino)ethane) (2.235 Å). The complexes $Fe(DEPE)_2Cl_2$ and $Fe(DPrPE)_2Cl_2$ are both diamagnetic in the solid state but give rise to paramagnetic solutions when dissolved. The solution paramagnetism varies with temperature and is ascribed to reversible dissociation (or partial dissociation) of one of the bidentate phosphine ligands from the iron. The tendency of iron(II) dichloride complexes with bis(dialkylphosphino)ethane ligands to form 6-coordinate complexes or complexes of lower coordination number is discussed in terms of the increasing steric demand of the alkyl-substituted ligands.

Introduction

During the course of our studies of iron bis(diphosphine) complexes, we have prepared a number of compounds of the general formula $Fe(PP)_2X_2$ (PP = 1,2-bis(dialkylphosphino)ethane, X = Br, Cl, I). Bis(dialkylphosphino)ethanes such as DMPE (bis(dimethylphosphino)ethane), DEPE (1,2-bis(diethylphosphino)ethane), and DPrPE (1,2-bis(di-*n*-propylphosphino)ethane) are versatile bidentate ligands that form strong

complexes with a number of transition metals. The synthesis and some properties of the iron(II) complexes $Fe(DMPE)_2Cl_2$ (**1**)^{1,2} and $Fe(DEPE)_2Cl_2$ (**2**)^{1,3} have been previously reported; however, the anomalous magnetic behaviors of **2** and the homologous compound $Fe(DPrPE)_2Cl_2$ (**3**) in solution have never been noted.

$Fe(DMPE)_2Cl_2$, $Fe(DEPE)_2Cl_2$, and $Fe(DPrPE)_2Cl_2$ are all green crystalline compounds that are diamagnetic in the solid state

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