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Transition-Metal Complexes with Sulfur Ligands. 45.[1] Model Reactions for Oxidoreductases with Metal-Sulfur Centers: Proton-Induced PPh_3/HCl Exchange in $[Ru(PPh_3)_2(L)]$ and Properties of the Resulting HCl Complexes $[Ru(ClH)(PPh_3)(L)]$ (L = 1,2-Bis((2-mercaptophenyl)thio)ethanato(2-); 1,2-Bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanato(2-))

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The ruthenium(II) complexes $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**) and $[Ru(PPh_3)_2(S_4)]$ (**3**) ($^{bu}S_4^{2-}$ = 1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanato(2-); S_4^{2-} = 1,2-bis((2-mercaptophenyl)thio)ethanato(2-)) react with gaseous HCl yielding the HCl complexes $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**) and $[Ru(ClH)(PPh_3)(S_4)]$ (**4**), respectively. Monitoring the reactions by ^1H and ^{31}P NMR spectroscopy yields evidence that the first step is a protonation of thiolato S atoms and the second step loss of one PPh_3 ligand. The protons in **2** and **4** exchange for deuterium when **2** or **4** are treated with CD_3OD/DCl. Reacting **4** with CH_3I leads to $[Ru(Cl)(PPh_3)(S_4\text{-}Me_2)]I$ (**5**). The HCl unit in **2** or **4** is extremely labile toward substitution. When reacted with CO, **4** forms $[Ru(CO)(PPh_3)(S_4)]$ (**7**); with N_2 as well as N_2O, however, paramagnetic $[Ru(Cl)(PPh_3)(S_4)]$ (**6**) is obtained. **4** reacts also with NEt_4N_3 in CH_2Cl_2, yielding a mixture of the cyano and azido complexes $[Ru(CN)(PPh_3)(S_4\text{-}CH_2Cl)]$ (**8**) and $[Ru(N_3)(PPh_3)(S_4\text{-}CH_2Cl)]$ (**9**) which contain the chloromethylated S_4^{2-} ligand. Upon treatment with bases, **4** forms the coordinatively unsaturated $[Ru(PPh_3)(S_4)]$ (**10**), having a five-coordinate, 16e configurated Ru center. **10** rapidly reacts with CO, PMe_3, SMe_2, SPhMe, and SPh_2, yielding the 18e complexes **7**, $[Ru(PMe_3)(PPh_3)(S_4)]$ (**11**), $[Ru(SMe_2)(PPh_3)(S_4)]$ (**12**), $[Ru(SPhMe)(PPh_3)(S_4)]$ (**13**), and $[Ru(SPh_2)(PPh_3)(S_4)]$ (**14**). Mechanisms for these reactions are suggested showing that protonation of thiolato atoms and deprotonation of thiol functions, respectively, allow the Ru centers to differentiate between hard and soft substrates as Cl^- or, e.g., CO or SMe_2. The relevance of these reactions for H^+-coupled substrate conversions catalyzed by oxidoreductases will be discussed.

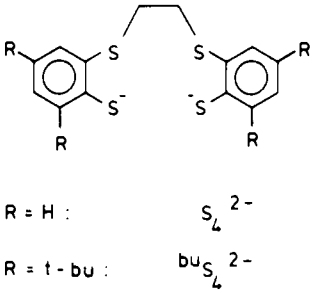
Introduction

In numerous oxidoreductases, e.g. hydrogenase, xanthineoxidase, or nitrogenase, the active centers consist of transition metals in a coordination sphere dominated by sulfur atoms.[2] In order to understand the function of these enzymes on the molecular level, investigations of the structure as well as the reactivity of transition-metal complexes with sulfur ligands are of considerable interest.[3] Substrate conversions being catalyzed by oxidoreductases comprise elementary reactions as coordination and decoordination of ligands, and usually, the electron flow is coupled to proton-transfer reactions. Substrate binding and release requires vacant sites at the active centers. Hard ligands, e.g. H_2O, are often assumed to function as auxiliary or protective ligands X that have to be released before the substrate Y can coordinate.[4]

$$M\text{-}X \underset{+X}{\overset{-X}{\rightleftharpoons}} \text{“M”} \underset{-Y}{\overset{+Y}{\rightleftharpoons}} M\text{-}Y \qquad (1)$$

The intermediate “M” must be always coordinatively unsaturated, i.e. must have a vacant site of coordination, and here the question arises as to how it may be generated and eventually stabilized. We recently showed that coordinatively unsaturated metal complexes can be stabilized by thiolate donors via π-donation, even in such extreme cases that contain five-coordinate 16e-configurated Cr^0, Mo^0, and W^0 centers as found in $[M(CO)_3(S_2C_6H_4)]^{2-}$ (M = Cr, Mo, W).[5] π-Donation also plays an important role in the substitution reactions of $[Ru(PPh_3)_2(S_4)]$ (S_4^{2-} = 1,2-bis((2-mercaptophenyl)thio)ethanato(2-)) and the isoelectronic $[Ru(PPh_3)_2(N_2S_2)]$ ($N_2S_2^{2-}$ = 1,2-bis(2-mercaptoanilino)ethanato(2-)). The former complex undergoes PPh_3 substitution in neutral media under standard conditions; in the latter case, PPh_3 is substituted only if the amine functions of the $N_2S_2^{2-}$ ligand are deprotonated in precursor reactions.[6] On the other hand, the reaction of $[Ru(PPh_3)_2(S_4)]$ with NEt_4N_3 in CH_2Cl_2 yielding $[Ru(N_3)(PPh_3)(S_4\text{-}CH_2Cl)]$[7] shows that substitutions at the $[Ru(PPh_3)(S_4)]$ core can be coupled with an electrophilic attack of carbenium ions at the thiolate atoms of the S_4^{2-} ligand.

This result was the major reason for investigating the reaction of $[Ru(PPh_3)_2(S_4)]$ with simple protonic acids, e.g. HCl. In this case, we obtained a very insoluble compound that analyzed for $[Ru(ClH)(PPh_3)(S_4)]$. In order to obtain more soluble and more easily characterizable compounds, we also studied the reactions of $[Ru(PPh_3)_2(^{bu}S_4)]$, where the Ru center is ligated by the sterically demanding thioether thiolate ligand $^{bu}S_4^{2-}$ (1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanato(2-)).



In this paper, we want to discuss the influence of thiolate ligands at metal-sulfur centers, in particular with respect to reactions involving protons. Aims of these investigations were the identification of the reaction products of $[Ru(PPh_3)_2(L)]$ (L = $^{bu}S_4^{2-}$, S_4^{2-}) with HCl, better insight into the reaction mechanisms, syntheses of new complexes with the [Ru(L)] fragments, and elucidation of potential bioinorganic relevances.

Experimental Section

General Data. All reactions were carried out under nitrogen by using Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Spectra were recorded on the following instruments: Perkin-Elmer infrared spectrophotometer Model 983 (solutions in CaF_2

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cuvettes with compensation for solvent bands, solids in KBr or polyethylene), JEOL JNM-GX 270 FT-NMR spectrometer, and Varian MAT 212 mass spectrometer. Magnetic moments were determined with a Johnson Matthey magnetic susceptibility balance.

$[Ru(PPh_3)_2(^{bu}S_4)]$,[1] $[Ru(PPh_3)_2(S_4)]$,[8] PMe_3,[9] and NEt_4N_3[10] were prepared as described in the literature. NEt_4OH (25% solution in MeOH) was purchased from Alfa; HBF_4 (54% solution in Et_2O) was obtained from Merck.

Syntheses. [Ru(ClH)(PPh$_3$)(^{bu}S$_4$)] (2). In a Schlenk tube, 1.158 g (1 mmol) of $[Ru(PPh_3)_2(^{bu}S_4)]$, (**1**) is largely dissolved in 100 mL of CH_2Cl_2. A gentle stream of HCl gas is bubbled through this mixture for 1 min, whereupon a clear solution forms. The Schlenk tube is closed, and the solution is stirred for 1 day under HCl gas. The volume of the solution is reduced to ca. 5 mL in a stream of HCl gas, whereupon yellow microcrystalline **2** precipitates. It is separated by filtration, washed twice with 5 mL of Et_2O, and dried in high vacuum for 1 day. Yield: 505 mg (54%). Anal. Calcd for $C_{48}ClH_{60}PRuS_4$ (mol wt 932.7): C, 61.81; H, 6.48; S, 13.75. Found: C, 61.30; H, 6.55; S, 13.70.

[Ru(ClH)(PPh$_3$)(S$_4$)]·CH$_2$Cl$_2$ (4). Into a suspension of 1.19 g (1.27 mmol) of $[Ru(PPh_3)_2(S_4)]$, (**3**) in 100 mL of CH_2Cl_2 is introduced gaseous HCl for 1 min. A clear solution forms, which is stirred for 1 day under HCl in the closed Schlenk tube. Needle-shaped yellow crystals of **4** precipitate, which are collected, washed three times with 10 mL of CH_2Cl_2, and dried in high vacuum for 1 day. Yield: 585 mg (65%). Anal. Calcd for $C_{33}Cl_3H_{30}PRuS_4$ (mol wt 793.2): C, 49.97; H, 3.81; S, 16.17. Found: C, 50.03; H, 3.21; S, 16.05.

[Ru(Cl)(PPh$_3$)(S$_4$–Me$_2$)]I·CH$_2$Cl$_2$ (5·CH$_2$Cl$_2$). To a suspension of 260 mg (0.37 mmol) of **4** in 20 mL of CH_2Cl_2 is added 1 mL (2.275 g, 16 mmol) of CH_3I. Within 10 min, complete dissolution takes place and the color turns from yellow to orange. The solution is stirred for 2 h, and 20 mL of *n*-hexane is added, precipitating yellow **5**, which is separated and recrystallized from CH_2Cl_2 covered by a layer of *n*-hexane at room temperature to give yellow needles of **5**·CH_2Cl_2. Yield: 275 mg (87%). Anal. Calcd for $C_{35}Cl_3H_{35}IPRuS_4$ (mol wt 949.2): C, 44.29; H, 3.72; S, 13.51. Found: C, 44.18; H, 3.10; S, 13.04.

H$^+$/D$^+$ Exchange of 2 and 4. About 50 mg of **2** and **4**, respectively, is suspended in 5 mL of a mixture of CD_3OD and DCl/D_2O, stirred for 2 h and evaporated to dryness. The procedure is completely repeated giving $[Ru(ClD)(PPh_3)(^{bu}S_4)]$ and $[Ru(ClD)(PPh_3)(S_4)]$, which were identified by IR spectroscopy.

[Ru(Cl)(PPh$_3$)(S$_4$)] (6). In an autoclave with a glass insert, 200 mg (0.28 mmol) of **4** is suspended in 20 mL of CH_2Cl_2 and stirred for 1 day under 100 bar of N_2. A clear green solution results, which is evaporated to dryness, yielding a green solid. The residue is recrystallized from CH_2Cl_2 (+20 to +5 °C) to give needle-shaped **6**, which is filtered off, washed twice with 5 mL of Et_2O, and dried in high vacuum for 1 day. Yield: 180 mg (91%). Anal. Calcd for $C_{32}ClH_{27}PRuS_4$ (mol wt 707.3): C, 54.34; H, 3.84; S, 18.13. Found: C, 53.92; H, 4.41; S, 18.49.

The same product forms when a gentle stream of N_2O is bubbled into a suspension of **4** in CH_2Cl_2.

[Ru(PPh$_3$)(S$_4$)] (10). To a yellow suspension of 355 mg (0.5 mmol) of **4** in 20 mL of MeOH is added 0.7 mL (1.05 mmol) of NEt_4OH (25% in MeOH). The suspension rapidly turns dark red, and after 2 h, the solvent is removed by filtration. The remaining dark red solid is washed with 30 mL of MeOH and 10 mL of Et_2O and dried in high vacuum for 1 day. Yield: 295 mg (87%). Anal. Calcd for $C_{32}H_{27}PRuS_4$ (mol wt 671.9): C, 57.21; H, 4.05; S, 19.09. Found: C, 57.29; H, 3.85; S, 18.70.

The following products, [Ru(CO)(PPh$_3$)(S$_4$)] (**7**),[8] [Ru(CN)(PPh$_3$)(S$_4$–CH$_2$Cl)] (**8**),[7] [Ru(N$_3$)(PPh$_3$)(S$_4$–CH$_2$Cl] (**9**),[7] and [Ru(PMe$_3$)(PPh$_3$)(S$_4$)] (**11**),[11] were identified by comparing their IR, NMR, and mass spectra to the spectra of authentic samples that previously were obtained by different routes.

(a) [Ru(CO)(PPh$_3$)(S$_4$)] (7) from 4 and CO. Through a suspension of 365 mg (0.52 mmol) of **4** in 25 mL of CH_2Cl_2, a gentle stream of CO is bubbled for 15 min. The resulting clear yellow solution is evaporated to dryness, the residue is redissolved in 10 mL of THF, and the solution is filtered. Evaporating the filtrate to dryness yields a yellow powder of **7**, which is dried in high vacuum for 1 day. Yield: 310 mg (86%).

(b) [Ru(CN)(PPh$_3$)(S$_4$–CH$_2$Cl)] (8) and [Ru(N$_3$)(PPh$_3$)(S$_4$–CH$_2$Cl)] (9) from 4 and NEt$_4$N$_3$. To 135 mg (0.19 mmol) of **4** in 10 mL of CH_2Cl_2 is added 92 mg (0.19 mmol) of NEt_4N_3, and the resulting clear brown-yellow solution is stirred for 1 day. Addition of 50 mL of *n*-hexane precipitates **8** and **9**, which were filtered off, washed three times with 10 mL of *n*-hexane, and dried in high vacuum for 1 day. **8** and **9** were not separated from each other. Yield: 70 mg.

(c) [Ru(CO)(PPh$_3$)(S$_4$)] (7) from 10 and CO. Through the red suspension of 50 mg (0.074 mmol) of **10** in 10 mL of MeOH is bubbled a gentle stream of CO for 15 min. Stirring under CO for 1 day gives a yellow solution, which is filtered and evaporated to dryness, yielding solid **7**, which is dried in high vacuum for 1 day. Yield: 38 mg (73%).

(d) [Ru(PMe$_3$)(PPh$_3$)(S$_4$)] (11) from 10 and PMe$_3$. To the red suspension of 20 mg (0.03 mmol) of **10** in 20 mL of MeOH is added 0.1 mL (0.1 mmol) of PMe_3. Within 10 min, the color of the suspension turns yellow. After 1 day of being stirred, the yellow solid is separated, washed three times with 15 mL of Et_2O, and dried in high vacuum for 1 day. Yield: 15 mg (67%).

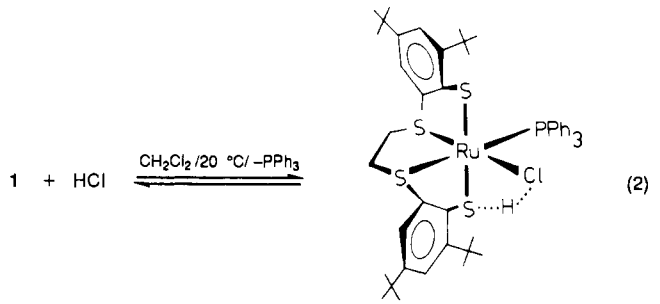
[Ru(SMe$_2$)(PPh$_3$)(S$_4$)] (12). To a red suspension of 125 mg (0.19 mmol) of **10** in 5 mL of MeOH is added 0.2 mL (2.73 mmol) of SMe_2. While the suspension is being stirred for 1 day its color changes to yellow. The solid product is separated by filtration, washed three times with 15 mL of MeOH and 15 mL of *n*-hexane, and dried in high vacuum for 1 day. Yield: 90 mg (65%). Anal. Calcd for $C_{34}H_{33}PRuS_5$ (mol wt 734.0): C, 55.64; H, 4.53; S, 21.84. Found: C, 56.19; H, 4.84; S, 19.68.

[Ru(SPhMe)(PPh$_3$)(S$_4$)] (13). First 250 mg (0.37 mmol) of **10** is suspended in 15 mL of MeOH. To it is added 0.1 mL (0.85 mmol) of SPhMe and the mixture stirred for 1 day, whereupon the color turns from deep red to yellow. Solid **13** is separated, washed with 30 mL of MeOH and 30 mL of *n*-hexane, and dried in high vacuum for 1 day. Yield: 240 mg (81%). Anal. Calcd for $C_{39}H_{35}PRuS_5$ (mol wt 796.1): C, 58.84; H, 4.43; S, 20.13. Found: C, 59.23; H, 4.17; S, 20.02.

[Ru(SPh$_2$)(PPh$_3$)(S$_4$)] (14). First 1 mL (5.9 mmol) of SPh_2 is added to the red suspension of 245 mg (0.36 mmol) of **10** in 15 mL of MeOH. After it was stirred for 1 day, the suspension, which turned ochre-orange, is filtered, the remaining solid is washed with 3 × 30 mL of MeOH and 30 mL of *n*-hexane and dried in high vacuum for 1 day. Despite several recrystallizations from CH_2Cl_2, the excess of SPh_2 could not be completely removed, giving rise to unsatisfactory analyses. Yield: 247 mg (80%). Anal. Calcd for $C_{44}H_{37}PRuS_5$ (mol wt 858.1): C, 61.59; H, 4.35; S, 18.80. Found: C, 63.24; H, 4.15; S, 18.36.

Results

When gaseous HCl is introduced into a yellow suspension of $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**) in CH_2Cl_2 according to eq 2, an immediate



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reaction takes place. Within less than a minute, the suspension turns into a clear yellow solution and $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**) forms. At this stage, the reaction is reversible: bubbling gaseous N_2 through the solution or evaporating the solvent, **1** is recovered. Accordingly, **2** can only be isolated if the reaction solution is concentrated in a HCl stream until solid **2** precipitates.

2 is very soluble in CH_2Cl_2, slightly soluble in THF, and practically insoluble in all other common solvents. All attempts to recrystallize **2** have led to decomposition. Since $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**) is a neutral and diamagnetic complex, the substitution of one PPh_3 ligand in **1** by chloride, which follows from elementary analyses as well as spectra of **2** (Table I), must be accompanied by the addition of a proton. Its presence is indicated in the KBr IR spectrum of **2** (Figure 1) by a broad band of medium intensity at 2174 cm^{-1}. This band is assigned to a ν(SH) vibration. Since in free $^{bu}S_4$–H_2 ν(SH) appears as a sharp absorption at 2480 cm^{-1} and gaseous HCl shows its ν(HCl) at 2886 cm^{-1},[12] the shape and frequency of the 2174-cm^{-1} band in **2** indicate that the SH bond is weakened by a S··H··Cl hydrogen

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Table I. Selected Spectroscopic Data for the New Complexes

compd (no.) [color]	KBr IR, cm^{-1}	^1H NMR δ, ppm[a]	^{31}P NMR δ, ppm[b]	FD MS, *m/e*
$[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**) [yellow]	2174 (ν(SHCl),[c] m, br) 319 (ν(RuCl),[d] w)	8.17–6.54 (m) (19; C_6H_2, PPh_3) 2.95–2.10 (m) (4; C_2H_4) 4.57 (s) (1; SHCl) 1.59 (s) (9; $C(CH_3)_3$) 1.40 (s) (9; $C(CH_3)_3$) 1.32 (s) (9; $C(CH_3)_3$) 1.18 (s) (9; $C(CH_3)_3$)	29.4	933 [M^+]
$[Ru(ClH)(PPh_3)(S_4)]$ (**4**) [yellow]	2190 (ν(SHCl),[c] m, br) 318 (ν(RuCl),[d] m)	7.88–7.17 (m) (23; C_6H_4, PPh_3)[e] 2.78–2.21 (m) (4; C_2H_4)	29.2[e]	708 [M^+]
$[Ru(Cl)(PPh_3)(S_4\text{–}Me_2)]I$ (**5**) [yellow-orange]	319 (ν(RuCl),[d] m)	8.05–7.35 (m) (23; C_6H_4, PPh_3) 3.47–2.10 (m) (4; C_2H_4) 3.16 (s) (3; SCH_3) 2.24 (s) (3; SCH_3)	25.2	737 [M^+ – I] 722 [M^+ – I – Me] 707 [M^+ – I – 2Me]
$[Ru(Cl)(PPh_3)(S_4)]$ (**6**) [green]	308 (ν(RuCl),[d] m)	*f*	24.0	707 [M^+]
$[Ru(SMe_2)(PPh_3)(S_4)]$ (**12**) [yellow]		7.61–6.55 (m) (23; C_6H_4, PPh_3) 2.90–1.82 (m) (4; C_2H_4) 2.14 (s) (6; SCH_3)	38.2	734 [M^+]
$[Ru(SPhMe)(PPh_3)(S_4)]$ (**13**) [yellow]		7.60–6.54 (m) (31; C_6H_4, PPh_3, SPh) 2.75–1.90 (m) (4; C_2H_4) 2.29 (s) (3; SCH_3)	36.6	796 [M^+][h]
$[Ru(SPh_2)(PPh_3)(S_4)]$ (**14**) [ochre-yellow]		7.58–6.54 (m) (33; C_6H_4, PPh_3, SPh) 3.00–1.53 (m) (4; C_2H_4)	29.2	*g* 644 [M^+ – SPh_2 – C_2H_4][h]

[a] In CD_2Cl_2, m = multiplet, s = singlet. [b] In CD_2Cl_2, ref. to ext. H_3PO_4. [c] m = medium, b = broad, w = weak. [d] PE pellet. [e] In situ (reaction solution). [f] No ^1H NMR spectrum. [g] No [M^+] observed. [h] Weak.

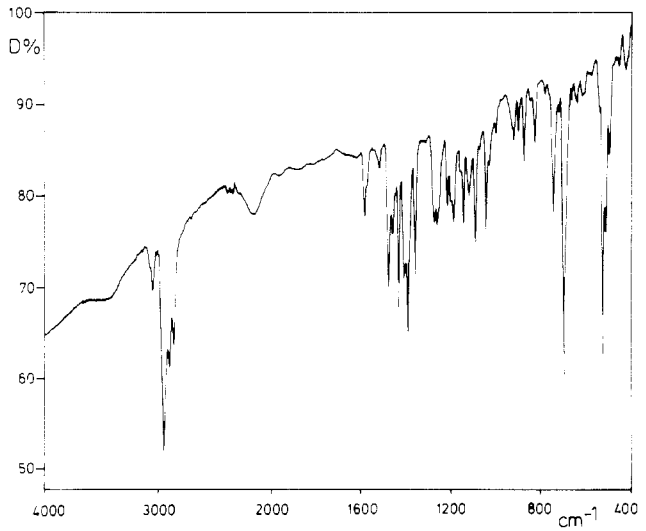

Figure 1. KBr IR spectrum of $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**).

bridge. Because of steric reasons, we assume an intramolecular S··H··Cl bridge as indicated in eq 2. Formation of intramolecular hydrogen bridges between coligands and thiolato S atoms of the $[Ru(PPh_3)(S_4)]$ core was previously detected in the diazene complex $[(\mu\text{-}N_2H_2)\{Ru(PPh_3)(S_4)\}_2]$[13] where the diazene ligand is stabilized by N_2H_2··S bonds.

Substitution reactions of thiolato complexes in the presence of catalytic amounts of acids are well-known and are usually attributed to protonation of thiolate donors.[14] On the contrary, **1** reacts with HCl stoichiometrically, and additionally, the protons play an important role concerning the exchanging ligand. In the absence of protons, **1** preferably exchanges PPh_3 for soft ligands, e.g. CO; in the presence of protons, PPh_3 can also be substituted by the very hard chloride ion. Such a substitution could never be observed under neutral conditions, e.g. by reacting **1** with NR_4Cl (R = Me, Et) in CH_2Cl_2 or THF.

Thus, details of the reaction pathway of eq 2 become important and two extreme alternatives may be considered:

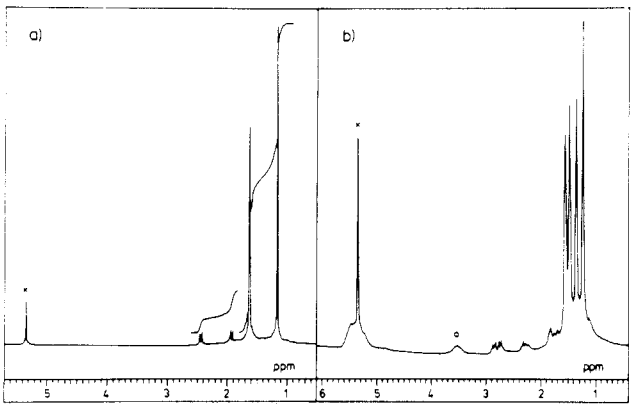

Figure 2. Sections of the ^1H NMR spectra in CD_2Cl_2 of (a) $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**) and (b) **1** immediately after introduction of HCl (× = CD_2Cl_2, O = H_2O).

1. The primary step is the substitution of PPh_3 by chloride, forming a negatively charged species, which is subsequently protonated in order to yield the neutral **2** (eq 3).

$$\mathbf{1} \underset{+PPh_3,\,-Cl^-}{\overset{-PPh_3,\,+Cl^-}{\rightleftharpoons}} [Ru(Cl)(PPh_3)(^{bu}S_4)]^- \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \mathbf{2} \qquad (3)$$

2. The initiating reaction is an H^+ attack at one thiolato S atom so that a positively charged intermediate is yielded in which one Ru–PPh_3 bond becomes labile, and in the second step, PPh_3 is substituted by chloride (eq 4). This would be a proton-induced substitution.

$$\mathbf{1} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [Ru(PPh_3)_2(^{bu}S_4\text{–}H)]^+ \underset{-Cl^-,\,+PPh_3}{\overset{+Cl^-,\,-PPh_3}{\rightleftharpoons}} \mathbf{2} \qquad (4)$$

In order to distinguish between these alternatives, we monitored the reaction by ^1H and ^{31}P NMR spectroscopy and obtained clear evidence for the second alternative. Due to its C_2 symmetry, $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**) shows two sharp singlets for the four *tert*-butyl groups in the ^1H NMR spectrum in CD_2Cl_2 (Figure 2a)), two pseudodoublets for the C_2H_4 group, and a multiplet for the aromatic protons.

When gaseous HCl is introduced into the CD_2Cl_2 solution of **1**, the *tert*-butyl signals immediately split up into four, clearly separated, peaks (Figure 2b)). Likewise, the splitting of the C_2H_4 and aromatic signals becomes more complex, and additionally,

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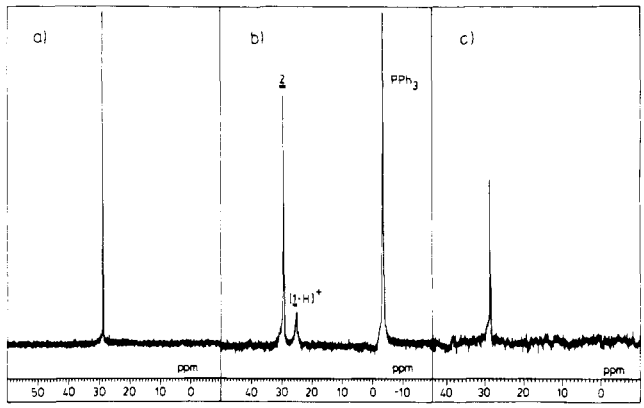


Figure 3. $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 of (a) $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**), (b) **1** ca. 15 min after addition of HCl, and (c) $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**).

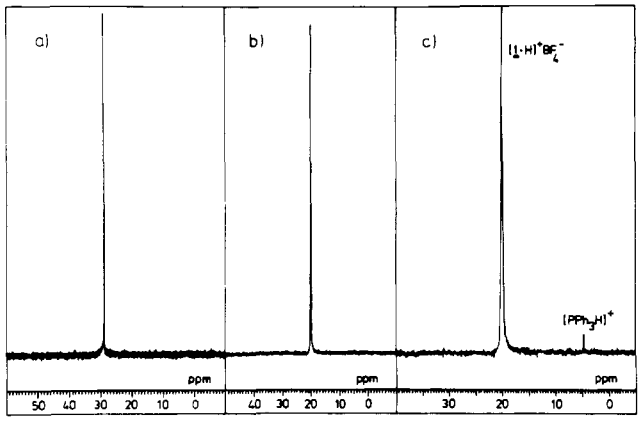


Figure 4. $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 of (a) $[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**), (b) **1** immediately after addition of HBF_4, and (c) **1** after 1 h.

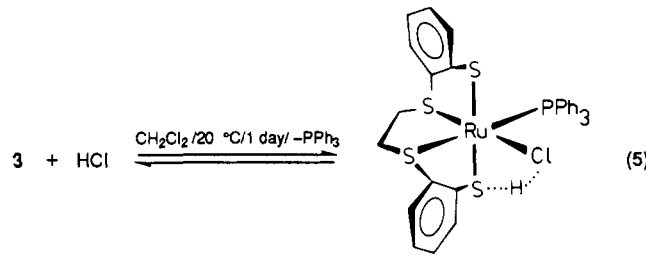
a small broad signal appears at 5.46 ppm. These signals are attributed to the primary product, which, we assume, is protonated educt, $[(\mathbf{1})H]^+$, having C_1 symmetry only. $[(\mathbf{1})H]^+$ still carries two PPh_3 ligands, and the small signal at 5.46 ppm is assigned to SH bond formation. This assignment was corroborated by reacting **1** with an excess of HBF_4, whereupon a similar signal is observed at 5.68 ppm. On the contrary, isolated **2** does not show this signal but a resonance at 4.57 ppm, which is due to the S···H···Cl entity. This interpretation could be confirmed further by ^{31}P NMR spectroscopy.

Figure 3a displays the $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 showing only a single ^{31}P signal at 29.2 ppm. When the NMR tube is filled with HCl gas and the ^{31}P NMR spectrum is recorded again (about 15 min later), the signal at 29.2 ppm disappears and three new peaks are observed at 29.4, 25.3, and −3.6 ppm (Figure 3b)). They are assigned to **2** (29.4 ppm) (Figure 3c)) and free PPh_3 (−3.6 ppm) by comparison with authentic samples and to the protonated species $[(\mathbf{1})H]^+$ (25.3 ppm), because this signal decreases in the course of the reaction and simultaneously the peaks at 29.4 and −3.6 ppm increase. This interpretation was supported by monitoring the reaction of **1** with HBF_4/Et_2O (Figure 4). Upon addition of HBF_4, the signal of **1** disappears again, but now only one new signal emerges at 19.9 ppm. We assign it also to the protonated educt $[(\mathbf{1})H]^+$ and attribute the difference in chemical shift to the acid strength and dissociation of HCl vs HBF_4. Moreover, because BF_4^- is only very weakly nucleophilic, $[Ru(PPh_3)_2(^{bu}S_4\text{–}H)]BF_4$ persists for a much longer period than $[Ru(PPh_3)_2(^{bu}S_4\text{–}H)]Cl$ (Figure 4b)), and only after more than 1 h, does a very small signal at 4.8 ppm arise, due to PPh_3H^+ (Figure 4c)). This indicates that, after protonation of **1**, PPh_3 is released.

The formation of PPh_3H^+ is to be expected in the presence of an excess of acid, and PPh_3H^+ is also observed in the reaction of **1** with HCl when the HCl gas is bubbled through the reaction solution for a longer period.

These results show that the first step of the reaction of **1** with acids is the protonation of **1** and the second step is the formation of a coordinatively unsaturated species by loss of PPh_3. Different nucleophilicities of the acid anion influence the reaction rate, and as a result, in the HCl reaction the ^{31}P signal of the protonated species $[(\mathbf{1})H]^+$ is always accompanied by the signals of PPh_3 or PPh_3H^+, respectively, and the product **2**.

Analogous reactions are observed for $[Ru(PPh_3)_2(S_4)]$ (**3**), containing the parent ligand S_4^{2-}. $[Ru(ClH)(PPh_3)(S_4)]$ (**4**) forms according to eq 5, when gaseous HCl is introduced into a sus-



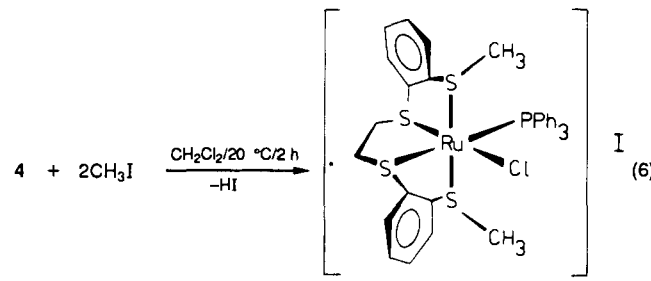
4

pension of **3** in CH_2Cl_2. In this case, the microcrystalline yellow product separates directly from the reaction mixture since **4** is insoluble in all common solvents. Spectroscopic data of **4** are listed in Table I.

When **2** and **4**, respectively, are treated with CD_2Cl_2, $CDCl_3$, or a mixture of CD_3OD and DCl, H^+/D^+ exchange is observed and the deuterated complexes $[Ru(ClD)(PPh_3)(^{bu}S_4)]$ and $[Ru(ClD)(PPh_3)(S_4)]$ form. They do not show the broad ν(SHCl) bands of the educts in the IR spectrum any longer; ν(SDCl) bands, however, cannot be observed, since they are obscured by $^{bu}S_4$ as well as S_4 ligand absorptions.

2 as well as **4** represent species we had looked for over a long time. They contain Ru(II) centers that can be expected to have a high electron density, due to the "soft" sulfur and phosphorus donors, and the "hard" Cl^- ligand should be easily exchangeable even under mild conditions. Another reactive site is expected to be the S–H···Cl bond since it is supposed to be susceptible to acid–base reactions. Both types of reactions could be observed.

The respective reactions were carried out with **4**, which is more easily accessible than **2**, and despite its poor solubility, **4** is highly reactive, even when only suspended. When **4** is reacted with CH_3I, according to eq 6, $[Ru(Cl)(PPh_3)(S_4\text{–}Me_2)]I$ (**5**), with a doubly methylated S_4 ligand, forms in high yield. In contrast to **2**, **5**



5

is very soluble in CH_2Cl_2 and THF; it was characterized spectroscopically as well as by elemental analyses.

Since the cation of **5** has only C_1 symmetry, the magnetically nonequivalent S–CH_3 groups give rise to two singlets in the ^1H NMR spectrum (Table I).

It was not possible to isolate the monoalkylated complex $[Ru(ClH)(PPh_3)(S_4\text{–}Me)]I$ or $[Ru(Cl)(PPh_3)(S_4\text{–}Me)]$. When only 1 equiv of CH_3I is used, **5** forms again, part of **4** remaining unreacted. This observation is in agreement with previous results obtained with related compounds.[15] **4** was of special interest as

(15) Sellmann, D.; Waeber, M.; Huttner, G.; Zsolnai, L. *Inorg. Chim. Acta* **1986**, *118*, 49.

an educt for the synthesis of compounds that could not be achieved with $[Ru(PPh_3)_2(S_4)]$ (**3**). One of these complexes would be $[Ru(N_2)(PPh_3)(S_4)]$, being one of the rare N_2 complexes with sulfur-dominated metal centers.[16]

When, however, the Ru(II) complex **4** is reacted with N_2 under various conditions up to pressures of 100 bar (eq 7), only the

$$4 + N_2 \xrightarrow{CH_2Cl_2/\text{room temp}/100\ \text{bar}/1\ \text{day}} \underline{\mathbf{6}} + \text{other products} \quad (7)$$

Ru(III) species $[Ru(Cl)(PPh_3)(S_4)]$ (**6**) is obtained. A redox reaction takes place in which eventually the proton of **4** may act as oxidant.

6 is very soluble in CH_2Cl_2 or THF; it is paramagnetic (μ_{eff} = 1.59 μ_B, 295 K), and no resolved ^1H NMR spectrum could be obtained. **6** was characterized by elemental analysis, its mass spectrum ($[M^+]$ = 707), and a ν(RuCl) absorption at 308 cm^{-1} in the IR spectrum. The same product also forms if a gentle stream of N_2O is bubbled through a CH_2Cl_2 suspension of **4**.

The easy loss of the HCl unit in **4** is shown by its reaction with CO, yielding instantaneously $[Ru(CO)(PPh_3)(S_4)]$ (**7**) (eq 8). **7**

$$4 + CO \xrightarrow[-HCl]{CH_2Cl_2/\text{room temp}/15\ \text{min}} \underset{\mathbf{7}}{[Ru(CO)(PPh_3)(S_4)]} \quad (8)$$

was previously synthesized from **3** and CO,[8] but much longer reaction times up to 12 h were required. The reaction according to eq 8 is irreversible, and even with an excess of HCl, no regeneration of **4** can be achieved.

The HCl unit is also lost when **4** is reacted with NEt_4N_3 in CH_2Cl_2. Simultaneously, the cyano complex $[Ru(CN)(PPh_3)(S_4\text{–}CH_2Cl)]$ (**8**) and the azido complex $[Ru(N_3)(PPh_3)(S_4\text{–}CH_2Cl)]$ (**9**) are formed, which have chloromethylated S_4 ligands since the CH_2Cl_2 solvent acts as an alkylating agent (eq 9). **8** and **9**, too, were previously obtained when **3** was reacted

$$2\,\mathbf{4} + 2NEt_4N_3 \xrightarrow[-2NEt_4Cl,\ -4HCl,\ -N_2]{CH_2Cl_2/\text{room temp}/1\ \text{day}} \mathbf{8} + \mathbf{9} \quad (9)$$

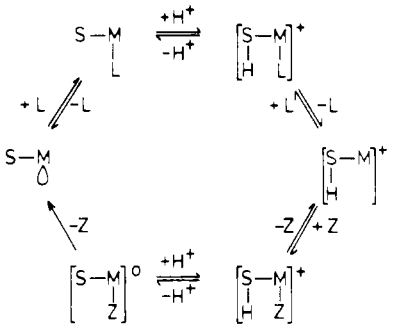
with NEt_4N_3 in boiling CH_2Cl_2 for several days; a mechanism for their formation was proposed, suggesting nitrene intermediates and their reaction with CH_2Cl_2.[7]

Loss of HCl finally occurs also when **4** is reacted with bases, e.g. NEt_4OH, according to eq 10. The yellow suspension of **4**

$$4 + NEt_4OH \xrightarrow[-H_2O]{MeOH/\text{room temp}/2\ \text{h}} \underline{\mathbf{10}} + NEt_4Cl \quad (10)$$

(16) Yoshida, T.; Adachi, T.; Kaminaka, M.; Ueda, T. *J. Am. Chem. Soc.* **1988**, *110*, 4872.

Scheme I. Protonation and Deprotonation Reactions of Metal Thiolate Centers Influencing Ligand Exchange[a]



[a] Key: S = thiolate ligand; M = metal center; L = soft ligand; Z = hard ligand.

instantaneously turns deep red when NEt_4OH is added, and the coordinatively unsaturated 16e species $[Ru(PPh_3)(S_4)]$ (**10**), as well as NEt_4Cl, is isolated.

10 is highly reactive, even when only suspended, and thus it could be characterized solely by elemental analysis, IR spectroscopy, and its reactions.

In the KBr IR spectrum of **10**, the ν(RuCl) and ν(SHCl) absorptions at 318 and 2190 cm^{-1} of **4** are absent. Solutions of **10**, e.g. in CH_2Cl_2, rapidly change color from red to yellow, and subsequently, besides unidentified products, $[Ru(PPh_3)_2(S_4)]$ (**3**) is isolated.

The reactions of **10** with either CO, PMe_3, or thioethers according to eq 11 yield the 18e-configurated derivatives **7** and **11**–**14**. The thioether complexes could not be obtained from

$$\mathbf{10} + L \xrightarrow{MeOH/\text{room temp}/1\ \text{day}} [Ru(L)(PPh_3)(S_4)] \quad (11)$$

L = CO (**7**), PMe_3 (**11**), SMe_2 (**12**), SPhMe (**13**), SPh_2 (**14**)

$[Ru(PPh_3)_2(S_4)]$ (**3**) and the corresponding thioethers, even under vigorous conditions. They were characterized by elemental analyses and IR, NMR, and mass spectra (Table I).

N_2 could not be reacted with **10**; a MeOH suspension of **10** stays unchanged even after 12 h at 60 °C and 60 bar of N_2. In Table I, selected spectroscopic data of the new complexes are listed.

Discussion and Conclusion

$[Ru(PPh_3)_2(^{bu}S_4)]$ (**1**) and $[Ru(PPh_3)_2(S_4)]$ (**3**) react with gaseous HCl to yield $[Ru(ClH)(PPh_3)(^{bu}S_4)]$ (**2**) as well as $[Ru(ClH)(PPh_3)(S_4)]$ (**4**). **2** and **4** can be considered HCl complexes with HCl ligands, being stabilized by intramolecular hydrogen bridges to the thiolate ligands; vice versa, they may also be described as thiol complexes with SH functions, being stabilized by hydrogen bonding to the chloride ligand. In either case, **2** and **4** represent very unusual complexes, since, as far as we are aware, no stable complexes with HCl ligands are known yet, and thiol complexes, although known, are rare because they usually deprotonate.[14]

Substitution of PPh_3 by HCl in **2** or **4** proceeds via protonation of the thiolate ligand and subsequent release of PPh_3, generating a vacant site of coordination at the metal center. This vacant site can be occupied by hard ligands of proper size, e.g. chloride, but only if the SH function persists (eq 2, 5). As soon as the proton is removed, the Ru center becomes so soft that hard ligands are expelled (eq 10).

The electronic unsaturation of the Ru center is diminished by S(thiolate) → Ru π-donation, so that $[Ru(PPh_3)(S_4)]$ (**10**) becomes an insolable species, which preferably binds σ–π ligands, e.g. CO.

Thus, protonation of thiolate atoms and deprotonation of thiol functions allow the Ru center to differentiate between hard and soft substrates. This sheds a new light on the role protons can play in oxidoreductases having transition-metal–sulfur centers.

Other effects, exerted by protons in oxidoreductases, concern, e.g., redox potentials,[17] oxidation states,[18] geometries,[19] and coupling to electron-transfer reactions.[20] Here, the reactions of $[Ru(PPh_3)(S_4)]$ complexes yield models for H^+-coupled substitution reactions. Ligand exchange at transition-metal–sulfur centers is much more complicated than expressed by eq 1 and can involve several protonation and deprotonation steps.

As shown by Scheme I, the protons take over a definite role in the release and coordination of ligands (substrates), which becomes important when L and Z represent *soft* and *hard* substrates, respectively. The state of protonation determines which kind of substrate is bound.

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Instability of the Nitrite/Iron(III) Porphyrinate System

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Reactions of (porphinato)iron(III) complexes (porphyrin = H_2TPP, H_2TTP, and H_2OEP) with nitrite ion have been investigated by means of attempted product isolation, UV–visible spectroscopy, solution IR and EPR spectroscopy, and a study of the time dependence of the reaction system. All observations are consistent with an instability of this system that leads not to coordinated nitrite species but rather to the production of iron nitrosyl complexes. These nitrosyl species appear to be formed by single oxygen atom transfer from a coordinated nitrite ion to an uncoordinated nitrite ion.

Hemoprotein reactions of nitrite ion are widespread. Assimilatory nitrite reductases catalyze the six-electron reduction of nitrite ion to ammonia,[1] while the dissimilatory nitrite reductases[2] reduce nitrite ion to nitrous oxide, nitric oxide, or dinitrogen. The assimilatory enzymes possess a heme prosthetic group of the isobacteriochlorin type, called siroheme, which serves as the binding and reactive site.[3] Introduction of nitrite to the reduced enzyme results in the rapid formation of a nitrosyl complex of the heme.[4] The nitrosyl complex is also observed as the steady-state species during enzyme turnover. The dissimilatory nitrite reductases contain four hemes, two of *c* and two of d_1. Heme d_1 has recently been shown to be a dioxoisobacteriochlorin,[5] and again there is the probable intermediacy of a nitrosyl complex in the catalytic reaction.

The reduction of nitrite to ammonia has been mimicked electrochemically in aqueous solution by utilizing a number of iron or ruthenium complexes, including water-soluble iron porphyrinate complexes.[6] These systems also suggest the intermediacy of a nitrosyl complex in the reductive pathway. Adler et al.[7] have described reactions of nitrite with hemoproteins that are suggested as potentially harmful. Finally, nitrite interactions with hemoproteins form seemingly important complexes in meat-curing processes.[8]

Despite the apparent importance of the interaction of nitrite with hemoproteins, there appeared to have been little work done on the interaction of nitrite with iron porphyrinate complexes. Several years ago, we began such an investigation with a primary goal of synthesizing nitrite-coordinated iron porphyrinate complexes. Questions that we wanted to resolve included a determination of stoichiometry, spin state of the species, mode of ligand binding (N- or O-bound; mono- or bidentate), the possible effects of other axial ligands, and the assignment of definitive spectroscopic parameters. Although the formation of such nitrite species should be possible by means of straightforward metathesis processes, we found that iron(III) porphyrinate/nitrite systems do not yield the expected nitrite complexes. Rather, the systems yield nitrosyl complexes under a variety of conditions. Our finding of this apparent instability of the desired nitrite complex seems to be in distinct contrast to a report that appeared while this work was in progress. This paper[9] implies that (porphinato)iron(III) nitrite complexes are relatively stable. While we concur with at least some of the spectroscopic properties reported, which are reasonably interpreted in terms of forming nitrite complexes, we also believe that these complexes undergo subsequent reaction rather quickly.

Our work leads us to conclude that the dominating feature of the porphinatoiron(III)/nitrite system is the loss of an oxygen atom from coordinated nitrite to yield an iron NO complex. These conclusions about this reaction system are derived from product isolation, time-dependent solution EPR and IR spectroscopy, UV–visible spectra and a kinetic analysis of the (porphinato)iron(III)/nitrite system. We have also briefly explored reactions related to this system. We have examined the reaction of nitrosyliron complexes with excess nitrite ion and finally we have

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