Synthesis, NMR and kinetic behaviour of rhodoximes containing bulky phosphine ligands

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Abstract

We report here an efficient method to obtain the chlororhodoximes $[Rh(dh)_2(PR_3)Cl]$ and the aquorhodoximes $[Rh(dh)_2(PR_3)H_2O]^+$, where $(dh)_2$ is the bis(dimethylglyoximate) ligand and PR_3 the bulky phosphines PPr^i_3 and $PChx_3$. The axial water is both more acidic and more labile toward the substitution reactions than in the corresponding cobaloximes; these results are in line with those previously found for the organometallic derivatives. The $^1J(Rh, P)$ values follow the *trans* influence of the other axial ligand. The temperature dependence of the cyclohexyl ^1H and ^{13}C spectra suggests that in the $[Rh(dh)_2(PChx_3)X]$ compounds the rotation around the Rh–P bond is hindered, likely owing to the steric bulk of the phosphine.

Introduction

Recent studies on the organometallic $[Rh(dh)_2(py)R]$ complexes (R = alkyl group, py = pyridine) have provided further advances in the understanding of these molecules and their better known cobalt analogues pyridine-cobaloximes [1, 2]. The availability of a series of $[Rh(dh)_2(L)X]$ compounds with X = Cl and L = tertiary phosphine is a good opportunity to extend the comparison between rhodoximes and cobaloximes to their non-organometallic derivatives.

The difficulties in obtaining the non-organometallic neutral rhodoximes have been discussed long ago [3], and the catalytic effect of small amounts of Rh(I) has been evidenced. We report here an efficient method to obtain chloro and aquorhodoximes containing bulky phosphine ligands (PPr^i_3 and $PChx_3$) (Fig. 1), their NMR properties and a preliminary kinetic study on the water substitution reactions.

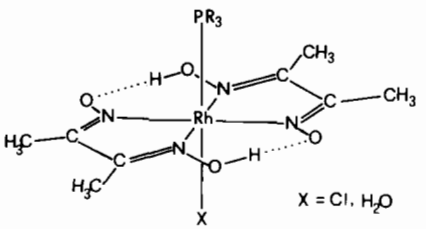

Fig. 1.

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Experimental

Syntheses of the metal complexes

[Rh(dh)(dh$_2$(Cl)$_2$], [Rh(dh)$_2$(PPh$_3$)Me] and [Rh(dh)$_2$(PPh$_3$)Cl]

These complexes were prepared as previously described [4–6]. The synthesis of $[Rh(dh)_2(PPh_3)Cl]$ in the presence of an excess of phosphine gives some $[Rh(dh)_2(PPh_3)_2]^+$ as a by-product.

[Rh(dh)$_2$(PPh$_3$)Me]. ^1H NMR ($CDCl_3$): δ 0.55 (dd, 3H, $^3J(P, H) = 6.1$ Hz, $^2J(Rh, H) = 2.2$ Hz), 1.88 (d, 12H, $^5J(P, H) = 2.1$ Hz), 7.45–7.75 (m, 15H); (C_6D_6): δ 1.12 (dd, 3H, $^3J(P, H) = 6.1$ Hz, $^2J(Rh, H) = 2.2$ Hz), 1.60 (d, 12H, $^5J(P, H) = 2$ Hz), 6.85–7.10 (m, 9H, *meta* + *para* H), 7.40–7.65 (m, 6H, *ortho* H).

[Rh(dh)$_2$(PPh$_3$)Cl]. ^1H NMR ($CDCl_3$): δ 1.94 (s, 12H), 7.35–7.75 (m, 15H); (C_6D_6): δ 1.56 (d, 12H, $^5J(P, H) = 0.5$ Hz), 6.82 (m, 9H, *meta* + *para* H), 7.40–7.75 (m, 6H, *ortho* H).

[Rh(dh)$_2$(PPh$_3$)$_2$]$^+$Cl$^-$. ^1H NMR ($CDCl_3$): δ 1.42 (t, 12H, $^5J(P, H) = 1.4$ Hz), 7.35–7.55 (m, 15H).

[Rh(dh)$_2$(PPr$^i_3$)Cl]

(a) 0.52 g of rhodium trichloride hydrate was refluxed in methanol with 0.48 g of dimethylglyoxime and a strong excess (about 1 ml) of PPr^i_3 for 45 min. Evaporation of the solvent under reduced pressure produced a yellow crystalline precipitate of the insoluble

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$[Rh(dh)(dh_2)(Cl)_2]$ complex, which was filtered out. The remaining red solution was allowed to stand until a yellow precipitate of $[Rh(dh)_2(PPr^i_3)Cl]$ formed. The ratio of the two products is very variable. *Anal.* Calc. for $[Rh(dh)_2(PPr^i_3)Cl]$: C, 38.6; H, 6.7; N, 10.6. Found: C, 37.9; H, 7.0; N, 8.5%.

(b) 0.32 g of $[Rh(dh)(dh_2)(Cl)_2]$ was suspended in 100 ml of methanol and some drops of concentrated aqueous NaOH were added until dissolution. The solution was stirred under nitrogen for 10 min and then less than the stoichiometric amount of $NaBH_4$ in water was added. The solution turned black and the colour did not change after addition of a slight excess of phosphine. During a period of 2 h under inert atmosphere the colour changed slowly to red–brown. In the presence of air the solution turned yellow quickly; neutralization with HNO_3 gave an orange solution, which was allowed to stand until a yellow precipitate appeared. Yield 40%. *Anal.* Calc. for $[Rh(dh)_2(PPr^i_3)Cl]$: C, 38.6; H, 6.7; N, 10.6. Found: C, 38.4; H, 6.7; N, 10.3%. ^{1}H NMR ($CDCl_3$): δ 1.23 (dd, 18H, ^3J(H, H) = 7.3 Hz, ^3J(P, H) = 14.2 Hz), 2.27 (m, 3H, ^2J(P, H) = 11 Hz, ^3J(H, H) = 7.3 Hz, ^3J(Rh, H) = 1 Hz), 2.27 (s, 12H).

$[Rh(dh)_2(PChx_3)Cl]$

0.405 g of $[Rh(dh)(dh_2)(Cl)_2]$ was suspended in 150 ml of methanol and some drops of concentrated aqueous NaOH were added until dissolution. The solution was stirred under nitrogen for 10 min an then less than the stoichiometric amount of $NaBH_4$ in water was added. The solution turned black and the colour did not change after addition of a twofold excess of the phosphine dissolved in methanol. The mixture was stirred under nitrogen for several hours; during this time a highly insoluble red–brown solid separated from the solution. This precipitate, likely the dimer $[Rh(II)(dh)_2(PChx_3)]_2$, was filtered out and dried under vacuum. Yield 20%. *Anal.* Calc. for $[Rh(II)(dh)_2(PChx_3)]_2$: C, 50.9; H, 7.7; N, 9.1. Found: C, 50.7; H, 7.8; N, 9.1%. In contact with the air the colour of the remaining solution turned red–brown. After neutralization (pH about 6) with diluted $HClO_4$ the resulting red–orange solution was evaporated nearly to dryness, giving yellow crystals of the desired product. Yield 40%. *Anal.* Calc. for $[Rh(dh)_2(PChx_3)Cl]$: C, 48.1; H, 7.3; N, 8.6. Found: C, 47.6; H, 7.3; N, 8.2%. ^{1}H NMR ($CDCl_3$): δ 1.11 (m, 6H, 3ax), 1.31 (m, 3H, 4ax), 1.47 (m, 6H, 2ax), 1.65–1.90 (m, 18H, 1ax + 2eq + 3eq + 4eq), 2.27 (s, 12H); (DMSO-d_6): δ 1.23 (m, 6H, 3ax), 1.27 (m, 3H, 4ax), 1.47 (m, 6H, 2ax), 1.60–1.90 (m, 18H, 1ax + 2eq + 3eq + 4eq), 2.21 (s, 12H).

$[Rh(dh)_2(PR_3)(H_2O)]^+X^-$ ($R = Ph$, Chx, Pr^i; $X^- = ClO_4^-$, NO_3^-)

About 0.5 g of the parent chloro complex was suspended in 150 ml of methanol warmed up to 40–50 °C under stirring. A stoichiometric amount of aqueous $AgNO_3$ was added. The suspension was stirred until the chloro complex dissolved and the precipitate of AgCl was well separated. After filtration a concentrated aqueous solution of $NaClO_4$ or $NaNO_3$ was added and the solvent was evaporated until the precipitation of the desired compound began. Yield 80%. *Anal.* Calc. for $[Rh(dh)_2(PPh_3)(H_2O)]^+ClO_4^-$: C, 43.8; H, 4.4; N, 7.9. Found: C, 43.1; H, 4.6; N, 7.5%. ^{1}H NMR ($(CD_3)_2CO$): δ 2.05 (s, 12H), 7.55–7.65 (m, 15H). *Anal.* Calc. for $[Rh(dh)_2(PChx_3)(H_2O)]^+ClO_4^-$: C, 42.7; H, 6.8; N, 7.7. Found: C, 40.6; H, 6.9; N, 7.0%. ^{1}H NMR ($(CD_3)_2CO$): δ 1.24 (m, 6H, 3ax), 1.35 (m, 3H, 4ax), 1.61 (m, 6H, 2ax), 1.69 (m, 3H, 4eq); 1.75–2.0 (m, 15H, 1ax + 2eq + 3eq), 2.35 (s, 12H); (DMSO-d_6): δ 1.17 (m, 6H, 3ax), 1.29 (m, 3H, 4ax), 1.47 (m, 6H, 2ax), 1.66 (m, 3H, 4eq), 1.76 (m, 12H, 2eq + 3eq), 1.8 (m, 3H, 1ax), 2.33 (s, 12H). *Anal.* Calc. for $[Rh(dh)_2(PPr^i_3)(H_2O)]^+NO_3^-$: C, 35.6; H, 6.5; N, 12.2. Found: C, 34.9; H, 6.7; N, 12.0%. ^{1}H NMR ($(CD_3)_2CO$): δ 1.26 (dd, 18H, ^3J(H, H) = 7.1 Hz, ^3J(P, H) = 14.4 Hz), 2.26 (s, 12H), 2.39 (m, 3H, ^2J(P, H) = 11 Hz, ^3J(H, H) = 7.1 Hz, ^3J(Rh, H) = 1 Hz).

Equilibrium studies

The deprotonation constants of the $[Rh(dh)_2(PR_3)(H_2O)]^+X^-$ complexes were determined by potentiometric titrations of air free solutions of the compounds (about 5×10^{-3} M) with NaOH 5×10^{-2} M in methanol (30%)–water at 25 °C. The titration curves show two sufficiently well separated inflexions. The corresponding pK_1 and pK_2 values were calculated from each titration point in the buffer region. The final values are the average of at least ten points.

The detection of the second inflexion for $[Rh(dh)_2(PChx_3)(H_2O)]^+$ is prevented by the precipitation of a highly insoluble product after the first neutralization process. The precipitate has a composition corresponding to $[Rh(dh)_2(PChx_3)(OH)]$. *Anal.* Calc. for $[Rh(dh)_2(PChx_3)(OH)]$: C, 49.5; H, 7.7; N, 8.9. Found: C, 48.8; H, 7.7; N, 8.3%.

For the pH measurements a Radiometer pHM4 pH meter was used.

Kinetic measurements

The reactions between $[Rh(dh)_2(PR_3)(H_2O)]^+X^-$ complexes and HSO_3^- were monitored spectrophotometrically at 420–430 nm by a Hi-Tech SF3 series stopped flow apparatus. The kinetic runs were performed at 35 °C, $I = 1$ M ($NaNO_3$), pH range 4.2–4.8 (acetate buffer). At these pH values the compounds

are present in solution as aquo complexes and the incoming ligand as HSO_3^- (for sulfurous acid $pK_{a1} = 1.89$ and $pK_{a2} = 7.21$ [7]). The reactions were carried out under pseudo first order conditions, in the presence of a large excess of HSO_3^-. The initial concentration of complexes was $2\text{–}4 \times 10^{-4}$ M; the ligand concentrations ranged from 5×10^{-2} to 2.5×10^{-1} M.

The plots of $\log(A_t - A_\infty)$, where A_t is the absorbance at the time t and A_∞ is the final absorbance, versus time are linear and allow the calculation of k_{obs}.

The $NaHSO_3$ solutions were prepared fresh each day by addition of HNO_3 to a solution containing an equivalent amount of analytical grade Na_2SO_3. The sulfite concentration was determined by titration with iodine.

NMR measurements

The NMR spectra were recorded on a Bruker WP80 spectrometer (^1H at 80 MHz, ^{13}C at 20.12 MHz, ^{31}P at 32.4 MHz) equipped with an ASPECT 2000 computer and on a Jeol EX-400 spectrometer (^1H at 400 MHz, ^{13}C at 100.4 MHz, ^{31}P at 161.7 MHz). For the ^1H and ^{13}C spectra TMS was used as internal standard in $CDCl_3$ and $(CD_3)_2CO$ solutions, DSS in DMSO-d_6 solutions. For the ^{31}P spectra H_3PO_4 10% was used as external standard.

Variable temperature ^1H and ^{13}C spectra were recorded through the Jeol NM-EVTS3 variable temperature unit.

Results and discussion

Synthesis

The synthesis of $[Rh(dh)_2(L)Cl]$ complexes (L= phosphine) is hampered by the inertness and the insolubility of the corresponding dichloro complex $[Rh(dh)(dh_2)(Cl)_2]$.

The PPh_3 derivative can be prepared directly from rhodium trichloride, dimethylglyoxime and a stoichiometric amount of phosphine [6], but our attempts to extend this synthesis to other phosphines gave unsatisfactory results, leading to mixtures of products.

The PPr^i_3 derivative may be synthesized by this method in the presence of an excess of phosphine, but the product is often contaminated by the dichloro complex.

With $PChx_3$, besides $[Rh(dh)(dh_2)(Cl)_2]$, a not well identified species appears, whose ^{31}P NMR spectrum consists of a broad signal. The same result has been obtained in the presence of a small amount of H_3PO_2, even if the hypophosphorous acid has been previously found to catalyze the synthesis of the $[Rh(dh)_2(py)Cl]$ compound from the dichloro complex and pyridine [3].

The inertness of the $[Rh(dh)(dh_2)(Cl)_2]$ derivative and the reported evidence that the substitution reactions are catalyzed by a small amount of the corresponding Rh(I) complex [3], led us to attempt the synthesis by reducing the dichloro complex to Rh(I), adding the phosphine and oxidizing in air. Through this route the neutral *trans* compounds $[Rh(dh)_2(PR_3)Cl]$ were obtained for $PChx_3$ and PPr^i_3, but with better donor and less bulky phosphines this method led to complexes with a modified equatorial ligand [8].

The red–brown by-product isolated during the synthesis of $[Rh(dh)_2(PChx_3)Cl]$ and supposed to be the dimer $[Rh(II)(dh)_2(PChx_3)]_2$ has low solubility and reacts with most solvents; therefore it could not be studied by NMR spectra. It is well known that the dimeric species $[Rh(II)(dh)_2(PPh_3)]_2$ is formed by decomposition under nitrogen of the corresponding hydridorhodoxime both through heterolytic and homolytic pathways [9]. The same mechanism could account for the formation of $[Rh(II)(dh)_2(PChx_3)]_2$ from the Rh(I) complex and $PChx_3$; indeed it is likely that significant amounts of hydrido complex are present also in our basic solutions, as for the strictly related PPh_3 derivative a $pK_a = 9.5$ has been found for equilibrium (1).

$$[Rh(dh)_2(PPh_3)H] \rightleftharpoons [Rh(dh)_2(PPh_3)]^- + H^+ \qquad (1)$$

NMR spectra

In the $[Rh(III)(dh)_2(PR_3)]$ compounds the $^1J(Rh, P)$ shows a heavy dependence on the *trans* ligand X (Table 1) and follows the changes expected for the Fermi term [12]*. The dependence of the ^{31}P complexation shift on X parallels that of the coupling constants. Furthermore there is a good quantitative correspondence between the ^{31}P complexation shifts in chlororhodoximes and chlorocobaloximes [11] (for PPh_3, 28.8 in the Rh derivative and 30.1 in the Co derivative; for PPr^i_3, 17.1 and 14.2; for $PChx_3$, 12.7 and 9.9).

The spectra of the phosphino aquo derivatives were run in acetone, as the ^{31}P resonances showed that they are unstable in chloroform. The high values of the rhodium–phosphorus coupling constants and of the phosphorus complexation shifts suggest that in the cationic aquo complexes the phosphine interacts with rhodium stronger than in the corresponding neutral chloro derivatives.

In the $\{^1H\}^{13}C$ spectra (Table 1) of the $[Rh(dh)_2(PChx_3)X]$ complexes the phosphine C-1 and C-2 carbons are broadened. The broadening is much stronger at 100 MHz than at 20 MHz, and, in the spectra run in DMSO-d_6 at 35.5 and 75 °C, it decreases with increasing temperature. Likely this is due to a hindered rotation around the Rh–P bond, which does

*The $^1J(Rh, P)$ values of $[Rh(dh)_2(PPh_3)Cl]$ and of $[Rh(dh)_2(PPh_3)_2]^+$ are similar to those of the phosphorus atom *trans* to chlorine and *trans* to phosphorus, respectively, in the *mer* and *fac* $[Rh(PR_3)_3(Cl)_3]$ complexes [13]. This is noteworthy especially if one considers the extreme difference of the equatorial situations.

TABLE 1. ^{31}P and ^{13}C NMR parameters of $[Rh(dh)_2(L)X]$ and $[Rh(dh)(dh_2)(Cl)_2]$[a]

L	X	Solvent	Phosphine					dh	
			^{31}P	C-1	C-2	C-3	C-4	C=N	CH_3
PPh_3	H_2O/ClO_4^-	$(CD_3)_2CO$	29.7 (139)	125.7 (58.8)	135.0 (11)	129.8 (12.9)	133.4	155.3	12.7
PPh_3	Cl	$CDCl_3$	23.8 (122.8)	127.0 (53)	134.0 (9.6)	128.4 (10.3)	131.6 (3)	151.5	12.3
PPh_3	PPh_3/Cl^-	$CDCl_3$	17.6 (92)		134.1 vt	128.9 vt	132.1	153.7	12.1
PPh_3	Me	$CDCl_3$	8.8 (66)					150.8[b]	12.3[b]
$PChx_3$	H_2O/ClO_4^-	$(CD_3)_2CO$	43.9 (133.1)	38.2 bs	obs	28.75 (9)	26.9	155.9	12.9
$PChx_3$	H_2O/ClO_4^-	DMSO	42.2 (128.1)	38.4 (20)	30.2 bs	29.1 (10.5)	27.3	156.0	14.0
$PChx_3$	Cl	$CDCl_3$	26.7 (119)	36.8 (20)	29.35 bs	28.5 (10)	26.4	152.0	12.6
$PChx_3$	Cl	DMSO	27.3 (118.4)	37.4 bs	30.1	29.3	27.4	153.2	13.6
PPr^i_3	H_2O/NO_3^-	$(CD_3)_2CO$	49.5 (128.1)	26.3 (25.8)	19.5			154.5	12.6
PPr^i_3	Cl	$CDCl_3$	37.9 (119)	25.1 (22)	19.2			152.3	12.7
Cl	Cl/H^+	DMSO						156.8	14.7
PPh_3	free	$CDCl_3$	−5[c]	137.4 (11)	133.8 (19)	128.5 (7.3)	128.6		
$PChx_3$	free	$CDCl_3$	14[c]	31.54 (14.7)	31.1 (11)	27.6 (9.5)	26.5		
PPr^i_3	free		20.8[c]						

[a] δ values in ppm; $|J|$ values in Hz in parentheses, first column $J(Rh, P)$, other columns $J(C, P)$; vt = virtual triplet, obs = obscured, bs = broad signal. [b] From ref. 10. [c] From ref. 11.

not allow a complete averaging of the inequivalences within the C-1 and the C-2 carbons of the various rotamers.

The ^1H data are reported in 'Experimental'. In the PPh_3 derivatives the equatorial methyl protons are 0.3 ppm more shielded than in the corresponding derivatives with aliphatic phosphines (compare $[Rh(dh)_2(PPr^i_3)Cl]$, $[Rh(dh)_2(PChx_3)Cl]$ and $[Rh(dh)_2(PPh_3)Cl]$ in $CDCl_3$; $[Rh(dh)_2(PChx_3)(H_2O)]^+$ and $[Rh(dh)_2(PPh_3)(H_2O)]^+$ in acetone). This has to be attributed to the magnetic anisotropy of the phosphine phenyls. An effect of close magnitude was found also for the cobaloximes [14, 15]. The further shielding of the equatorial methyls observed in the $[Rh(dh)_2(PPh_3)_2]^+$ cationic compound is related to the increased number of aromatic rings. On going from $CDCl_3$ to C_6D_6 the equatorial methyls both in $[Rh(dh)_2(PPh_3)Me]$ and $[Rh(dh)_2(PPh_3)Cl]$ are about 0.3–0.4 ppm more shielded, while the axial methyl of the former is 0.6 ppm deshielded; these findings reflect the tendency of the benzene molecules to lie parallel to the equatorial plane.

The resonances of the cyclohexyl protons in $[Rh(dh)_2(PChx_3)X]$ observed at 400 MHz were assigned by comparison with the spectra of cyclohexylamine [16] and $[Pt(trans\text{-}MeO_2CCH{=}CHCO_2Me)_2PChx_3]$ [17]. Interestingly, the resolution of the cyclohexyl proton signals, particularly of 2ax, is poor and improves by raising the temperature. This behaviour is similar to that described above for the ^{13}C spectra and likely it has the same origin, i.e. a slow rotation around the Rh–P bond.

Equilibrium studies

The two consecutive ionization processes evidenced in the potentiometric titrations of $[Rh(dh)_2(PPh_3)(H_2O)]^+X^-$ and $[Rh(dh)_2(PPr^i_3)(H_2O)]^+X^-$ complexes have been ascribed to equilibria (2) and (3).

$$[Rh(dh)_2(PR_3)(H_2O)]^+ \rightleftharpoons [Rh(dh)_2(PR_3)(OH)] + H^+ \quad (2)$$

$$[Rh(dh)_2(PR_3)(OH)] \rightleftharpoons [Rh(dh)(d)(PR_3)(OH)]^- + H^+ \quad (3)$$

The corresponding pK_1 and pK_2 values are reported in Table 2. For $[Rh(dh)_2(PChx_3)(H_2O)]^+$ only the first ionization could be evidenced (see 'Experimental').

TABLE 2. pK values for the deprotonation of $[M(dh)_2(L)(H_2O)]^+$ at 25 °C in methanol (30%)–water

L	pK_1		pK_2
	Rh(III)	Co(III)[a]	Rh(III)
PPr^i_3	6.4±0.1	8.23±0.01	9.4±0.1
$PChx_3$	6.7±0.2	8.10±0.03	
PPh_3	6.2±0.1	7.53±0.01	9.7±0.1

[a]From ref. 18.

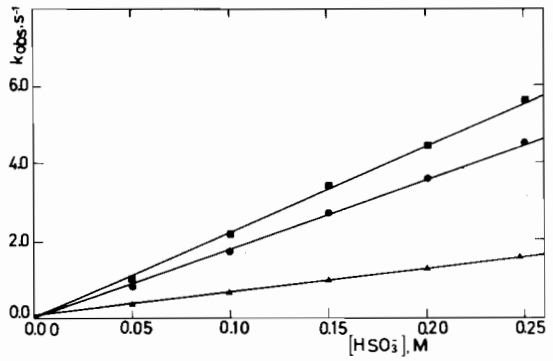

Fig. 2. Dependence of k_{obs} on $[HSO_3]^-$ for L = PPr^i_3 (■), $PChx_3$ (●) and PPh_3 (▲).

The pK_1 values are 2–3 units lower than in the organoaquorhodoximes [19], in agreement with the lower *trans* effect of the phosphine groups and with the positive charge of these complexes. A comparison with the deprotonation constants of the axial water in the corresponding $[Co(dh)_2(PR_3)(H_2O)]^+$ complexes shows a higher acidity in the rhodium complexes (Table 2); the same behaviour was previously observed in the alkyl derivatives [19].

A quantitative comparison between the equatorial proton acidities of rhodoximes and cobaloximes is not possible because the bulky phosphines in the latter dissociate very fast in strongly alkaline medium [18]. However both the lack of evidence of a second dissociation process for the cobaloximes in the explored pH range (at least until pH 9.0) and the inspection of the pK values for the dissociation of the equatorial proton in the methylbis(dimethylglyoximato)pyridine derivatives (9.65 for Rh [20], 13.61 for Co [21]) suggest that also the equatorial proton should be more acidic in the phosphinorhodoximes than in the phosphinocobaloximes.

Kinetic results

The k_{obs} values for reaction (4) show a linear dependence on $[HSO_3^-]$ in the examined concentration range (Fig. 2), according to eqn. (5).

$$[Rh(dh)_2(PR_3)(H_2O)]^+ + HSO_3^- \rightleftharpoons [Rh(dh)_2(PR_3)(SO_3)]^- + H_3O^+ \quad (4)$$

$$k_{obs} = k_1[HSO_3^-] + k_{-1} \quad (5)$$

The k_1 and k_{-1} values are reported in Table 3.

Even if the substitution reactions of the organorhodoximes have been studied for different entering ligands a comparison can be made with the phosphinorhodoximes, as the k_1 values in the former are almost independent of the nature of the incoming group [22], in line with a dissociative mechanism. The lability of the axial water appears to be considerably lower in the phosphino than in the alkyl complexes [19] in agreement with the higher acidity of the former, which suggests a stronger metal–water bond in the ground state.

Both in the phosphino and in the alkyl aquo rhodoximes the axial water is at the same time more acidic and more labile than in the corresponding cobaloximes, which constitutes a rather unusual result. These features seem peculiar to the bis(dimethylglyoximato) derivatives, as in general considerable similarity exists between the pK values of coordinated water for corresponding Rh(III) and Co(III) complexes and the former are more inert than the latter toward the substitution reactions [19, 20]. Finally, in the $[Rh(dh)_2(PR_3)(H_2O)]^+$ rhodoximes only substitution of the water occurs, whereas in the corresponding Co(III) complexes the phosphine is also substituted through a multistep mechanism in the presence of highly *trans* labilizing ligands such as HSO_3^- or thiourea [18]. Moreover during the potentiometric titrations it has been observed that the $[Rh(dh)_2(PR_3)(OH)]$ compounds are much more inert toward the dissociation of the phosphine than the

TABLE 3. Kinetic constants at 35 °C and I = 1 M ($NaNO_3$) for the reaction $[M(dh)_2(L)(H_2O)]^+ + HSO_3^- \rightleftarrows [M(dh)_2(L)(SO_3)]^- + H_3O^+$

L	k_1 (M^{-1} s^{-1})		k_{-1} (s^{-1})	
	Rh(III)	Co(III)[a]	Rh(III)	Co(III)[a]
PPr^i_3	22.5±0.5	1.61±0.04		$(6.2\pm0.5)10^{-3}$
$PChx_3$	18.6±0.3	3.37±0.07		
PPh_3	5.78±0.02	$(1.44\pm0.03)10^{-1}$	$(4.0\pm0.3)10^{-2}$	$(4.1\pm0.9)10^{-3}$

[a]From ref. 18.

corresponding Co compounds. Both these findings suggest an Rh–P bond stronger than the Co–P bond, in accord with the softness of the phosphine ligands.

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