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Possible Cooperative Bonding between the Ru-Bonded and the S-Bonded SO_2 Groups in $CpRu(PPh_3)(SO_2)(S(SO_2)\text{-}4\text{-}C_6H_4Me)$

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The complexes $CpRu(PPh_3)_2SR$, where R = 4-C_6H_4Me, 1-C_3H_7, and $CHMe_2$, react with SO_2 to give two types of products; one, $CpRu(PPh_3)_2(S(SO_2)R)$, possesses a labile S-bonded SO_2 group, and the other type, $CpRu(PPh_3)(SO_2)(S(SO_2)R)$, possesses both S-bonded and Ru-bonded SO_2 groups neither of which are labile. The structure of $CpRu(PPh_3)(SO_2)(S(SO_2)\text{-}4\text{-}C_6H_5Me)$ was determined: $P2_1/C$, $a = 9.954$ (2) Å, $b = 18.423$ (5) Å, $c = 16.111$ (4) Å, $\beta = 95.13$ (2)°, $V = 2942.6$ Å^3, and $Z = 4$. During the initial stages of the reaction, complexes with two SO_2 groups are favored at low SO_2 concentrations, while those with only S-bonded SO_2 are favored at high concentrations. This observation and the differences in the relative ease of SO_2 loss between the two types of complexes is discussed in terms of cooperativity between the two SO_2 groups. This leads to reduced lability of the S-bonded SO_2 group when the complex contains a Ru-bonded SO_2 ligand (or a CO ligand).

Introduction

Interest in the transition metal chemistry of sulfur oxides in general, and SO_2 in particular, remains high. Environmental concerns about SO_2 in the atmosphere spurs studies into potential fixing reactions.[2] The SO_2 molecule shows a broad and diverse range of reactivity and types of bonding with complexes[3] that illustrates many fundamental concepts. The molecule can enter the coordination sphere as a ligand much like CO. It can also form Lewis acid adducts with a free lone pair of a coordinated ligand atom such as iodide. The insertion reactions[4] of SO_2 into metal–carbon bonds have been well studied.

As part of a research program on complexes containing catenated polysulfur and polysulfur oxide ligands, we have prepared complexes of the type $CpRu(PPh_3)(CO)E$, where E = S_xR,[5] where x = 1–3, and E = $SS(O)_nR$,[6] where n = 1 and 2. The parent complexes $CpRu(PPh_3)_2SR$[5a] are activated with respect to loss of PPh_3, easily forming $CpRu(PPh_3)(CO)(SR)$ or, in the absence of additional ligands, trimers[7] of the type $[CpRuSR]_3$. In the presence of CS_2, insertion[5a] into the Ru–S bond occurs to give the thioxanthates $CpRu(PPh_3)(S_2CSR)$. Thus, the complexes $CpRu(PPh_3)_2SR$ are excellent candidates for reaction with SO_2 via substitution of PPh_3. Moreover, Kubas[8] has shown that certain transition metal thiolates form labile adducts with SO_2 at the sulfur atoms. We have observed labile adduct formation[9] at the sulfur atom of $CpW(CO)_2(PPh_3)SR$. Finally, there are reports[10] of SO_2 insertion into metal–nitrogen and metal–oxygen bonds which raise the interesting possibility of insertion into M–SR bonds. We report here the rich chemistry[11] of the thiolato complexes $CpRu(PPh_3)_2SR$ with SO_2 which has resulted in the isolation and structural characterization of $CpRu(PPh_3)(SO_2)(S(SO_2)$-4-

Table I. Crystallographic Data for $CpRu(PPh_3)(SO_2)(S(SO_2)\text{-}4\text{-}C_6H_4Me)$ (**2a**)

chem formula $C_{30}H_{27}O_4PRuS_3$	fw = 676.73
$a = 9.954$ (2) Å	space group: $P2_1/c$
$b = 18.423$ (5) Å	$T = 20 \pm 1$ °C
$c = 16.111$ (4) Å	$\lambda = 1.54056$ Å
$\beta = 95.13$ (2)°	$\rho_{calcd} = 1.528$ g cm^{-3}
$V = 2942.6$ (12) Å^3	μ(Cu Kα) = 7.18 mm^{-1}
$Z = 4$	$R^a = 0.062$, $R_w{}^b = 0.057$

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

Table II. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $CpRu(PPh_3)(SO_2(S(SO_2)\text{-}4\text{-}C_6H_4Me)$

	x	y	z	$B_{iso}{}^a$
Ru	0.06569 (7)	0.35464 (4)	0.63700 (5)	2.57 (3)
S(1)	0.11166 (25)	0.22874 (14)	0.62128 (17)	3.32 (12)
S(2)	0.0982 (3)	0.38191 (15)	0.51244 (17)	3.34 (12)
S(3)	0.0482 (5)	0.15372 (23)	0.76701 (24)	7.15 (23)
P	0.29254 (24)	0.37175 (14)	0.68744 (16)	2.72 (11)
O(1)	0.2128 (7)	0.3705 (5)	0.4692 (4)	6.7 (5)
O(2)	−0.0077 (8)	0.4202 (4)	0.4603 (5)	5.5 (4)
O(3)	0.1218 (15)	0.0903 (7)	0.7496 (8)	14.4 (11)
O(4)	−0.0832 (12)	0.1437 (10)	0.7543 (9)	19.7 (13)
C(1)	0.5067 (10)	0.4628 (6)	0.6529 (7)	4.4 (6)
C(2)	0.5616 (12)	0.5262 (7)	0.6286 (9)	5.8 (7)
C(3)	0.4816 (12)	0.5843 (6)	0.6044 (7)	4.7 (6)
C(4)	0.3461 (12)	0.5770 (6)	0.6023 (7)	5.0 (6)
C(5)	0.2885 (10)	0.5134 (6)	0.6247 (7)	3.9 (5)
C(6)	0.3673 (9)	0.4551 (5)	0.6502 (6)	2.9 (4)
C(7)	0.3470 (10)	0.4489 (6)	0.8371 (7)	3.9 (5)
C(8)	0.3490 (12)	0.4568 (8)	0.9235 (8)	5.8 (8)
C(9)	0.3157 (14)	0.4011 (10)	0.9730 (8)	6.2 (9)
C(10)	0.2771 (12)	0.3365 (8)	0.9367 (8)	5.7 (8)
C(11)	0.2717 (10)	0.3270 (6)	0.8508 (7)	4.1 (6)
C(12)	0.3049 (9)	0.3839 (6)	0.7998 (6)	3.2 (5)
C(13)	0.4461 (10)	0.2914 (7)	0.5855 (7)	4.5 (6)
C(14)	0.5378 (13)	0.2412 (8)	0.5655 (8)	6.2 (7)
C(15)	0.6041 (12)	0.1958 (7)	0.6290 (10)	5.4 (7)
C(16)	0.5736 (13)	0.2067 (7)	0.7088 (9)	6.7 (8)
C(17)	0.4835 (13)	0.2600 (7)	0.7304 (7)	5.4 (6)
C(18)	0.4147 (9)	0.3008 (5)	0.6670 (7)	3.2 (5)
C(19)	−0.0052 (10)	0.4257 (7)	0.7326 (7)	4.5 (6)
C(20)	−0.0277 (10)	0.3548 (7)	0.7543 (7)	3.9 (6)
C(21)	−0.1217 (11)	0.3255 (7)	0.6952 (7)	4.5 (6)
C(22)	−0.1546 (10)	0.3824 (8)	0.6315 (8)	5.5 (7)
C(23)	−0.0803 (11)	0.4425 (6)	0.6572 (8)	4.5 (6)
C(24)	−0.0207 (11)	0.1137 (6)	0.5488 (8)	4.2 (6)
C(25)	−0.1098 (13)	0.0773 (6)	0.4928 (8)	5.0 (7)
C(26)	−0.1979 (12)	0.1161 (7)	0.4343 (8)	4.5 (6)
C(27)	−0.1913 (10)	0.1908 (7)	0.4375 (7)	4.2 (6)
C(28)	−0.1041 (11)	0.2282 (6)	0.4941 (7)	3.8 (5)
C(29)	−0.0147 (10)	0.1872 (6)	0.5509 (6)	3.2 (5)
C(30)	−0.2966 (12)	0.0767 (7)	0.3663 (7)	5.3 (3)

$^a B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

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Table III. ^{1}H NMR Data for $CpRu(PPh_3)(SO_2)(S(SO_2)R)$ (**2a–c**) and $CpRu(PPh_3)_2(S(SO_2)R)$ (**3a–c**)[a,b]

complex	C_5H_5	CH_3	C_6H_4	$CHMe_2$	$\mathit{CH_2}CH_2CH_3$	$CH_2\mathit{CH_2}CH_3$
2a, R = $4\text{-}C_6H_4Me$	5.01	2.09	6.94[c]			
2b, R = $1\text{-}C_3H_7$	4.94	0.80[d]			2.33[e] 2.46[e]	1.50[f]
2c, R = $CHMe_2$	5.06	1.32[g] 1.26[g]		2.85[h]		
3a	4.48	2.13[i]				
3b	4.60	0.70[j]			2.20[f]	1.50[f]
3c[k]	4.77	1.51[l] 1.48[m]		2.83[h]		

[a] In C_6D_6, under SO_2(g), reported in ppm. [b] Phenyl resonances of PPh_3 appeared in the range 6.82–7.82 ppm. [c] Doublet, relative intensity = 1, *J*(H–H) = 8.4 Hz; the other doublet not observed due to overlap of other peaks. [d] Triplet, *J*(H–H) = 7.4 Hz. [e] Multiplet, relative intensity = 1. [f] Multiplet. [g] Doublet, *J*(H–H) = 6.7 Hz. [h] Septet. [i] Not observed due to overlap of other peaks. [j] Triplet, *J*(H–H) = 7.2 Hz. [k] Excess PPh_3 present. [l] Doublet, *J*(H–H) = 6.0 Hz. [m] Doublet, *J*(H–H) = 8.4 Hz.

C_6H_4Me), a molecule with apparent cooperative bonding between the Ru-bonded and the S-bonded SO_2 groups.

Results

Treatment of a concentrated THF solution of $CpRu(PPh_3)_2S\text{-}4\text{-}C_6H_4Me$ (**1a**) with SO_2, pouring the solution into SO_2-saturated ether, and filtering gave a red solution from which $CpRu(PPh_3)(SO_2)(S(SO_2)\text{-}4\text{-}C_6H_4Me)$ (**2a**) was obtained. Elemental analysis was consistent with the formulation above, and the infrared spectrum displayed bands[12] attributed to SO stretching modes at 1283 and 1258 cm^{-1}. The structure is depicted in Figure 1; the crystal data and atomic coordinates appear in Tables I and II, respectively.

The structure is a piano stool with two SO_2 groups. One, a ligand, is bonded to the ruthenium atom which is coplanar with the plane formed by the sulfur and the two oxygen atoms (the ruthenium atom lies 0.053 Å above the plane). The Ru–S(2) bond distance is 2.121 (3) Å, close to the range observed for similar complexes[3a] but a little shorter than that observed for $[Ru(NH_3)_4(SO_2)Cl]^+$[13] (Ru–S = 2.223 Å). The thiolato sulfur-to-ruthenium distance (Ru–S(1)) is normal[14] at 2.382 (3) Å. The Ru–P distance is 2.352 (3) Å, slightly longer than for analogous compounds.[5a,15]

The other SO_2 is bonded to the sulfur atom of the thiolato group. The thiolato sulfur atom (S(1)) lies well out of the plane formed by the sulfur atom S(3) and the two oxygen atoms (S(1) lies 2.719 (18) Å above the plane). Thus, the geometry about S(3) is strongly pyramidal. The $S\text{–}SO_2$ distance, 2.844 (5) Å, is much longer than that in $Cu(PPh_2Me)_3S(SO_2)Ph$ (2.530 Å),[8] which also contains a SO_2 group attached to a thiolato ligand, but is much shorter than the sum of the van der Waals radius (3.70 Å). The $X\cdots SO_2$ distances where X = O[16a] are close to that seen in **2a** ($Me_2O\cdot SO_2$, 2.87 Å; $H_2O\cdot SO_2$, 2.82 Å), while for X = N[16b,c] the distances are much shorter ($Me_3N\cdot SO_2$, 2.26 Å; $Me_2HN\cdot SO_2$, 2.34 Å; pyridine·SO_2, 2.61 Å; tetramethyl-*p*-phenylenediamine·$2SO_2$,[16c] 2.39 Å).

The central sulfur atom of the S-bonded SO_2 group in **2a** is much more pyramidal than that in the copper complex. The angle α between the S–S vector and the SO_2 plane is only 17° in **2a** while it is 35° in the copper adduct. In the adducts $Me_2O\cdot SO_2$ and $H_2O\cdot SO_2$ the values of α are 4 and 20°, respectively, while in the amine adducts α is in the range 9–22°. In comparison α is 89° for the Ru-bonded SO_2 ligand. Also of interest is the S(2)–Ru–S(1)–S(3) dihedral angle, which, at 171°, makes the Ru-bonded SO_2 group's plane nearly parallel to the S(1)–S(3) vector. Furthermore, the two SO_2 planes are mutually orthogonal (91°).

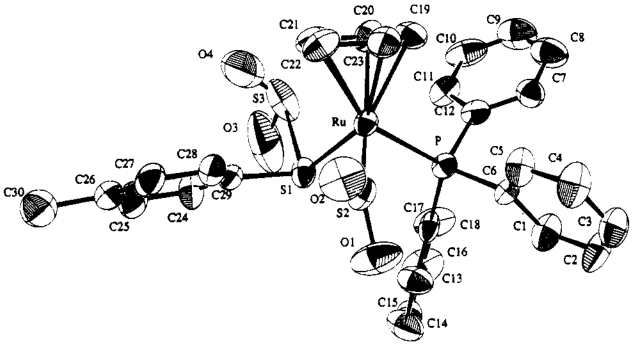
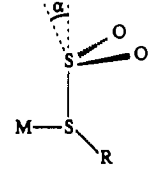


Figure 1. ORTEP drawing of $CpRu(PPh_3)(SO_2)(S(SO_2)\text{-}4\text{-}C_6H_4Me)$ (**2a**). Bond lengths (Å) and angles (deg) are as follows: S(1)–S(3), 2.844 (5); Ru–S(1), 2.382 (3); Ru–S(2), 2.121 (3); Ru–P, 2.352 (3); S(1)–C(29), 1.788 (10); S(3)–O(4), 1.319 (13); S(3)–O(3), 1.420 (14); S(2)–O(2), 1.469 (7); S(2)–O(1), 1.405 (8); S(1)–Ru–S(2), 94.76 (11); S(1)–Ru–P, 88.83 (9); S(2)–Ru–P, 94.14 (10); O(1)–S(2)–O(2), 111.2 (5); Ru–S(2)–O(1), 129.3 (3); Ru–S(2)–O(2), 119.5 (3); O(3)–S(3)–O(4), 112.1 (9); S(1)–S(3)–O(3), 94.6 (6); S(1)–S(3)–O(4), 103.3 (9); Ru–S(1)–S(3), 109.05 (13); Ru–S(1)–C(29), 110.7 (4); S(3)–S(1)–C(29), 96.9 (4).



In order to determine the events leading to **2a** the interactions of $CpRu(PPh_3)_2SR$ with SO_2 were monitored in C_6D_6 via ^{1}H NMR spectroscopy (5 mg of **1a–c** in 0.7 mL C_6D_6), where R = $4\text{-}C_6H_4Me$ (**1a**), $1\text{-}C_3H_7$ (**1b**), and $CHMe_2$ (**1c**). The results are consistent with Scheme I. In the case of **1a,b**, a rapid stream of SO_2 for 15 min led to their consumption and the appearance in the NMR spectra of Cp peaks corresponding to intermediates **3a,b** together with those corresponding to the final products **2a,b** and free PPh_3 in the appropriate integrated intensity. For **1c** only one Cp peak, assigned to the final product **2c**, was observed. Further bubbling of SO_2 led to more **2a,b** at the expense of peaks due to **3a,b**. Complete conversion of **1a** to **2a** required 4 h, while 15 min gave a final **2b**:**3b** ratio of 6. When excess PPh_3 was added to NMR samples of **1a** and **1c**, followed by treatment with SO_2 for 15 min, peaks due to **2a** and **2c** were not observed. In the case of **1a**, peaks due to a mixture of **1a** and **3a** were observed, while for **1c** only peaks due to **3c** were observed.

The NMR data for **2a–c** and **3a–c** are given in Table III. Diastereotopic methyl groups were observed for **3c**, suggesting

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(12) Four bands are expected, two from each SO_2 moiety;[3b] however, the bands in the neighborhood of 1100 cm^{-1} are obscured by those due to PPh_3.

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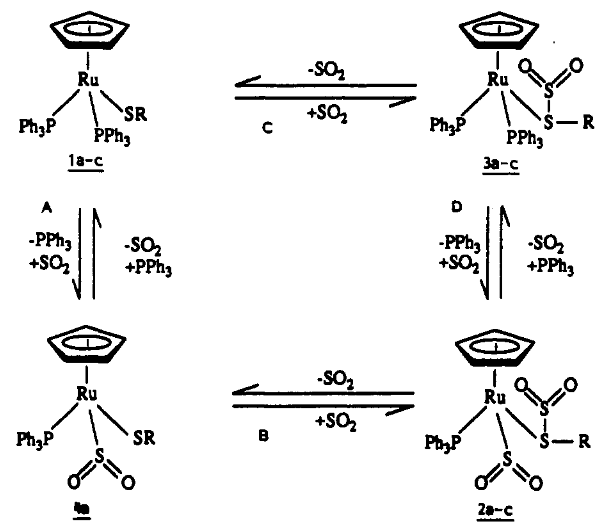
Scheme I



a, R = $4\text{-}C_6H_4Me$
b, R = $1\text{-}C_3H_7$
c, R = $CHMe_2$

that the rate of exchange of the SO_2 group is slow on the NMR time scale in contrast to the SO_2 adduct of $CpW(CO)_2(PPh_3)SCHMe_2$.[9] Similarly, diastereotopic methyl groups were observed for **2c**. On the other hand, no evidence for the presence of diastereomers of **2a–c** was detected despite the presence of two chiral sites. The Cp resonance of pure **2a** was invariant between room temperature and –65 °C. Characterization of the infrared ν(SO) bands of the complexes was not possible due to the presence of excess SO_2, which was always present except in the case of pure **2a**.

Treatment of a more concentrated solution of **1a** in C_6D_6 (10 mg in 0.7 mL) with SO_2 (10 min) gave an orange precipitate in a red solution. An NMR spectrum was taken of this slurry as formed, and equal amounts of **2a** and **3a** but no **1a** were detected in the red mother liquors. The slurry was rapidly evaporated to dryness under vacuum and the residue redissolved in C_6D_6 whereupon no **3a** was present but **1a** and **2a** were detected in equal amounts. When SO_2 was again passed through the solution, the precipitate formed again and only **2a** and **3a** in equal amounts were detected in the NMR spectrum. The re-formed slurry was filtered. The NMR spectrum of the orange precipitate revealed the presence of **3a** and **1a**, the latter presumably due to loss of SO_2 from **3a**. The red filtrate contained **2a**. The experiment indicates the facile interconversion of **1a** and **3a** and the relatively high stability of **2a** with respect to loss of SO_2.

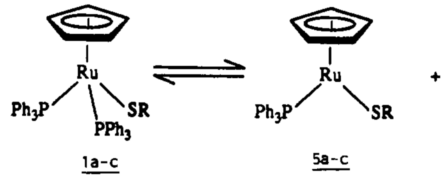
The reaction of **1a** with SO_2 was monitored as a function of time at high and at low concentrations of SO_2. At a high concentration of SO_2 (continuous rapid flow of SO_2 for 10 min), the NMR spectrum revealed only equal amounts of **2a** and **3a** after 10 min. After 1 h the ratio **2a**:**3a** was 9:1. On the other hand, at a low concentration of SO_2 (0.5 mL of SO_2(g) in 0.7 mL of C_6D_6) the reaction mixture consisted of only **1a** and **2a** in the ratio 1:6 after only 2 min. Addition of another 0.5 mL of SO_2(g) after 12 min gave enrichment of **2a** at the expense of **1a** without the presence of **3a**. The sample was purged with N_2 for 20 min whereupon **1a** and **2a** were detected in the NMR spectrum now in the ratio 3:2 (i.e. enriched in **1a**) with no sign of **3a**. The results suggests that significant concentrations of **3a** are possible only in presence of high concentrations of SO_2 and early in the reaction before much **1a** is converted to **2a**.

The facile loss of SO_2 from **3a–c** is consistent with the lability observed for all other thiolate-bonded SO_2 adducts observed[8,9] to date. Thus, the stability of **2a–c** is notable. During the determination of the melting point of **2a**, the crystals crumbled to powder at 125 °C and then melted at 138 °C with evolution of a pungent gas. Heating **2a** at 130 °C for 20 min gave a new complex, **4a**, which was characterized[17] by its NMR and infrared spectra. The presence of only one ν(SO) stretching band at 1261 cm^{-1} led to the tentative formulation[18] of **4a** as $CpRu(PPh_3)(SO_2)S\text{-}4\text{-}C_6H_4Me$.

The SO_2 ligand is similar to the CO group with respect to its σ-donor and strong π-acceptor abilities.[19] Thus, the CO complex $CpRu(PPh_3)(CO)SCHMe_2$ in C_6D_6 was treated with SO_2 to give a new adduct $CpRu(PPh_3)(CO)(S(SO_2)CHMe_2)$, as indicated by its NMR and infrared spectra.[20] The NMR sample was evaporated to dryness under vacuum and the residue redissolved in C_6D_6. The spectrum was unchanged, which suggests that the new adduct possesses the same high stability with respect to loss of SO_2 as do **2a–c**.

Discussion

The reactivity of **1a–c** is dominated[5a,7] by the influence of the thiolato ligand. The HOMO of such complexes[21] is thought to be high in sulfur-p character and to be antibonding due to π-donation by the thiolato ligand. The two relatively poor π-accepting and bulky PPh_3 groups appear unable to compensate for the buildup of electron density; steric acceleration may also contribute to greater reactivity. However, π-donation from the thiolato sulfur atom stabilizes the 16-electron intermediate[21,22] formed by loss of PPh_3. Thus, the lone pairs on the sulfur atom destabilize the ground state and stabilize the coordinatively unsaturated intermediate leading to an equilibrium between the two.



We have shown[5] that the presence of the strong π-accepting CO ligand stabilizes the complexes $CpRu(PPh_3)(CO)SR$ with respect to ligand loss. The results above suggest (1) that SO_2 can also stabilize the system and (2) that adduct formation between SO_2 and the thiolato sulfur atom greatly reduces the latter's influence.

The inhibitory effect of the presence of excess PPh_3 on the production of **2a** and **2c**, but not on **3a** and **3c**, is consistent with Scheme I. The SO_2 concentration dependence of the reaction is also understandable. For **1a**, SO_2 at low concentrations attacks the coordinatively unsaturated intermediate **5a** rapidly shifting the equilibrium and generating solely **2a**, presumably via **4a** (steps A and B in Scheme I). The spectra did not change beyond 2 min after addition of the first small aliquot of SO_2, and a further addition was required to produce more **2a**, **3a** never being detected. Thus, the product distribution is dependent on SO_2 concentration, as well as time, consistent with rapid attainment of equilibria which greatly favor **2a**. However, at high concentration, equilibrium C is also established, which produces **3a**. This depletes the concentration of **1a**, thus slowing the production of **2a** via steps A and B. The conversion of **3a** to **2a** (step D) is much slower than that of **1a**. This is due to the attack of the SO_2 on the thiolato sulfur atom's lone pair in **3a**. The resulting rehybridization would decrease the π-donation from this atom and concomitantly decrease the activation of **3a**. There would also be less stabilization

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(17) ^1H NMR (C_6D_6) for $CpRu(PPh_3)(SO_2)S\text{-}4\text{-}C_6H_4Me$: 7.63 (m, 6 H, PPh_3), 6.98 (m, 9 H, PPh_3), 7.26 and 6.59 (ABq, 4 H, J(H–H) = 8.3 Hz, $4\text{-}C_6H_4Me$), 4.66 (s, 5 H, C_5H_5), 1.89 (s, 3 H, $4\text{-}C_6H_4CH_3$).

(18) Thiolato-bonded SO_2 groups are easily removed;[8,9] therefore, the band at 1261 cm^{-1} is assigned to a Ru-bonded SO_2 group.

(19) Conway, P.; Garil, S. M.; Manning, A. R.; Stephens, F. S. *Inorg. Chem.* **1983**, *22*, 3714.

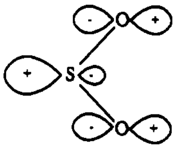
(20) Data for $CpRu(PPh_3)(CO)(S(SO_2)CHMe_2$ are as follows. ^1H NMR (C_6D_6): 7.61 (m, 6 H, PPh_3), 7.02 (m, 9 H, PPh_3), 4.86 (s, 5 H, C_5H_5), 2.87 (septet, 1 H, J(H–H) = 6.7 Hz, $CHMe_2$), 1.46 and 1.44 (dd, 6 H, $CH(CH_3)_2$). IR (Nujol) (SO): 1254 cm^{-1}. IR (C_6D_6) (CO): 1945 cm^{-1}.

(21) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191.

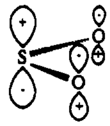
(22) (a) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730. (b) McCleverty, J. A.; Drane, A. S.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 91.

of the hypothetical 16-electron intermediate $CpRu(PPh_3)(S(SO_2)$-4-$C_6H_4Me)$ implied in step D.

The S–SO_2 bond distance in **2a** (2.844 (5) Å) is much longer than that in $Cu(PPh_2Me)_3(S(SO_2)Ph)$ (2.530 Å). The HOMO and LUMO of SO_2[3a] are shown as follows:



$8a_1$ (HOMO)



$3b_1$ (LUMO)

The Lewis acid character of an SO_2 adduct is inversely proportional to α defined above. At the extreme when α is 90°, as for the Ru-bonded SO_2 ligand, it acts as a Lewis base. At the other extreme, when α is 0°, the SO_2 group would be considered a Lewis acid. Consequently, the thiolate-bonded SO_2 in **2a** has higher Lewis acid character ($\alpha = 17°$) compared to that in $Cu(PPh_2Me)_3(S(SO_2)Ph)$ ($\alpha = 35°$). The $3b_1$ orbital is high in p character, while the $8a_1$ orbital is sp^2 hybridized. Therefore, a thiolate–SO_2 bond with a small α value would be high in p character and the S–SO_2 bond distance might be expected to be longer than a thiolate–SO_2 bond with a large α value. The interaction distances of SO_2 adducts have been shown[16] to be very sensitive to the relative basicities of the donor atoms.

Surprisingly, **2a** loses SO_2 much more reluctantly than the copper complex[8] despite the longer S–SO_2 bond distance of the former. Of interest is the possible effect of the Ru-bonded SO_2 ligand. In **2a** the Ru-bonded SO_2 ligand has its empty $3b_1$ π-orbital in the proper orientation to accept electron density from the metal. The SO_2 ligand is a strong π-acceptor,[19] and indeed if a different strong acceptor ligand is present as in $CpRu(PPh_3)(CO)(S(SO_2)CHMe_2)$ (**4a**), the complex is also unusually resistant to SO_2 dissociation. One might therefore postulate a cooperative interaction between the S-bonded and the Ru-bonded SO_2 groups, via the thiolato sulfur atom and the ruthenium atom.

The complexes **2a–c** have two chiral centers, one at the metal center assumed to be configurationally stable[23] and the other at S(1). Consequently there should be a pair diastereomers observable in their NMR spectra, but such was never the case. The observation of peaks due to the diastereomeric methyl groups of **2c** confirms the presence of at least one chiral site which is configurationally stable on the NMR time scale. This rules out rapid exchange of the S-bound and Ru-bound SO_2 groups, which would invert both centers and impose a time-averaged mirror plane on the molecule. One might postulate that rapid inversion occurs at S(1). However, $CpRu(PPh_3)_2(S(SO_2)CHMe_2)$ (**3c**), which possesses only the chiral site at the thiolato sulfur atom, also displayed diastereotopic methyl groups in the NMR spectrum. There is no compelling reason to assign to **2c** a lower inversion barrier at S(1) than to **3c**. It is also notable that the SO_2 adduct $CpRu(PPh_3)(CO)(S(SO_2)CHMe_2)$ also displayed only one set of peaks between room temperature and −65 °C and showed diastereotopic methyl groups. The tentative conclusion is that only one diastereomer is present. This may also be a reflection of the precise combination of electronic and steric factors leading to the enhanced stability of **2a–c**.

The complexes of Scheme I are models of hypothetical intermediates whereby SO_2 might "insert" into the Ru–SR bond to give a Ru–$S(O)_2SR$ moiety. Complexes containing a S-bonded SO_2 group model an insertion reaction wherein SO_2 first attacks the ligand to be followed by rearrangement, a process similar to that observed for insertion of SO_2 into a metal–carbon bond. The complexes containing a Ru-bound SO_2 group model an attack by SO_2 on the metal first, to be followed by migration of the ligand, a process analogous to carbonyl insertion into metal–carbon bonds. However, there was no evidence that any of the complexes reported here were precursors to insertion products.

Experimental Section

The general techniques used have been described in the literature.[5a] Tetrahydrofuran was refluxed over sodium/benzophenone and distilled under N_2 prior to use. The compound $RuCl_3{\cdot}3H_2O$ was kindly supplied by PGM Chemicals Ltd., New Germany, South Africa; SO_2, Linde, was used as received.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 or XL-300 spectrometer. All NMR samples were prepared under N_2 atmosphere using benzene-d_6, degassed by freeze–thaw degassing under vacuum. Chemical shifts are reported in ppm relative to tetramethylsilane, used as an internal standard. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Melting points were obtained on a Thomas Hoover capillary melting point apparatus in a sealed capillary tube under a nitrogen atmosphere and are uncorrected.

Cyclopentadienyl(triphenylphosphine)(4-methylbenzenethiolato)ruthenium(II) *Ru*,*S*-Bis(sulfur dioxide), $CpRu(PPh_3)(SO_2)(S(SO_2)$-4-$C_6H_4Me)$ (2a). A Schlenk tube was charged with **1a** (0.3710 g, 0.456 mmol) and THF (4 mL). Sulfur dioxide was bubbled through the solution for 1 h to give an orange precipitate in a red supernatant. The slurry was poured into 40 mL of diethyl ether which had been previously saturated with SO_2. The slurry was filtered under N_2 and the filtrate was left to stand under SO_2, whereupon deep red crystals slowly formed. The mother liquors were decanted and saved. The crystals were washed with hexanes (2 × 2 mL, at −78 °C) and briefly dried under vacuum. The mother liquors were cooled to −78 °C and, upon standing, gave a second crop of **2a** as crystallographic grade crystals, total yield = 34%. During the melting point determination the crystals lost their crystallinity at 125 °C and melted at 138 °C with evolution of SO_2, which was detected by its pungent smell when the melting point capillary was broken open. IR (Nujol): $\nu(SO)$ = 1283 (m), 1258 (m) cm^{-1}. ^1H NMR (C_6D_6): 7.87 (d, 2 H, $J(H$–$H)$ = 8.0 Hz, 4-$C_6H_4CH_3$), 7.65 (m, 6 H, PPh_3), 6.95 (m, 9 H, PPh_3), 6.88 (d, 2 H, 4-$C_6H_4CH_3$), 4.61 (s, 5 H, C_5H_5), 2.09 (s, 3 H, 4-$C_6H_4CH_3$). Anal. Calcd for $C_{30}H_{27}O_4PRuS_3$: C, 53.01; H, 4.00; S, 14.15. Found: C, 53.49; H, 3.70; S, 12.92.

X-ray Structure Determination. Table I contains the crystal parameters for **3a**. A thin rectangular red crystal (0.07 × 0.28 × 0.36 mm) was glued with epoxy to the inside of a thin-walled glass capillary which was sealed under N_2. All dimensions were obtained from 15 reflections with 2θ in the range 45.00–65.00°. A total of 4389 independent reflections having 2θ (Cu Kα) < 120.0° were collected ($-11 \le h \le 11$, $0 \le k \le 20$, $0 \le l \le 18$) using the $\theta/2\theta$ scan mode (merging R is 2.8%). A ψ correction was made for absorption.[24] The structure was solved by the Patterson method.[25] The resulting structural parameters were refined to convergence (R_w, based on counting statistics) for 3615 reflections for which $I > 3\sigma(I)$. An extinction correction was made. Anisotropic themal parameters for all non-hydrogen atoms were used except for C(30), which could not be refined anisotropically to give reasonable off-diagonal tensor elements. The large anisotropic thermal parameters observed for O(3) and O(4) are consistent with the large thermal motion observed in other SO_2 adducts.[16c] The S-bonded SO_2 group does not show the extreme structural distortions associated with disordered structures.[8] All hydrogen atoms, except those of C(30) were added in calculated positions with the mean isotropic thermal parameters of their carbon atoms.

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Supplementary Material Available: Listings of anisotropic temperature factors (Table IV), hydrogen atom coordinates and temperature factors (Table V), and bond length and angles (Table VI) (4 pages); a listing of observed and calculated structure factors for $CpRu(PPh_3)(SO_2)(S(SO_2)$-4-$C_6H_4Me)$ (Table VII) (22 pages). Ordering information is given on any current masthead page.

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(23) At least on the NMR time scale.

(24) The data, supplied by Crystalytics Co., Lincoln, NE, was collected on a computer-controlled four-circle Nicolet diffractometer. Atomic scattering factors were from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101.

(25) The solution and refinement was conducted using NRCVAX programs: Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.