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Preparation of ruthenium silanethiolato complexes and their reactions with sulfur dioxide; possible models for the activation of SO_2 in the homogeneously catalyzed Claus reaction☆

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Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday.

Abstract

$CpRu(PPh_3)_2SSi^iPr_3$ (**6a**) was prepared by reacting $[CpRu(PPh_3)_2(acetone)]BF_4$ and $NaSSi^iPr_3$. Complex **6a** is substitution-labile and readily gave the mixed-ligand derivatives $CpRu(PPh_3)(L)SSi^iPr_3$, where L = CO (**6b**), PMe_3 (**6c**), $P(OMe)_3$ (**6d**), upon treatment with the corresponding ligands. $CpRu(dppe)SSi^iPr_3$ (**6e**) was obtained from complex **6a** and dppe via the intermediate formation of $CpRu(PPh_3)(\eta^1\text{-dppe})SSi^iPr_3$. Treatment of complex **6a** with one equivalent of SO_2 gave primarily unstable $CpRu(PPh_3)(SO_2)SSi^iPr_3$ (**6f**). However, complexes **6b–e** inserted one equivalent of SO_2 solely at their S–Si^iPr_3 function to give the unstable *O*-silyl thiosulfito complexes $CpRu(PPh_3)(L)SS(O)OSi^iPr_3$ (L = CO (**8b**), PMe_3 (**8c**), $P(OMe)_3$ (**8d**)) as well as $CpRu(dppe)SS(O)OSi^iPr_3$ (**8e**). The S–H bonds of $CpRu(PPh_3)_2SH$ (**7a**) and CpRu(dppe)SH (**7b**) added to PhNSO to give $CpRu(PPh_3)_2SS(O)NHPh$ (**9a**) and CpRu(dppe)SS(O)NHPh (**9b**), respectively. The crystal structure of complex **6a** was determined. Crystallographic data for **6a**: triclinic, $P\bar{1}$, $a = 10.642(6)$ Å, $b = 11.068(8)$ Å, $c = 21.994(10)$ Å, $\alpha = 79.27(5)°$, $\beta = 89.22(5)°$, $\gamma = 62.32(4)°$, $V = 2246(2)$ Å^3, $Z = 2$.

Keywords: Catalysis; Claus process; Ruthenium; Silanethiolate; Sulfhydryl complex; Sulfur dioxide; Insertion; Addition; Thiosulfite

1. Introduction

Well-defined, soluble platinum complexes have been applied successfully in recent years for modeling possible surface reactions of the industrially important, heterogeneously catalyzed Claus process [1]. This led to the discovery that *cis*-$(PPh_3)_2Pt(SH)_2$ (**1**) effectively catalyzes the Claus reaction in homogeneous phase under ambient conditions [1a,2]. The homogeneous system provides a unique opportunity for studying possible mechanisms of the catalytic cycle, which is poorly understood due to obvious difficulties in monitoring chemical transformations directly on the surface of the commercial catalyst [3].

Preliminary investigations have shown that reaction of complex **1** with SO_2 gives $(PPh_3)_2PtS_3O$ (**4**), a stable intermediate in the catalytic cycle, which then recovers **1** upon treatment with H_2S [1a]. On the basis of these results, a plausible mechanism was suggested for the homogeneously catalyzed Claus reaction (Scheme 1) [1a].

In particular, the activation of SO_2 by complex **1** is believed to take place via intermediates **2** and **3**, which remain undetected. The intermediacy of complex **2** was assumed on the basis of analogies: alkylthiolato complexes, including *cis*-$(PPh_3)_2Pt(S^iPr)_2$, reportedly form similar, well-characterized SO_2-adducts [1a,4]. H_2S and SO_2 also form an adduct which has a considerably longer S–S distance (3.67 Å) than alkylthiolato adducts (average 2.61 Å) and contains hydrogen bridges [5]. A similar SH···O interaction cannot be ruled out in com-

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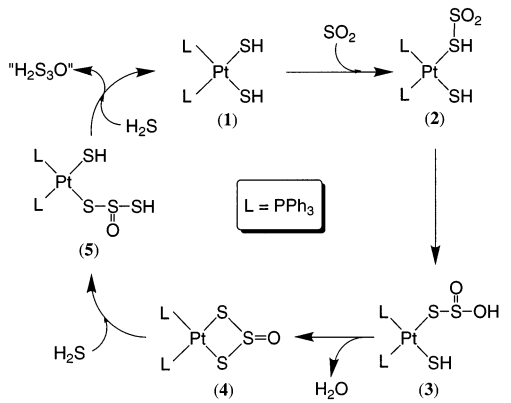


Scheme 1.

plex **2** either. Furthermore, the H_2S–SO_2 adduct supposedly transforms into thiosulfurous acid, HSS(O)OH, via proton transfer to oxygen [6], which may be an intermediate in the commercial Claus process [7]. The same transformation is likely to take place in complex **2** to give **3**, which then probably undergoes a rapid intramolecular thioesterification reaction to generate complex **4**. The high reactivity of complex **3** may originate from the intrinsic instability of the hydrothiosulfito ligand, as well as from the proximity of the hydrosulfido function. It is reasonable to assume that hydrothiosulfito complexes are generally unstable, given that the aforementioned thiosulfurous acid has yet to be independently identified [7], and no hydrothiosulfito complex has ever been reported.

In this study, we were interested in modeling the addition of the S–H bond in sulfhydryl complexes to SO_2 and eventually in obtaining evidence for the intermediacy of complex **3** in the homogeneously catalyzed Claus reaction. By proposing an analogy between the reactions of –SH and $–SSiR_3$ groups, silanethiolato complexes appeared to be suitable models. It has been demonstrated recently that deprotonation of sulfhydryl complexes [8] and desilation of a silanethiolato complex [9] gave similar products. They are also interconvertible: $[Ru(N)Me_3(SSiMe_3)]^-$ reportedly gives $[Ru(N)Me_3(SH)]^-$ via hydrolysis of the S–Si bond [9]. The well-known oxophilic nature of silicon and the substantial difference between the Si–S (54.2 kcal) and Si–O (88.2 kcal) bond energies were expected to become the driving force behind a formal 1,2-insertion of SO_2 into the S–Si bond, resulting in an *O*-silyl thiosulfito complex. Since organic thiosulfites, RSS(O)OR′, appear to be relatively stable compounds [10] compared to the parent thiosulfurous acid [7], analogous *O*-silyl esters of hydrothiosulfito complexes may also have some stability.

Here we report the synthesis and characterization of a series of new ruthenium(II) silanethiolato complexes, $CpRu(PPh_3)(L)SSi^iPr_3$ (L = PPh_3 (**6a**), CO (**6b**), PMe_3 (**6c**), $P(OMe)_3$ (**6d**)) and $CpRu(dppe)SSi^iPr_3$ (**6e**), including the crystal and molecular structure of $CpRu(PPh_3)_2SSi^iPr_3$ (**6a**). Their reactions with SO_2 and spectroscopic characterization of the resulting species are described. Results of a complementary study on the reactions of $CpRu(PPh_3)_2SH$ (**7a**) and CpRu(dppe)SH (**7b**) with *N*-thionylaniline are also presented.

2. Results and discussion

*2.1. Synthesis and characterization of $CpRu(PPh_3)(L)SSi^iPr_3$ (L = PPh_3 (**6a**), CO (**6b**), PMe_3 (**6c**), $P(OMe)_3$ (**6d**)), $CpRu(dppe)SSi^iPr_3$ (**6e**), $CpRu(PPh_3)_2SH$ (**7a**) and CpRu(dppe)SH (**7b**)*

Complexes **6a**,**b** were prepared by reacting $NaSSi^iPr_3$ with $[CpRu(PPh_3)_2(acetone)]BF_4$ and $[CpRu(PPh_3)(CO)(THF)]BF_4$, respectively. Complex **6b** was generated alternatively from **6a** via CO substitution. They were characterized by elemental analysis, IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. An X-ray crystallographic analysis of complex **6a** was also carried out (vide infra).

During the synthesis and characterization of complexes **6a**,**b** some of their fundamental chemical properties were revealed. First, as expected [11], the bulky isopropyl groups effectively stabilized the S–Si bond against hydrolysis by ubiquitous water. For comparison, this bond in $CpRu(PPh_3)_2SSiPh_3$, which contains less bulky phenyl groups, was readily hydrolyzed by wet acetone to give $CpRu(PPh_3)_2SH$, while complex **6a** remained stable under identical conditions. Its Ru–S bond, however, was readily cleaved by chloroform to give $CpRu(PPh_3)_2Cl$. This type of reactivity is common for $CpRu(PPh_3)_2SR$ (R = alkyl, aryl) complexes [12] owing to a high degree of nucleophilicity at the sulfur atom. In contrast, complex **6b** was stable in chlorinated solvents, suggesting that a substantial amount of electron density is pulled off from sulfur by the π-accepting CO ligand. Complexes **6a** and **6b** are also different in that, only the former underwent ligand substitution. Although this is common for complexes of the type $CpRu(PPh_3)_2SR$ (R = alkyl, aryl) [12], complex **6a** appears to be extraordinarily susceptible for ligand substitution. The facile loss of PPh_3 from $CpRu(PPh_3)_2SR$ complexes has previously been attributed to a combination of steric and electronic effects [13]. In complex **6a** both are expected to be strong due to the bulk and electron-donor capability of the silyl group. As a result, a number of ligands (CO, phosphorus and nitrogen donors, isonitriles, etc.) reacted with complex **6a** to give mono- or bis-substituted derivatives. However, PCy_3, which is more basic but also bulkier than PPh_3 [14], completely failed to substitute PPh_3. Interestingly, while the thiolato sulfur atom in $CpRu(PPh_3)_2SR$ (R = ^{n}Pr,

Table 1
Selected ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopic data

Compound	^{1}H-NMR data δ (ppm) [a]		^{13}C{^{1}H}-NMR data δ (ppm) [a]		
	^{i}Pr	Cp	CH	CH_3	Cp
$CpRu(PPh_3)_2SSi^iPr_3$ (**6a**)	1.39	4.37	16.1	19.8	80.7
$CpRu(PPh_3)_2SS(O)OSi^iPr_3$ (**8a**)	1.28	4.67			
$CpRu(PPh_3)_2SS(O)NHPh$ (**9a**)		4.67			83.1
$CpRu(PPh_3)_2SS(O)CH_2Ph$ [19b]		4.62			83.5
$CpRu(PPh_3)_2S(SO_2)R$ (R = ^{i}Pr, Me) [4b,c]		4.77 [b]			82.5[c]
$CpRu(PPh_3)(CO)SSi^iPr_3$ (**6b**)	1.34	4.67	15.5	19.6 19.7	87.1
$CpRu(PPh_3)(CO)SS(O)OSi^iPr_3$ (**8b**)	1.22	4.79	12.9	17.9	86.3
(two diastereomers)		4.88	12.8	17.9	87.3
$CpRu(PPh_3)(CO)SS(O)CH_2Ph$ [19b]		4.90			86.88
(two diastereomers)		4.87			86.90
$CpRu(PPh_3)(CO)S(SO_2)R$ (R = ^{i}Pr, Me) [4b,c]		4.86 [b]			85.6 [c]
$CpRu(PPh_3)(PMe_3)SSi^iPr_3$ (**6c**)	1.36	4.35	16.1	19.8	79.3
$CpRu(PPh_3)(PMe_3)SS(O)OSi^iPr_3$ (**8c**)	1.29	4.58	13.1	18.1	81.0
(two diastereomers)		4.75	13.0	18.1	81.2
$CpRu(PPh_3)[P(OMe)_3]SSi^iPr_3$ (**6d**)	1.36	4.63	16.1	19.8	81.5
$CpRu(PPh_3)[P(OMe)_3]SS(O)OSi^iPr_3$ (**8d**)	1.26	4.92	13.0	18.1	82.3
(two diastereomers)		4.93	13.0	18.1	82.8
$CpRu(dppe)SSi^iPr_3$ (**6e**)	1.13	4.66	15.7	19.7	79.5
$CpRu(dppe)SS(O)OSi^iPr_3$ (**8e**)	1.21	4.87			
CpRu(dppe)SS(O)NHPh (**9b**)		4.91			
$CpRu(PPh_3)(SO_2)SSi^iPr_3$ (**6f**)	1.30	4.77	15.6	19.5	90.5
$CpRu(PPh_3)(PhNSO)SSi^iPr_3$ (**6g**)		4.79			

[a] Recorded in C_6D_6.
[b] R = ^{i}Pr.
[c] R = Me, recorded in $CDCl_3$.

^{i}Pr) substituted one or both PPh_3 ligands to give thiolato-bridged dimers and trimers [13], no such reaction was observed for complex **6a**, possibly due to steric hindrance by the silyl group.

Complexes **6c**–**e** were readily prepared from **6a** by adding stoichiometric amounts of PMe_3, $P(OMe)_3$ and dppe, respectively. The reactions were monitored by NMR spectroscopy at room temperature and substitution of one PPh_3 ligand was found to be instantaneous and quantitative in all cases. Replacement of the second PPh_3 ligand, albeit at a slightly slower rate, also took place when the chelating dppe was applied. Due to the rate difference, the mixed-ligand intermediate $CpRu(PPh_3)(\eta^1$-dppe)SSi^iPr_3, which contains a monodentate dppe ligand, was detected in low concentrations by ^{1}H- and ^{31}P{^{1}H}-NMR (Table 2). The final product **6e** was isolated as an air-stable, orange crystalline material and characterized by elemental analysis and NMR spectroscopy. Complexes **6c**,**d** were also characterized by multinuclear NMR spectroscopy but not isolated; all were stable in solution for at least several days at room temperature.

^{1}H-NMR spectra of complexes **6a**–**e** exhibited a featureless upfield multiplet resonance attributable to all protons of the three ^{i}Pr groups attached to silicon, a doublet for the Cp protons in the range 4.35–4.67 ppm with weak (1 Hz) coupling to phosphorus and separate multiplet resonances for the *o*- as well as *m*,*p*-Ph protons of coordinated PPh_3. The methyl and methine carbons in the ^{i}Pr groups were easily recognizable in the ^{13}C{^{1}H}-NMR spectra, which also exhibited signals for the other ligands as expected. Proton and carbon NMR data for the ^{i}Pr and Cp groups are compiled in Table 1. The shielding of Cp protons and carbons is consistent with changes in the basicity of the ligand L in the $CpRu(PPh_3)(L)SSi^iPr_3$ system. Being distant from ruthenium, the ^{i}Pr proton and carbon resonances are practically insensitive to these changes. For complex **6b**, the methyl carbon resonances of the Si^iPr_3 group appeared as two closely spaced singlets, indicating that the chiral metal center rendered these methyl groups diastereotopic. The spectra of complexes **6c**,**d** did not indicate chirality, probably because the two methyl carbon resonances were overlapping.

^{31}P{^{1}H}-NMR spectra (Table 2) of complexes **6a**–**e** reflect changes in the ligand environment of ruthenium. For complexes **6c**,**d**, where two different phosphorus ligands are present, two mutually coupled doublets were observed with characteristic chemical shift values and coupling constants. The strong π-acceptor CO ligand in complex **6b** considerably deshielded the PPh_3 ligand (δ 51.2), similarly to the Cp ligand (Table 1).

The chelating effect in complex **6e** resulted in even more substantial deshielding at phosphorus (δ 78.6). Unlike the Cp proton and carbon NMR data, however, the PPh_3 phosphorus resonances of complexes **6a**,**c**,**d** were inconsistent with the anticipated electronic effects of the second phosphine or phosphite [14]. Most notably, this signal for complex **6a** shifted unusually upfield to δ 37.0. It may reflect a weakened interaction between PPh_3 and the ruthenium atom as manifested in the high substitution lability observed for this particular complex.

When an attempt was made to prepare $CpRu(PPh_3)_2SSiPh_3$, it was found that the product of the reaction of $NaSSiPh_3$ and $[CpRu(PPh_3)_2(acetone)]\text{-}BF_4$ was readily hydrolyzed by water present in commercial acetone (Eq. (1)).

$$CpRu(PPh_3)_2SSiPh_3 + H_2O \rightarrow \underset{\textbf{7a}}{CpRu(PPh_3)_2SH} + Ph_3SiOH \quad (1)$$

While this observation demonstrated the relative sensitivity of $CpRu(PPh_3)_2SSiPh_3$ toward hydrolysis in comparison with complex **6a**, it also provided an alternative method for the synthesis of hydrosulfido complex **7a** [12,15].

Complex **7b** was prepared from **7a** via thermal substitution with dppe. NMR spectroscopic studies on the substitution process showed that exchange of the first PPh_3 ligand readily took place to generate the mixed-ligand species $CpRu(PPh_3)(\eta^1\text{-dppe})SH$ containing a dangling $-PPh_2$ function. Unlike in the case of the conversion of complex **6a** to **6e**, the substitution of the second PPh_3 ligand took place at a considerably slower rate at room temperature to give complex **7b**. This resulted in a temporary accumulation of the mixed-ligand intermediate in $>95\%$ yield, which permitted its characterization by NMR (Table 2). Being quite persistent, this intermediate also reacted with a second equivalent of **7a** to give the diastereomeric binuclear

Table 2
$^{31}P\{^1H\}$-NMR spectroscopic data

Compound	δ (ppm) [a]
$CpRu(PPh_3)_2SSi^iPr_3$ (**6a**)	37.0
$CpRu(PPh_3)_2SS(O)OSi^iPr_3$ (**8a**)	41.5, 42.3 (both d, $J_{PP} = 39$ Hz)
$CpRu(PPh_3)_2SS(O)NHPh$ (**9a**)	41.4, 42.4 (both d, $J_{PP} = 38$ Hz)
$CpRu(PPh_3)_2SS(O)CH_2Ph$ [19b]	41.6, 42.9 (both d, $J_{PP} = 39$ Hz)
$CpRu(PPh_3)_2S(SO_2)Me$ [4b]	41.1 [b]
$CpRu(PPh_3)(\eta^1\text{-dppe})SSi^iPr_3$ [c]	-12.4 (d, $J_{PP} = 27$ Hz, free $-PPh_2$), 37.7 (dd, $J_{PP} = 45$ Hz, $J_{PP} = 27$ Hz, complexed PPh_2), 40.4 (d, $J_{PP} = 45$ Hz, PPh_3)
$CpRu(dppe)SSi^iPr_3$ (**6e**)	78.6
$CpRu(dppe)SS(O)OSi^iPr_3$ (**8e**)	81.0, 81.9 (both d, $J_{PP} = 27$ Hz)
$CpRu(dppe)SS(O)NHPh$ (**9b**)	80.1, 82.5 (both d, $J_{PP} = 27$ Hz)
$CpRu(PPh_3)(CO)SSi^iPr_3$ (**6b**)	51.2
$CpRu(PPh_3)(CO)SS(O)OSi^iPr_3$ (**8b**) (two diastereomers)	52.2 (65%), 52.5 (35%)
$CpRu(PPh_3)(CO)SS(O)CH_2Ph$ [19b] (two diastereomers)	51.4 (23%), 52.1 (77%)
$CpRu(PPh_3)(CO)S(SO_2)Me$ [4b]	49.2 [b]
$CpRu(PPh_3)(PMe_3)SSi^iPr_3$ (**6c**)	0.2 (d, $J_{PP} = 50$ Hz, PMe_3), 47.0 (d, $J_{PP} = 50$ Hz, PPh_3)
$CpRu(PPh_3)(PMe_3)SS(O)OSi^iPr_3$ (**8c**) (two diastereomers)	2.2 (d, $J_{PP} = 43$ Hz, PMe_3), 54.2 (d, $J_{PP} = 43$ Hz, PPh_3) (58%) 3.0 (d, $J_{PP} = 43$ Hz, PMe_3), 53.3 (d, $J_{PP} = 43$ Hz, PPh_3) (42%)
$CpRu(PPh_3)[P(OMe)_3]SSi^iPr_3$ (**6d**)	48.2 (d, $J_{PP} = 80$ Hz, PPh_3), 147.1 (d, $J_{PP} = 80$ Hz, $P(OMe)_3$)
$CpRu(PPh_3)[P(OMe)_3]SS(O)OSi^iPr_3$ (**8d**) (two diastereomers)	50.9 (d, $J_{PP} = 74$ Hz, PPh_3), 152.5 (d, $J_{PP} = 74$ Hz, $P(OMe)_3$) (50%) 51.7 (d, $J_{PP} = 71$ Hz, PPh_3), 153.1 (d, $J_{PP} = 71$ Hz, $P(OMe)_3$) (50%)
$CpRu(PPh_3)(SO_2)SSi^iPr_3$ (**6f**)	43.9
$CpRu(PPh_3)(PhNSO)SSi^iPr_3$ (**6g**)	45.0
$CpRu(PPh_3)_2SH$ (**7a**)	44.3
$CpRu(PPh_3)(\eta^1\text{-dppe})SH$ [d]	-12.6 (d, $J_{PP} = 29$ Hz, free $-PPh_2$), 43.6 (dd, $J_{PP} = 29$ Hz, $J_{PP} = 39$ Hz, complexed $-PPh_2$), 48.9 (d, $J_{PP} = 39$ Hz, PPh_3)
$[CpRu(PPh_3)SH]_2(\mu\text{-dppe})$ [e] (two diastereomers)	44.4 (d, $J_{PP} = 39$ Hz, dppe), 47.9 (d, $J_{PP} = 39$ Hz, PPh_3) (50%) 45.9 (d, $J_{PP} = 39$ Hz, dppe), 48.2 (d, $J_{PP} = 39$ Hz, PPh_3) (50%)
$CpRu(dppe)SH$ (**7b**)	86.2

[a] Recorded in C_6D_6.
[b] Recorded in $CDCl_3$.
[c] ^1H-NMR (C_6D_6): 4.39 (s, Cp).
[d] ^1H-NMR (C_6D_6): δ -3.21 (t, $J_{PH} = 7$ Hz, SH), 4.30 (s, Cp).
[e] ^1H-NMR (C_6D_6): δ -3.57, -3.89 (both t, $J_{PH} = 7$ Hz, SH), 4.17, 4.20 (both s, Cp).

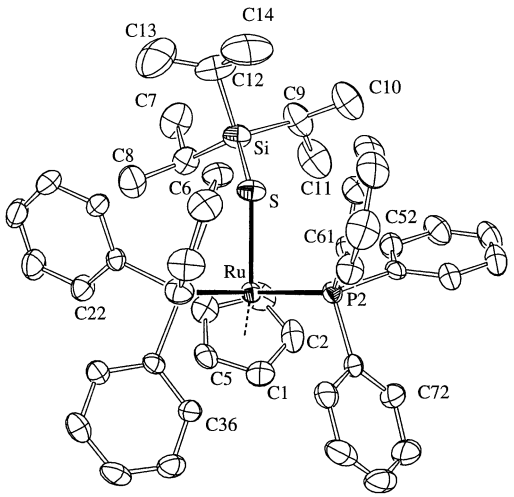


Fig. 1. ORTEP view of $CpRu(PPh_3)_2SSi^iPr_3$ (**6a**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru–S, 2.462(3); Ru–P(1), 2.317(3); Ru–P(2), 2.330(2); Ru–C(1), 2.203(7); Ru–C(2), 2.211(8); Ru–C(3), 2.228(7); Ru–C(4), 2.208(7); Ru–C(5), 2.196(7); S–Si, 2.114(3); Si–S–Ru, 127.63(11); P(1)–Ru–P(2), 99.81(8); P(1)–Ru–S, 87.75(9); P(2)–Ru–S, 87.74(8).

sulfhydryl complex $[CpRu(PPh_3)SH]_2(\mu\text{-dppe})$, which was characterized by ^1H and $^{31}P\{^1H\}$-NMR (Table 2) but was not further investigated.

2.2. Crystal and molecular structure of complex *6a*

The structure of complex **6a** is as expected and is depicted in Fig. 1, along with the selected bond distances and angles. The Ru–S and S–Si bond distances are 2.462(3) and 2.114(3) Å, respectively, while the Ru–S–Si bond angle is 127.6°. The large P–Ru–P angle (99.8°) compared with the P–Ru–S angles (both 87.7°) seems to be an indication of steric crowding about ruthenium. The $Ru–C_{ring}$ distance for carbon C3 close to the thiolato sulfur is longer than for those at the opposite side of the Cp ring, resulting in a slight ring-slippage.

Although a number of transition metal silanethiolato complexes have been reported [9,16–18], few contain a single, unsupported transition metal–S–Si moiety and only four have been characterized by X-ray crystallography: $Cp^*_2Ti(H)SSiHEt_2$ [18d], $(PPh_3)_2CuSSi(O^tBu)_3$ [16c,e], $(PPh_3)_2AgSSi(O^tBu)_3$ [16i] and $^tBuN=V(SSiPh_3)_3$ [17a]. The Ru–S–Si angle in complex **6a** is the largest of all five complexes. The Ru–S bond distance in complex **6a** also exceeds those observed for a large number of complexes of the type $CpRu(PPh_3)(L)X$ ($L = CO$, PPh_3, SO_2; $X = SH$, SR, SSR, SSSR, SS(O)R, $SS(O)_2R$, $S(SO_2)R$; R = alkyl, aryl), which are in the range 2.36–2.42 Å [4b,c,12,19]. The largest Ru–S–Y angle observed in these complexes (110.7°) is significantly smaller than that in complex **6a**.

2.3. Reaction of ruthenium silanethiolato complexes with SO_2

When a large excess of SO_2 gas [4] was passed through solutions of complexes **6a**–**e**, complete consumption of the starting materials and the formation of many decomposition products was observed. Therefore, all subsequent experiments were performed with carefully measured volumes of SO_2 and were closely monitored by multinuclear NMR spectroscopy. Complexes **6a**–**e** reacted instantly and quantitatively with one equivalent of SO_2 at room temperature to give a single product each. Upon gradual addition of SO_2, no intermediates were detected and no reactions between these products and their starting materials were observed. However, addition of even a small excess of SO_2 generated mixtures of unidentified secondary or decomposition products. The primary products are inherently unstable either at room temperature or at low temperatures and thus could only be characterized in solution by IR and NMR spectroscopic techniques, which provided a reasonable basis for their identification. Complex **6a** showed different reactivity toward SO_2 than **6b**–**e**.

2.3.1. Reaction of complex *6a* with SO_2

Upon injection of up to one equivalent of SO_2 into benzene-d_6 or acetone-d_6 solutions of complex **6a** at room temperature, a deep red color evolved instantly and formation of a 1:1 mixture of free PPh_3 and the new ligand-substituted derivative $CpRu(PPh_3)(SO_2)SSi^iPr_3$ (**6f**) (Eq. (2)) was observed. At this point, no reaction with the silanethiolato ligand had occurred.

$$\underset{\mathbf{6a}}{CpRu(PPh_3)_2SSi^iPr_3} + SO_2 \rightleftharpoons \underset{\mathbf{6f}}{CpRu(PPh_3)(SO_2)SSi^iPr_3} + PPh_3 \quad (2)$$

The phosphorus atom of complex **6f** resonated at δ 43.9 as a singlet and the Cp protons and carbon atoms at δ 4.77 as a doublet and 90.5 as a singlet, respectively. All were significantly deshielded compared to the respective nuclei in **6a** (Tables 1 and 2). Integrals of the proton signals indicated only one PPh_3 ligand in the molecule. The NMR data are fully consistent with the presence of the strong electron-accepting SO_2 ligand in the coordination sphere of the ruthenium atom. These data are comparable to those for complex **6b**, indicating that CO and SO_2 have similar σ-donor and π-acceptor characters [20], although the CO ligand in complex **6b** pulls more electron density from the phosphine, while the SO_2 ligand in complex **6f** attracts more electron density from the Cp ligand. Complex **6f** is chiral, which renders the methyl groups in the Si^iPr_3 moiety diastereotopic but this was not detected spectroscopically, similarly to complexes **6c**,**d** and probably due to overlapping signals (Table 1).

Complex **6f** spontaneously decomposes in benzene-d_6 to give the starting complex **6a**, $CpRu(PPh_3)_2SS(O)OSi^iPr_3$ (**8a**) and Ph_3PS, which were detected in relatively significant concentrations among other products. Complex **8a** was tentatively identified on the basis of a new ^{i}Pr multiplet at δ 1.28 and a Cp doublet at 4.67 in the proton spectrum, as well as of two mutually coupled doublets at δ 41.5 and 42.3 in the $^{31}P\{^1H\}$-NMR spectrum. In comparison with the respective data for complexes **6a** and **6f** (Tables 1 and 2), these data are consistent with the proposed structure wherein the SO_2 moiety has inserted into the S–Si bond. Careful integration of both the proton and phosphorus signals for complex **8a** supported the presence of two PPh_3 ligands in the molecule. The resulting *O*-silyl thiosulfito moiety $-S(O)OSi^iPr_3$ is chiral at the S atom and this renders the Ph_3P ligands non-equivalent, consistent with the observed AB phosphorus resonance pattern.

The reappearance of complex **6a** among the products suggests that Eq. (2) is reversible, but the release of SO_2 must be very slow compared to the forward process. It is probably the SO_2 present at equilibrium concentration, which attacks a thiolato sulfur atom to give complex **8a**. The latter is unstable and decomposes to yet unidentified species, among them to Ph_3PS. Curiously, the formation of complex **8a** was not accompanied by that of $CpRu(PPh_3)(SO_2)SS(O)OSi^iPr_3$ in detectable amounts even though complex **6f** was continuously present in the reaction mixture. This is supported by an independent observation that treatment of complex **6f** with SO_2 did not give $CpRu(PPh_3)(SO_2)SS(O)OSi^iPr_3$.

2.3.2. Reactions of complexes *6b–e* with SO_2

Unlike complex **6a**, its more robust ligand-substituted derivatives **6b–e** did not undergo reaction with SO_2 at the ruthenium center but instead reacted exclusively at the silanethiolato ligand. The reactions were accompanied by a color change to dark yellow or yellow–brown and no free ligand could be detected by NMR spectroscopy. Most reaction mixtures eventually became green and paramagnetic in a few hours, suggesting a relatively fast oxidation process. The primary products of the reaction of SO_2 with complexes **6b–e** were spectroscopically identified as the *O*-silyl thiosulfito complexes $CpRu(PPh_3)(L)SS(O)OSi^iPr_3$ (L = CO (**8b**), PMe_3 (**8c**), $P(OMe)_3$ (**8d**)) and $CpRu(dppe)SS(O)OSi^iPr_3$ (**8e**) (Eq. (3)).

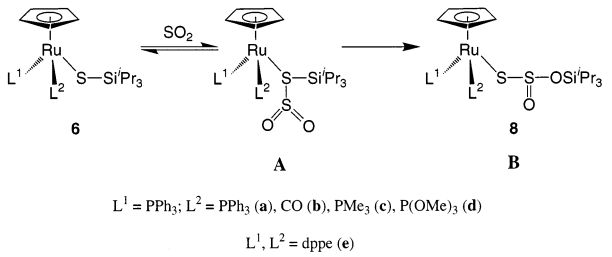
$$CpRu(PPh_3)(L)SSi^iPr_3 + SO_2 \rightarrow CpRu(PPh_3)(L)SS(O)OSi^iPr_3 \quad (3)$$

The IR spectrum of complex **8b** exhibited a broad ν_{SO} band at 1110 cm^{-1} and a ν_{CO} band at 1960 cm^{-1}. The former is different from that of SO_2 found in the adducts $CpRu(PPh_3)(L)S(SO_2)R$ (L = CO, PPh_3, SO_2; R = alkyl, aryl) [4b,c], which typically has two strong bands in the regions 1210–1218 cm^{-1} (asymmetric) and 1060–1069 cm^{-1} (symmetric). The band at 1110 cm^{-1} is rather similar to the single band at 1080 cm^{-1} calculated for HSS(O)OH [7] and to that observed for $CpRu(PPh_3)(CO)SS(O)CH_2Ph$ at 1030 cm^{-1} [19b]. The ν_{CO} band is shifted to higher wavenumbers compared to that of the parent compound (1941 cm^{-1}) due to the electron-withdrawing effect of SO_2.

A combination of ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy confirmed the structures of complexes **8b–e** (Tables 1 and 2). Each of the mixed-ligand complexes **8b–d** gave two very similar sets of resonances in the NMR spectra consistent with the presence of diastereomers as expected. The ratio of diastereomers was 50:50 for **8d**, 58:42 for **8c**, and 65:35 for **8b,** and the latter showed no solvent-dependency in benzene-d_6, acetone-d_6, or $CDCl_3$. The different phosphorus environments in complexes **8c,d** gave rise to two pairs of mutually coupled doublets in the $^{31}P\{^1H\}$-NMR spectra, while only two singlet resonances were detected for complex **8b** (Table 2). Comparing the Cp and ^{i}Pr proton and carbon resonances of complexes **8b–d** to those of the respective starting materials (Table 1), it is evident that the Cp nuclei are only slightly affected while the ^{i}Pr group is considerably shielded, consistent with SO_2 addition. The extent of the changes in shielding is quite uniform for all complexes regardless of their different ligand sphere. These observations clearly point to the silanethiolato ligand as the reactive site.

Complex **6e**, which contains magnetically equivalent phosphorus nuclei, was designed to model the reaction of the thiolato sulfur of **6a** with SO_2 while preventing any ligand exchange. Indeed, upon addition of one equivalent of SO_2, complex **8e** was obtained as the sole product. Since the ruthenium center in **8e** is achiral, no diastereomeric mixture is possible. However, the phosphine sites are non-equivalent as indicated by an AB spin pattern in the $^{31}P\{^1H\}$-NMR spectrum (Table 2). This is consistent with the presence of a chiral sulfur atom in the –SS(O)OSi moiety, which renders the phosphorus atoms diastereotopic. This spectroscopic feature is identical to that observed for complex **8a**.

It is proposed that the reaction of complexes **6a–e** with SO_2 results in a formal 1,2-insertion of SO_2 into the S–Si bond to give the novel *O*-silyl thiosulfito complexes **8a–e** of the general structure **B** and not simply formation of an SO_2-adduct as depicted in **A** (Scheme 2). Such adducts of ruthenium thiolato complexes are well known and have been characterized by X-ray crystallography [4b,c]. However, they do not undergo subsequent insertion into the S–C bond and adduct formation is always reversible [4], which contrasts to the rapid and irreversible reaction of complexes **6b–e** with SO_2. For example, complex **8b** was



L^1 = PPh_3; L^2 = PPh_3 (**a**), CO (**b**), PMe_3 (**c**), $P(OMe)_3$ (**d**)

L^1, L^2 = dppe (**e**)

Scheme 2.

kept under vacuum at room temperature for one day and no complex **6b** could be detected.

Structures of type **A** and that proposed for complexes **8a**–**e** (**B**) both possess a stereogenic sulfur, which should render the chemically equivalent phosphorus environments in **8a**,**e** magnetically non-equivalent (Table 2) as observed. This was also observed for $CpRu(PPh_3)_2SS(O)CH_2Ph$ [19b] and $CpRu(PPh_3)_2SS(O)NHPh$ (**9a**) as well as in CpRu(dppe)SS(O)NHPh (**9b**) (vide infra), which may be viewed as functional derivatives of complexes **8a**,**e** and are of **B**-type. In contrast, only one type of phosphorus environment was detected in the **A**-type complexes $CpRu(PPh_3)_2S(SO_2)R$ (R = Me, ^{n}Pr, ^{i}Pr, *p*-Tol) [4b,c] (Table 2). Furthermore, complexes **8b**–**d** exist as a pair of diastereomers owing to the presence of two chiral centers in the molecules (Tables 1 and 2) and the same behavior was reported for $CpRu(PPh_3)(CO)SS(O)CH_2Ph$ [19b]. However, the **A**-type adducts $CpRu(PPh_3)(CO)S(SO_2)R$ (R = Me, ^{i}Pr) [4b,c] and $CpRu(PPh_3)(SO_2)S(SO_2)$-*p*-Tol [4c] did not show diastereomerism in their NMR spectra. In general, it appears that the chirality at sulfur of type **A** SO_2-adducts of ruthenium thiolato complexes is not detected via NMR spectroscopy, possibly due to exchange. This may also be invoked in support of the structure **B** suggested for complexes **8a**–**e**. Note, however, that although all the evidence supports the formation of **B**-type complexes and no **A**-type adducts were detected, formation of short-lived **A**-type intermediates in fast equilibrium with the starting silanethiolato complexes cannot be ruled out and, as suggested in Scheme 2, are probably intermediates in the formation of **8a**–**e**.

2.4. Reactions of complexes *2a*,*b* with SO_2 and PhNSO

Since the original goal was to model the addition of the S–H bond of hydrosulfido complexes to SO_2, complex **7a** was also treated with SO_2. Complex **7a** readily reacted with SO_2 but no product was detected by NMR spectroscopy. The reaction mixture remained homogeneous but changed color from orange to green, possibly due to oxidation of Ru(II) to paramagnetic and NMR-silent Ru(III). No evidence for the formation of intermediates such as $CpRu(PPh_3)_2SS(O)OH$, $CpRu(PPh_3)(SO_2)SH$, or $CpRu(PPh_3)_2SS(O)SRu(PPh_3)_2Cp$ was detected. If any $CpRu(PPh_3)_2SS(O)OH$ was formed, it must be very unstable.

Attention then turned to *N*-thionylaniline, which appeared to be a possible alternative to SO_2. In order to test the analogy between SO_2 and *N*-thionylaniline in the Claus reaction, a reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ (**1**) with PhNSO was performed. As outlined in Scheme 1, the reaction between complex **1** and SO_2 gave $(PPh_3)_2PtS_3O$ (**4**) and H_2O. Notably, the reaction of complex **1** with PhNSO proceeded similarly to give complex **4** and aniline (Eq. (4)).

$$\underset{\mathbf{1}}{cis\text{-}(PPh_3)_2Pt(SH)_2} + PhNSO \rightarrow \underset{\mathbf{4}}{(PPh_3)_2PtS_3O} + PhNH_2 \quad (4)$$

Upon treatment of complex **7a** with one equivalent of *N*-thionylaniline at room temperature, an instantaneous reaction took place giving a single product (Eq. (5)), which was identified spectroscopically as

$$\underset{\mathbf{7a}}{CpRu(PPh_3)_2SH} + PhNSO \rightarrow \underset{\mathbf{9a}}{CpRu(PPh_3)_2SS(O)NHPh} \quad (5)$$

$CpRu(PPh_3)_2SS(O)NHPh$ (**9a**) and which decomposed in a few hours to paramagnetic, green colored solutions even at low temperatures. Its $^{31}P\{^1H\}$-NMR spectrum exhibited an AB spin pattern at δ 41.4 and 42.4 (Table 2), consistent with diastereotopism due to a stereogenic sulfur center. The proton and carbon NMR spectra exhibited singlet resonances at δ 4.64 and 83.1, respectively, attributed to the Cp ligand. All the NMR data are practically identical with the respective data for complexes **8a** and $CpRu(PPh_3)_2SS(O)CH_2Ph$ [19b] (Tables 1 and 2). The reaction of complex **7b** with PhNSO was carried out in a similar manner and gave CpRu(dppe)SS(O)NHPh (**9b**). Its ^1H- and $^{31}P\{^1H\}$-NMR data are similar to those of complex **8e** (Tables 1 and 2). On the basis of analogies between complexes **9a**,**b** and **8a**,**b** and the ways they were formed, the reactions outlined in Eqs. (3) and (5) are mutually supportive. They also mimic the addition of the S–H bond of sulfhydryl complexes to SO_2 to give hydrothiosulfito complexes.

When reactions of *N*-thionylaniline were attempted with complexes **6a**,**b** at room temperature, **6b** remained unchanged at least for 3 days, while **6a** immediately gave red colored $CpRu(PPh_3)(PhNSO)SSi^iPr_3$ (**6g**) via an equilibrium ligand substitution (Eq. (6)). Unlike the

$$\underset{\mathbf{6a}}{CpRu(PPh_3)_2SSi^iPr_3} + PhNSO \rightleftharpoons \underset{\mathbf{6g}}{CpRu(PPh_3)(PhNSO)SSi^iPr_3} + PPh_3 \quad (6)$$

substitution reaction of complex **6a** with SO_2 (Eq. (2)), this equilibrium favors the starting complex; at least a fourfold increase in the concentration of PhNSO and longer reaction times were necessary to achieve a substantial (38%) conversion of complex **6a** into **6g**, indicating that PhNSO is a poor ligand compared with

SO_2. Complex **6g** was only identified in the reaction mixture by its Cp proton (δ 4.79) and phosphorus (δ 45.0) resonances, which closely resemble to those of the SO_2-substituted complex **6f** (Tables 1 and 2). No evidence for insertion of PhNSO into the S–Si bond was detected.

3. Summary

Ruthenium silanethiolato complexes of the general formula $CpRu(PPh_3)(L)SSi^iPr_3$ and $CpRu(dppe)SSi^iPr_3$ are easily accessible and all react instantly with SO_2 to give $CpRu(PPh_3)(SO_2)SSi^iPr_3$, when $L = PPh_3$, as well as $CpRu(PPh_3)(L)SS(O)OSi^iPr_3$, when $L = CO$, PMe_3, $P(OMe)_3$, and $CpRu(dppe)SS(O)OSi^iPr_3$ as the primary products. This is the first observation of a formal 1,2-insertion of SO_2 into the S–Si bond. The S–H bond of $CpRu(PPh_3)_2SH$ and CpRu(dppe)SH also add readily to PhNSO to give the corresponding complexes $CpRuL_2SS(O)NHPh$. Both the anilides and the *O*-silyl esters are derivatives of a hypothetical hydrosulfito complex. These reactions support suggestions that similar intermediates may also form in the reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 as a step in the Claus chemistry catalyzed by that complex.

4. Experimental

All manipulations were carried out under an inert atmosphere (N_2 or Ar), using standard Schlenk technique and a drybox. Solvents were dried and freshly distilled under nitrogen prior to use. $CpRu(PPh_3)_2Cl$ [21], $CpRu(PPh_3)(CO)Cl$ [22], $NaSSi^iPr_3$ [11] and $NaSSiPh_3$ [23] were prepared according to reported procedures. IR spectra were recorded on a Bruker IFS 48 spectrometer in solutions using a 0.1 mm NaCl cell. ^{1}H-, ^{13}C-, and ^{31}P-NMR measurements were performed on a Jeol CPF 270 spectrometer. Selected ^{1}H- and $^{13}C\{^1H\}$-NMR data are listed in Table 1 and the $^{31}P\{^1H\}$-NMR data are compiled in Table 2. Elemental analyses were carried out by the Laboratoire d'Analyse Elementaire at the University of Montreal.

4.1. *$CpRu(PPh_3)_2SSi^iPr_3$ (**6a**)*

A suspension of $CpRu(PPh_3)_2Cl$ (2.00 g, 2.75 mmol) and $AgBF_4$ (0.60 g, 3.1 mmol) in a solvent mixture of 100 ml THF and 30 ml acetone was stirred overnight at room temperature (r.t.). The resulting dark yellow solution containing a yellow precipitate was filtered through Celite and the precipitate was washed with acetone until it became off-white. The combined washings were concentrated to about 100 ml under vacuum. To this $NaSSi^iPr_3$ was added (0.65 g, 3.1 mmol) and the color changed quickly to red–orange as stirring started. The resulting mixture was stirred at r.t. for 2 h, filtered through Celite and evaporated to dryness. The remaining solid was dissolved in warm acetone and crystallized upon slow cooling as well-formed red–orange crystals. Yield: 1.64 g (1.9 mmol, 68%). The crystalline form is indefinitely stable in air but was found to decompose if kept in a closed vial under acetone vapors. The crystals must be washed with hexane and dried carefully for storage. Anal. Calc. for $C_{50}H_{56}P_2RuSSi$: C, 68.23; H, 6.41; S, 3.64. Found: C, 67.78; H, 6.25; S, 3.68. ^{1}H-NMR (acetone-d_6): δ 1.11 (m, 21H, ^{i}Pr), 4.27 (s, 5H, Cp), 7.13 (m, 12H, *m*-Ph), 7.26 (m, 6H, *p*-Ph), 7.41 (m, 12H, *o*-Ph). $^{13}C\{^1H\}$-NMR (acetone-d_6): δ 16.0 (CH), 19.5 (Me), 80.1 (Cp), 127.2 (*m*-Ph), 128.5 (*p*-Ph), 134.2 (*o*-Ph), 139.2 (t, $J_{PC} = 20$ Hz, *ipso*-Ph).

4.2. *$CpRu(PPh_3)(CO)SSi^iPr_3$ (**6b**)*

A mixture of $CpRu(PPh_3)(CO)Cl$ (1.50 g, 3.0 mmol) and $AgBF_4$ (0.66 g, 3.4 mmol) was stirred in 100 ml of THF at r.t. overnight. The resulting precipitateous yellow solution was filtered through Celite and the solid was washed with THF until colorless washings were obtained. $NaSSi^iPr_3$ (0.72 g, 3.4 mmol) was added and the yellow color changed to orange almost instantly. Stirring was continued for 2 h and the reaction mixture was filtered again through Celite and evaporated to dryness. The product crystallized as yellow plates from ether or acetone at -30°C. Yield: 1.47 g (2.3 mmol, 76%). Anal. Calc. for $C_{33}H_{41}OPRuSSi$: C, 61.37; H, 6.40; S, 4.96. Found: C, 61.27; H, 6.50; S, 4.70. IR (CH_2Cl_2): ν_{CO} 1941 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.04 (m, 21H, ^{i}Pr), 4.86 (s, 5H, Cp), 7.36 (m, 9H, *m*,*p*-Ph), 7.56 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.4 (CH), 19.40 and 19.46 (Me), 87.4 (Cp), 128.0 (d, $J_{PC} =$ 10 Hz, *m*-Ph), 129.9 (*p*-Ph), 133.9 (d, $J_{PC} = 10$ Hz, *o*-Ph), 135.7 (d, $J_{PC} = 48$ Hz, *ipso*-Ph), 205.7 (d, $J_{PC} =$ 23 Hz, CO).

4.3. *$CpRu(PPh_3)(PMe_3)SSi^iPr_3$ (**6c**)*

This compound was generated in situ by adding PMe_3 (3.5 μl, 0.034 mmol) in two portions to complex **6a** (30 mg, 0.034 mmol) dissolved in 0.7 ml of benzene-d_6. The ligand substitution process, closely monitored by NMR spectroscopy, gave quantitative formation of complex **6c**, accompanied by a color change from orange to yellow upon mixing. ^{1}H-NMR (C_6D_6): δ 1.09 (d, $J_{PH} = 9$ Hz, 9H, PMe), 1.36 (m, 21H, ^{i}Pr), 4.35 (br d, 5H, Cp), 7.05 (m, 9H, *m*,*p*-Ph), 7.79 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 16.1 (CH), 19.8 (Me), 20.7 (d, $J_{PC} = 28$ Hz, PMe), 79.3 (Cp), 128.9 (*p*-Ph), 134.6 (d, $J_{PC} = 10$ Hz, *o*-Ph), 139.4 (d, $J_{PC} = 38$ Hz, *ipso*-Ph), the *m*-Ph resonance was covered by that of the solvent.

4.4. $CpRu(PPh_3)[P(OMe_3)]SSi^iPr_3$ (6d)

As for complex **6c**, $P(OMe)_3$ (4 μl, 0.034 mmol) and **6a** (30 mg, 0.034 mmol) were dissolved in 0.7 ml of benzene-d_6. ^{1}H-NMR (C_6D_6): δ 1.36 (m, 21H, ^{i}Pr), 3.32 (d, $J_{PH} = 10$ Hz, 9H, POMe), 4.63 (d, $J_{PH} = 1$ Hz, 5H, Cp), 7.09 (m, 9H, *m*,*p*-Ph), 7.89 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 16.1 (CH), 19.8 (Me), 81.5 (Cp), 127.1 (d, $J_{PC} = 9$ Hz, *m*-Ph), 128.8 (*p*-Ph), 134.8 (d, $J_{PC} = 9$ Hz, *o*-Ph), 138.7 (d, $J_{PC} = 42$ Hz, *ipso*-Ph), 152.6 (d, $J_{PC} = 8$ Hz, POMe).

4.5. $CpRu(dppe)SSi^iPr_3$ (6e)

Complex **6a**, generated from 2.0 g $CpRu(PPh_3)_2Cl$ as described above, in the final filtered red–orange reaction solution in THF–acetone was treated with bis-diphenylphosphinoethane (dppe) (1.10 g, 2.7 mmol) under ambient conditions. The resulting solution was stirred for 1 day while the color changed to yellow–orange. The solvent was evaporated under vacuum and the resulting solid was washed thoroughly with a 1:1 hexane–ether solvent mixture to remove PPh_3. The product crystallized as orange needles from acetone at low temperature. Yield: 1.32 g (1.75 mmol, 64%). Anal. Calc. for $C_{40}H_{50}P_2RuSSi$: C, 63.72; H, 6.68; S, 4.25. Found: C, 62.99; H, 6.66; S, 4.35. ^{1}H-NMR (acetone-d_6): δ 0.80 (m, 21H, ^{i}Pr), 2.26, 2.91 (both m, 2H, CH_2P), 4.65 (s, 5H, Cp), 7.15 (m, 4H, *o*-Ph), 7.29 (m, 12H, *m*,*p*-Ph), 7.88 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$-NMR (acetone-d_6): δ 15.2 (CH), 19.1 (Me), 79.2 (Cp), 127.3 (t, $J_{PC} = 4$ Hz, *m*-Ph), 127.8 (t, $J_{PC} = 4$ Hz, *m*-Ph), 128.7 (*p*-Ph), 128.9 (*p*-Ph), 132.1 (t, $J_{PC} = 4$ Hz, *o*-Ph), 133.8 (t, $J_{PC} = 4$ Hz, *o*-Ph), 137.2 (t, $J_{PC} = 22$ Hz, *ipso*-Ph).

4.6. $CpRu(PPh_3)(SO_2)SSi^iPr_3$ (6f)

Complex **6a** (40 mg, 0.045 mmol) in an NMR sample tube in 0.7 ml of benzene-d_6 was treated with 1.2 ml of SO_2 gas, added in two portions at r.t. by means of a gas-tight Hamilton syringe. The color of the reaction mixture became deep red instantly and the NMR spectra revealed formation of complex **6f** as well as one equivalent of free PPh_3. The product had significantly decomposed after 2 h at r.t. ^{1}H-NMR (C_6D_6): δ 1.30 (m, 21H, ^{i}Pr), 4.77 (d, $J_{PH} = 0.5$ Hz, 5H, Cp), 7.02 (m, 9H, *m*,*p*-Ph), 7.70 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 15.6 (CH), 19.5 (Me), 90.5 (Cp), 130.1 (*p*-Ph), 134.4 (d, $J_{PC} = 9$ Hz, *o*-Ph); the *m*-Ph resonance was covered by that of the solvent, the *ipso*-Ph resonance could not be distinguished unambiguously.

4.7. $CpRu(PPh_3)_2SH$ (7a) and CpRu(dppe)SH (7a)

$NaSSiPh_3Et_2O$ (1.10 g, 2.8 mmol) was added at once to a filtered solution of $[CpRu(PPh_3)_2(acetone)]BF_4$ in THF–acetone (wet). The reaction mixture became red–orange instantly as expected for $CpRu(PPh_3)_2SSiPh_3$. However, it gradually changed color to yellow upon stirring overnight at r.t. The precipitateous solution was filtered through Celite and concentrated. Complex **7a** spontaneously separated as a yellow microcrystalline solid during this process. Yield: 1.90 g (2.62 mmol, 95%). This compound has been described [15]. ^{1}H-NMR (C_6D_6): δ -3.12 (t, $J_{PH} = 6$ Hz, 1H, SH), 4.28 (s, 5H, Cp), 6.94 (m, 18H, *m*,*p*-Ph), 7.57 (m, 12H, *o*-Ph).

Complex **7b** was obtained in benzene-d_6 solution by heating an equimolar mixture of **7a** (40 mg, 0.07 mmol) and dppe. ^{1}H-NMR (C_6D_6): δ −4.22 (t, $J_{PH} = 8$ Hz, 1H, SH), 1.96, 2.71 (both m, 2H, CH_2), 4.68 (s, 5H, Cp), 6.96, 7.15 (both m, 8H, Ph), 7.78 (m, 4H, Ph).

4.8. $CpRu(PPh_3)(L)SS(O)OSi^iPr_3$ (L = CO (8b), PMe_3 (8c), $P(OMe)_3$ (8d) and $CpRu(dppe)SS(O)OSi^iPr_3$ (8e))

Complexes **6b**–**d** (0.034 mmol) in 0.7 ml of benzene-d_6 in an NMR sample tube were treated with one equivalent of SO_2 at r.t. by means of a gas-tight Hamilton syringe. The gas was added in two to three portions and the reactions were closely monitored by NMR spectroscopy. Each portion of SO_2 reacted instantly and completely with concomitant proportional consumption of the starting complexes. The reaction mixtures changed color from yellow to dark yellow or brown. In each case, two diastereomers of the single products **8b**–**d** were identified. Complex **8b** slowly decomposed to various unidentified species. The reaction mixtures containing **8c** and **8d** changed color to green upon standing either at r.t. or at −30°C. The NMR spectra of the green solutions indicated extensive decomposition of the reaction products and formation of Ph_3PS as the only identifiable decomposition product.

Complex **8b**: IR (CH_2Cl_2): ν_{SO} 1110, ν_{CO} 1960 cm^{-1}. Diastereomer (65%): ^{1}H-NMR (C_6D_6): δ 1.22 (m, 21H, ^{i}Pr), 4.79 (s, 5H, Cp), 7.00 (m, 9H, *m*,*p*-Ph), 7.50 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 12.6 (CH), 17.8 (Me), 87.5 (Cp), 128.3 (d, $J_{PC} = 10$ Hz, *m*-Ph), 130.3 (*p*-Ph), 133.5 (d, $J_{PC} = 11$ Hz, *o*-Ph), 135.0 (d, $J_{PC} = 49$ Hz, *ipso*-Ph); the CO resonance could not be distinguished. Diastereomer (35%): ^{1}H-NMR (C_6D_6): δ 1.22 (m, 21H, ^{i}Pr), 4.88 (br s, 5H, Cp), 7.00 (m, 9H, *m*,*p*-Ph), 7.50 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 12.8 (CH), 17.9 (Me), 86.5 (Cp), 128.3 (d, $J_{PC} = 10$ Hz, *m*-Ph), 130.3 (*p*-Ph), 133.5 (d, $J_{PC} = 11$ Hz, *o*-Ph), 135.1 (d, $J_{PC} = 50$ Hz, *ipso*-Ph); no CO resonance could be observed.

Complex **8c**: Diastereomer (58%); ^{1}H-NMR (C_6D_6): δ 1.10 (dd, $J_{PH} = 7$ Hz, $J_{PH} = 1$ Hz, 9H, PMe), 1.29 (m, 21H, ^{i}Pr), 4.75 (d, $J_{PH} = 1$ Hz, 5H, Cp), 7.02 (m, 9H, *m*,*p*-Ph), 7.59 (m, 6H, *o*-Ph). Diastereomer (42%); ^{1}H-NMR (C_6D_6): δ 1.14 (dd, $J_{PH} = 7$ Hz, $J_{PH} = 1$ Hz, 9H,

Table 3
Crystallographic data and structure refinement for complex **6a**

	6a
Empirical formula	$C_{50}H_{56}P_2RuSSi$
Formula weight	880.11
Temperature (K)	293 (2)
Radiation, λ (Å)	Mo–K_α, 0.70930
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.642 (6)
b (Å)	11.068 (8)
c (Å)	21.994 (10)
α (°)	79.27 (5)
β (°)	89.22 (5)
γ (°)	62.32 (4)
V (Å^3)	2246 (2)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.301
μ (mm^{-1})	0.514
$F(000)$	920
Crystal size (mm)	$0.38 \times 0.25 \times 0.08$
Transmission range	0.90–1.00
Reflections collected	9106
Independent reflections (R_{int})	8823 (0.042)
Goodness-of-fit on F^2	1.053
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0750$, $wR_2 = 0.1452$ [a]
R indices (all data)	$R_1 = 0.1519$, $wR_2 = 0.1677$ [a]

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$.

PMe), 1.29 (m, 21H, ^{i}Pr), 4.58 (d, $J_{PH} = 1$ Hz, 5H, Cp), 7.02 (m, 9H, *m*,*p*-Ph), 7.59 (m, 6H, *o*-Ph).

Complex **8d**: Diastereomer (50%): ^{1}H-NMR (C_6D_6): δ 1.26 (m, 21H, ^{i}Pr), 3.24 (d, $J_{PH} = 11$ Hz, 9H, POMe), 4.93 (d, $J_{PH} = 1$ Hz, 5H, Cp), 7.04 (m, 9H, *m*,*p*-Ph), 7.73 (m, 6H, *o*-Ph). ^{13}C{^{1}H}-NMR (C_6D_6): δ 13.0 (CH), 18.1 (Me), 51.9 (d, $J_{PC} = 7$ Hz, POMe), 82.8 (Cp), 134.4 (d, $J_{PC} = 10$ Hz, *o*-Ph); the missing carbon resonances could not be distinguished unambiguously. Diastereomer (50%): ^{1}H-NMR (C_6D_6): δ 1.26 (m, 21H, ^{i}Pr), 3.28 (d, $J_{PH} = 11$ Hz, 9H, POMe), 4.92 (d, $J_{PH} = 1$ Hz, 5H, Cp), 7.04 (m, 9H, *m*,*p*-Ph), 7.73 (m, 6H, *o*-Ph). ^{13}C{^{1}H}-NMR (C_6D_6): δ 13.0 (CH), 18.1 (Me), 52.0 (d, $J_{PC} = 8$ Hz, POMe), 82.3 (Cp), 134.3 (d, $J_{PC} = 11$ Hz, *o*-Ph); the missing carbon resonances could not be distinguished unambiguously.

As described above, complex **6e** (50 mg, 0.066 mmol) and 1.6 ml of SO_2 gave **8e** in quantitative yield, which readily decomposed to give a green solution. ^{1}H-NMR (C_6D_6): δ 1.21 (m, 21H, ^{i}Pr), 1.65–2.6 (complex m, 4H, CH_2P), 4.87 (s, 5H, Cp), 6.9–7.8 (complex m, 20H, PPh).

4.9. Reactions of complexes *7a*,*b* with N-thionylaniline

To a solution of complex **7a** (30 mg, 0.05 mmol) in 0.7 ml of benzene-d_6, *N*-thionylaniline (6 μl, ≈ 0.05 mmol) was injected in two portions. The starting yellow solution became brown and formation of complex **9a** was established by NMR spectroscopy. However, the solution changed color to green and decomposition of the product started in < 1 h at r.t. The decomposition process was complete overnight even at -30°C. ^{1}H-NMR (C_6D_6): δ 4.63 (br s, 5H, Cp), 6.95 (m, 18H, *m*,*p*-Ph), 7.42 (m, 12H, *o*-Ph); the –NHPh resonances were partially hidden under those of PPh_3.

4.10. Reaction of cis-$(PPh_3)_2Pt(SH)_2$ (*1*) with N-thionylaniline

A solution of complex **1** (25 mg, 0.032 mmol) in 0.6 ml of CD_2Cl_2 was treated with *N*-thionylaniline (4 μl, 0.035 mmol). The reaction was monitored by NMR spectroscopy at r.t. Formation of $(PPh_3)_2PtS_3O$ started in 1 h and a complete reaction took place overnight. This compound was obtained in 90% yield, accompanied by small amounts of Ph_3PS and Ph_3PO side-products, which formed in an approximately 3:1 ratio. Small amounts of a white precipitate also appeared in the reaction mixture, accountable for the missing platinum. Similar observations were made during the reaction of complex **1** with SO_2 under similar conditions [1a].

4.11. Reactions of complex *6a* with N-thionylaniline

Complex **6a** (30 mg, 0.034 mmol) in 0.7 ml of benzene-d_6 was treated with *N*-thionylaniline (4 μl, 0.035 mmol) and the reaction was monitored by ^{1}H-NMR spectroscopy at r.t. The reaction solution changed color upon mixing from orange to red and about 17% of the starting material was consumed to give a 1:1 mixture of complex **6g** and free PPh_3. Addition of two and four equivalents of *N*-thionylaniline resulted in a deeper red color and 23 and 38% conversions, respectively. Extensive decomposition of the reaction mixture occurred in 3 days at r.t.

4.12. Crystal-structure determination of complex *6a*

Large red–orange crystals of complex **6a** were obtained from a concentrated acetone-d_6 solution at room temperature. Intensity data were collected on a Rigaku AFC6S diffractometer. Data collection and structure solution parameters are listed in Table 3.

Data were collected on three different crystals. The first two were twinned and although the structure was solved, the R factors were unacceptable at 15%. The third crystal was thinner and showed no obvious sign of twinning, although the faces were still not perfectly defined. The measured intensities were weak as reflected by $R(\sigma)$ of 13.9%. Data were corrected for absorption using psi-scans (transmission range 0.90–1.00). The structure was solved by direct methods using SHELXS-96 and difmap synthesis using SHELXL-96 [24]. All non-hydrogen atoms were refined anisotropically, while the

hydrogen atoms were calculated at idealized positions using a riding model with C–H distances depending on the type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to a value 50% higher than U_{eq} of the parent carbon atom for methyl hydrogens and 20% higher for others. The crystal structure of **6a** is shown in Fig. 1. Selected bond distances and angles are listed in the figure captions.

5. Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 134376. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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