New Aspects of Rhodium(III)–Dimethyl Sulfoxide Chemistry: Synthesis and Molecular Structure of $[NEt_4][cis\text{-}RhCl_4\{(CH_3)_2SO\}_2]$ and Chemical Behaviour in Aqueous Solution of $[RhCl_n\{(CH_3)_2SO\}_{6-n}]^{3-n}$ (n = 3 or 4) Complexes†

Enzo Alessio,* Andrea Sessanta o Santi, Paolo Faleschini, Mario Calligaris and Giovanni Mestroni
Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy

A careful reinvestigation of the synthesis of the long known complex $[H(dmso)_2][trans\text{-}RhCl_4(dmso\text{-}S)_2]$ **2a** has resulted in the isolation of the unprecedented *cis* isomer $[H(dmso)_2][cis\text{-}RhCl_4(dmso\text{-}S)_2]$ **2b**. The new isomer has been characterized spectroscopically and the crystal structure of the anion determined as the tetraethylammonium salt. Crystal data: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.500(4)$, $b = 17.054(3)$, $c = 13.304(5)$ Å, $\beta = 114.19(2)°$. As in the case of the neutral isomers, *mer,cis*- and *mer,trans*-$[RhCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$ **1a** and **1b**, respectively, the anionic *trans* derivative is thermodynamically unstable and isomerizes to the *cis* isomer in dmso solution with first order kinetics; the reverse *cis* to *trans* isomerization is promoted by visible light. A comparative investigation of the chemical behaviour of the two pairs of isomers **1** and **2** in aqueous solution, determined by ^1H and ^{13}C NMR spectroscopy, has also been carried out. In both cases dissociation of the ligand *trans* to an S-bonded dmso ligand is the first step.

Our interest in the chemistry of rhodium(III) chloride dimethyl sulfoxide (dmso) complexes of general formula $[RhCl_n(dmso)_{6-n}]^{3-n}$ (n = 3 or 4) derives mainly from their structural analogies with the corresponding Ru^{III} derivatives that we are using as precursors in the synthesis of antitumour-active compounds.[1–4] The crystal structure of $[trans,cis,cis\text{-}RhCl_2(dmso\text{-}S)_2(dmso\text{-}O)_2]BF_4$[5] and, more recently, the photochemical synthesis and crystal structure of a new isomer of the long known compound *mer,cis*-$[RhCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$ **1a**,[6,7] namely *mer,trans*-$[RhCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$ **1b** have already been described.[8] Since the thermodynamic instability of **1b** compared to **1a** was attributed to the electronic competition between the two *trans* S-bonded dmso ligands, we suggested that in the case of the well known anionic derivative *trans*-$[RhCl_4(dmso\text{-}S)_2]^-$,[9] a *cis* isomer of greater or comparable stability might also exist. Several crystal structures of the *trans*-$[RhCl_4(dmso\text{-}S)_2]^-$ anion with different cations have been determined,[10–13] but the presence of a *cis* isomer has only been reported in solution, based upon NMR evidence.[14] The synthesis of a similar *cis* isomer has been described for iridium(III), where a complex of formula $[H(dmso)_2][cis\text{-}IrCl_4(dmso\text{-}S)_2]$ was proposed upon spectroscopic evidence.[15,16] However, only the *trans* isomer, $[H(dmso)_2][trans\text{-}IrCl_4(dmso\text{-}S)_2]$, has been structurally characterized.[17]

In this paper we have carefully reinvestigated the synthesis of $[H(dmso)_2][trans\text{-}RhCl_4(dmso\text{-}S)_2]$ **2a**. This has led to the isolation of the *cis* isomer, $[H(dmso)_2][cis\text{-}RhCl_4(dmso\text{-}S)_2]$ **2b**, which was structurally characterized as the tetraethylammonium derivative $[NEt_4][cis\text{-}RhCl_4(dmso\text{-}S)_2]$ **2b′**.

We also present a detailed ^1H NMR investigation of the chemical behaviour of complexes **1** and **2** in aqueous solution. This was undertaken not only because water is a common solvent for these complexes and their behaviour in this medium would give useful information about their reactivity, but also for comparison with the corresponding isostructural ruthenium(III) complexes. The investigation of the chemical behaviour of Ru^{III} derivatives in solution is, in fact, relatively more difficult, as the paramagnetism of the metal atom does not allow extensive use of NMR spectroscopy. Studies concerning antitumour-active ruthenium(III) complexes in aqueous solution, particularly with regard to their interactions with biologically relevant molecules, might benefit greatly from the results obtained for isostructural diamagnetic rhodium(III) models.

Results and Discussion

The compound $[H(dmso)_2][trans\text{-}RhCl_4(dmso\text{-}S)_2]$ **2a** was synthesized by the reaction of hydrated $RhCl_3$ with concentrated warm HCl (70 °C), followed by addition of dmso to the cooled solution.[9] The D_2O ^1H NMR spectrum of the crude complex was often contaminated by a minor peak in the region of the *S*-bonded dmso (δ 3.48), the intensity of which varied slightly from preparation to preparation. This resonance does not correspond to any known species and might be attributed to a complex bearing one or more equivalent dmso-*S* ligands with magnetically equivalent methyl groups. The symmetry requirements for such species to give a single NMR resonance obviously increase with increasing number of co-ordinated dmso-*S* molecules. The new complex **2b** was first isolated by us as an almost pure compound from the mother-liquor in the synthesis of **1a**,[7] after removal of most of the solvent and addition of small amounts of dmso and acetone. Later we found that **2b** was the major product of the reaction between hydrated $RhCl_3$, concentrated HCl and dmso at temperatures higher than those used in the synthesis of **2a**, *i.e.* under similar conditions to those adopted for the synthesis of the ruthenium analogue $[H(dmso)_2][trans\text{-}RuCl_4(dmso\text{-}S)_2]$.[1] Also recrystallization of **2a** from warm dmso yielded **2b** in high yield upon addition of acetone.

Complex **2b** analysed quite well for $[H(dmso)_2][RhCl_4\text{-}$

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

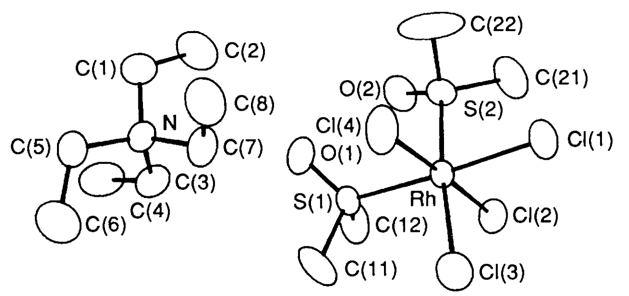


Fig. 1 An ORTEP drawing of $[NEt_4][cis\text{-}RhCl_4(dmso\text{-}S)_2]$ **2b′** with the atom labelling scheme

Table 1 Positional parameters and estimated standard deviations for complex **2b′**

Atom	*x*	*y*	*z*
Rh	0.988 33(3)	0.124 22(2)	0.250 66(2)
Cl(1)	0.903 8(1)	0.086 34(8)	0.383 08(8)
Cl(2)	0.817 4(1)	0.048 32(8)	0.115 33(9)
Cl(3)	0.829 9(1)	0.230 44(8)	0.202 7(1)
Cl(4)	1.157 7(1)	0.203 11(8)	0.380 83(9)
S(1)	1.085 2(1)	0.164 89(6)	0.132 11(7)
S(2)	1.121 2(1)	0.015 02(6)	0.295 01(8)
O(1)	1.237 9(3)	0.165 4(3)	0.178 3(3)
O(2)	1.184 1(3)	−0.007 6(2)	0.219 4(3)
C(11)	1.028 6(6)	0.260 1(3)	0.083 5(4)
C(12)	1.027 3(6)	0.111 9(3)	0.007 2(4)
C(21)	1.030 5(7)	−0.067 3(3)	0.309 9(5)
C(22)	1.252 4(9)	0.019 3(5)	0.430 7(6)
N	1.494 5(3)	0.355 8(2)	0.310 8(3)
C(1)	1.611 3(5)	0.298 2(3)	0.368 9(4)
C(2)	1.568 1(7)	0.213 1(4)	0.359 2(5)
C(3)	1.419 8(5)	0.337 1(3)	0.190 1(4)
C(4)	1.510 7(6)	0.340 1(4)	0.126 4(4)
C(5)	1.561 8(5)	0.436 0(3)	0.328 2(4)
C(6)	1.468 1(7)	0.503 4(3)	0.269 8(4)
C(7)	1.384 3(5)	0.352 8(3)	0.357 8(4)
C(8)	1.434 7(6)	0.369 6(4)	0.477 6(4)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2b′**

Rh–Cl(1)	2.364(1)	S(1)–O(1)	1.463(3)
Rh–Cl(2)	2.343(1)	S(1)–C(11)	1.759(5)
Rh–Cl(3)	2.363(1)	S(1)–C(12)	1.766(5)
Rh–Cl(4)	2.334(1)	S(2)–O(2)	1.464(4)
Rh–S(1)	2.306(1)	S(2)–C(21)	1.752(6)
Rh–S(2)	2.256(1)	S(2)–C(22)	1.768(7)
Cl(1)–Rh–Cl(2)	91.06(4)	S(1)–Rh–S(2)	91.63(4)
Cl(1)–Rh–Cl(3)	88.47(5)	Rh–S(1)–O(1)	115.4(2)
Cl(1)–Rh–Cl(4)	90.52(4)	Rh–S(1)–C(11)	110.6(2)
Cl(1)–Rh–S(1)	175.74(3)	Rh–S(1)–C(12)	114.3(2)
Cl(1)–Rh–S(2)	87.72(5)	O(1)–S(1)–C(11)	107.2(3)
Cl(2)–Rh–Cl(3)	89.03(4)	O(1)–S(1)–C(12)	107.1(3)
Cl(2)–Rh–Cl(4)	178.01(5)	C(11)–S(1)–C(12)	101.1(2)
Cl(2)–Rh–S(1)	93.11(4)	Rh–S(2)–O(2)	116.3(1)
Cl(2)–Rh–S(2)	86.67(4)	Rh–S(2)–C(21)	112.6(2)
Cl(3)–Rh–Cl(4)	89.80(5)	Rh–S(2)–C(22)	111.9(3)
Cl(3)–Rh–S(1)	92.48(5)	O(2)–S(2)–C(21)	106.6(3)
Cl(3)–Rh–S(2)	174.20(5)	O(2)–S(2)–C(22)	109.3(3)
Cl(4)–Rh–S(1)	85.33(4)	C(21)–S(2)–C(22)	98.6(4)
Cl(4)–Rh–S(2)	94.61(4)		

$(dmso)_2]$ and was apparently a pure compound, being composed of very thin needle-shaped light orange crystals. The solid state IR spectrum confirmed the presence of exclusively S-bonded dmso (ν_{S-O} at 1155, ν_{Rh-S} at 425 cm^{-1}) and of the $[H(dmso)_2]^+$ cation, as clearly indicated by the characteristic broad O•••H•••O stretching band centred around 700 cm^{-1}.[11] The NMR spectrum of the complex in D_2O, however, always showed the presence of variable amounts of **2a** (peak at δ 3.58, see below), ranging from 5 to 15% depending on the preparation. From integration, after subtraction of the contributions of **2a**, a ratio of free to S-bonded dmso of 1 : 1 resulted for **2b**. Combined IR and NMR evidence strongly suggested the presence of the isomer $[H(dmso)_2][cis\text{-}RhCl_4(dmso\text{-}S)_2]$. Several attempts to recrystallize the product in order to obtain crystals of **2b** suitable for X-ray analysis were unsuccessful, usually yielding a mixture of already known compounds, such as **1a** and $[Hdmso][trans\text{-}RhCl_4(dmso\text{-}S)_2]$ (which differs from **2a** only in the nature of the cation),* together with crystals of **2b** always contaminated by **2a**. The two isomers **2a** and **2b** can apparently cocrystallize in variable ratios without noticeably affecting the shape of the crystals.

Crystals of the pure *cis* isomer were eventually obtained upon substitution of $[H(dmso)_2]^+$ for the tetraethylammonium cation, by abstraction of the anion from an aqueous solution of **2b** into CH_2Cl_2 with NEt_4Cl. The crystal structure of $[NEt_4][cis\text{-}RhCl_4(dmso\text{-}S)_2]$ **2b′** is shown in Fig. 1. The positional parameters are listed in Table 1 and selected bond lengths and angles are given in Table 2. The Rh–S distances in **2b′** [2.256(1) and 2.306(1) Å] are significantly different and are both close to the limiting values of the range 2.254(7)–2.290(2) Å found for Rh^{III}-S distances *trans* to Cl.[6,21–24] Their average value of 2.279(8) Å is considerably shorter than that of 2.323(3) Å for mutually *trans* Rh–S bonds.[8,13,21] Significant differences between the M–S bond lengths of two *cis*-dmso-*S* ligands, even though less pronounced than in **2b′** have already been found in Ru^{II} derivatives.[25,26]

In agreement with previous suggestions that dmso-*S* behaves essentially as a pure σ donor towards Rh^{III},[8] the lengthening of the Rh–S bond distance in the *trans* isomers can be ascribed to the higher σ-*trans* influence of S compared to Cl. It is notable that for the Rh^{III} derivatives a Rh–S bond lengthening of 0.052 Å is observed from *cis* to *trans* dmso-*S* isomers, while a more marked lengthening (0.073 Å) is found for isoelectronic Ru^{II}–dmso-*S* complexes. In the case of ruthenium, the difference in the Ru–S bond distances between *cis* and *trans* geometries is enhanced by the π back-bonding contribution. Accordingly, the average value for the S–O bond length of 1.477(2) Å in *cis*-$[Ru^{II}Cl_2(dmso\text{-}S)_2]$ compounds is slightly greater than that of 1.466(2) Å in similar Rh^{III} moieties, in agreement with a significant π back-bonding contribution that weakens the S–O bond in Ru^{II} compounds.

As was already apparent from the synthesis of **2b**, and as we had expected from the nature of the Rh–S bond, the *trans* derivative is thermodynamically less stable than the *cis* isomer in dmso solution and isomerizes with first order kinetics. The thermal isomerization has been followed spectrophotometrically (Fig. 2) and a clean isosbestic point at 512 nm is maintained during the process. The rate constants have been determined at six temperatures in the range 35–60 °C (Table 3) and the activation parameters were calculated: $\Delta H^\ddagger = 93 \pm 3$ kJ

---

* $[Hdmso][trans\text{-}RhCl_4(dmso\text{-}S)_2]$ is reported here for the first time. Similar compounds, with a single protonated sulfoxide as cation, have already been reported for ruthenium(III), *i.e.* $[Hdmso][trans\text{-}RuCl_4(dmso\text{-}S)_2]$[18] and $[Htmso][trans\text{-}RuCl_4(tmso\text{-}S)_2]$[19] (tmso = tetramethylene sulfoxide). Of particular interest is the S–O stretching frequency in the cation, which falls considerably below the usual range (930–900 cm^{-1}) for O-bonded sulfoxide ligands: 863 cm^{-1} in $[Hdmso][trans\text{-}RhCl_4(dmso\text{-}S)_2]$, 870 cm^{-1} in the ruthenium analogue[18] and 897 cm^{-1} in the tmso derivative. In agreement with the bonding model for sulfoxides,[20] such low stretching frequencies suggest that the interaction of dmso (and tmso) with H^+ is considerably stronger than with a metal centre. In order to establish the S–O bond distance in the protonated dmso cation, we also determined the crystal structure of $[Hdmso][trans\text{-}RhCl_4(dmso\text{-}S)_2]$.[21] However, the static disorder of $[Hdmso]^+$ prevented an accurate determination of the structural parameters of the cation.

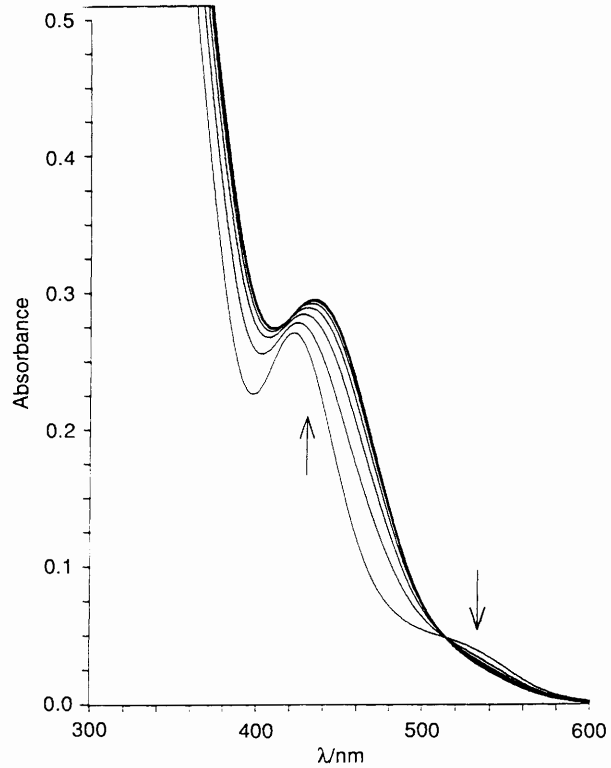


Fig. 2 Spectral changes observed in dmso solution during the thermal isomerization of **2a** to **2b**. [**2a**] = 1 × 10^{-3} mol dm^{-3}, T = 40 °C, scan-time interval 60 min

Table 3 First order kinetic constants measured in dmso solution for the thermal isomerization of **2a** to **2b**

T/°C	k/s^{-1}
35.0	7.78 × 10^{-5}
40.2	1.53 × 10^{-4}
44.9	2.74 × 10^{-4}
49.6	4.21 × 10^{-4}
54.5	8.29 × 10^{-4}
59.8	1.22 × 10^{-3}

mol^{-1}; $\Delta S^{\ddagger} = -21 \pm 6$ J K^{-1} mol^{-1}; $k_{25 °C} = 2.15 \times 10^{-5}$ s^{-1}. A negative value for the entropy of activation has also been measured for the thermal isomerization of *mer,trans*-[$RhCl_3$(dmso-*S*)$_2$(dmso-*O*)] to *mer,cis*-[$RhCl_3$(dmso-*S*)$_2$(dmso-*O*)].[8] It should be noted that the *cis* derivative of the iridium analogue is also presumed to be the most thermodynamically stable isomer, as it is formed at higher temperature.[15,16]

As for the neutral isomers,[8] the reverse isomerization process from *cis* to *trans* is promoted by visible light. In fact, while a chloroform solution of **2b** is quite stable in the dark,* exposure to the diffuse light of the laboratory induced its complete isomerization to [NEt_4][*trans*-$RhCl_4$(dmso-*S*)$_2$] **2a′** in a few hours. This latter complex, being less soluble than the *cis* isomer, can precipitate during the isomerization. The process could be easily monitored by ^1H NMR spectroscopy, the singlet of **2b′** at δ 3.52 being gradually replaced by the resonance of **2a′** at δ 3.56; a very small signal for free dmso was observed throughout the isomerization. The small difference in the ^1H $CDCl_3$ chemical shift between **2b′** and **2a′** is in agreement with the resonances reported for the corresponding NPr^n_4 salts in CD_2Cl_2.[14] The same light-promoted isomerization process, monitored by visible spectroscopy, occurs also in dmso.

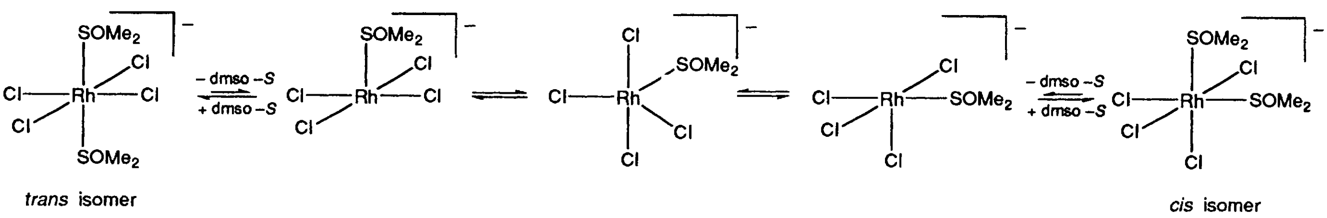
An isomerization mechanism, involving the dissociation of a dmso-*S* as the first step followed by reorganization of the five-co-ordinate intermediate and re-co-ordination of dmso-*S*, can be proposed (Scheme 1). Due to the negative value of $\Delta S^{\ddagger}$ observed in the thermal isomerization process, the dissociation step is very likely not rate determining. On the other hand, in agreement with the observations in aqueous solution (see below), the role of light might be the promotion of the dissociation of dmso-*S* from the thermodynamically more stable *cis* isomer. There is no evidence for chloride dissociation during the process.

Chemical Behaviour in Aqueous Solution of Complexes **1** *and* **2**.—The chemical behaviour of neutral and anionic rhodium chloride dmso complexes in aqueous solution is summarized in Scheme 2. The reactions have been followed mainly by ^1H NMR spectroscopy on light-protected solutions. The ^1H and ^{13}C chemical shifts of the species identified are reported in Tables 4 and 5, respectively. Due to the paucity of signals, a single NMR spectrum was seldom sufficient for an unambiguous assignment and a careful comparative study of the spectral evolution with time of different species was often required. The rhodium derivatives, unlike the corresponding ruthenium complexes,[1] are stable in aqueous solution and have no tendency to form polymeric aggregates.

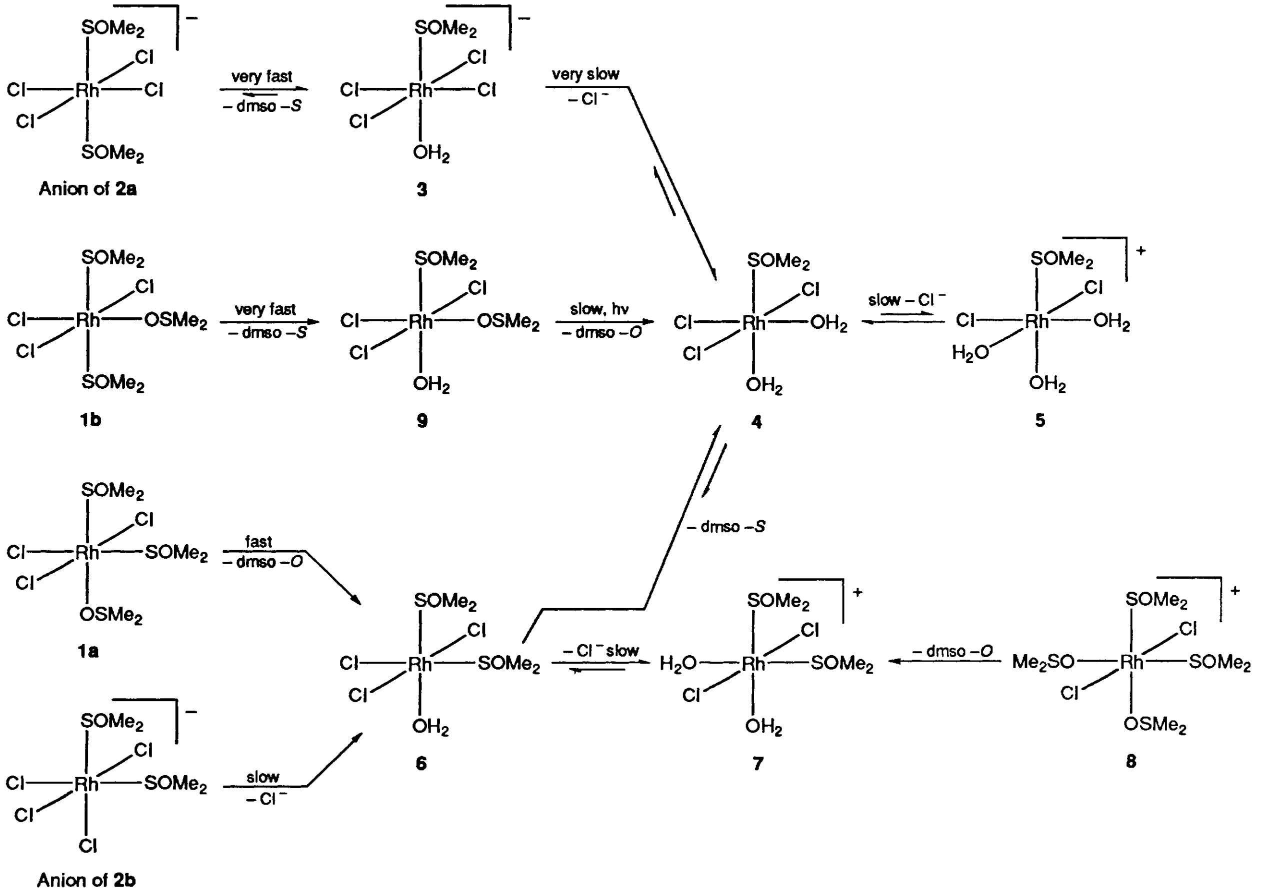
As already reported by James and Morris,[7] upon dissolution in water **2a** immediately loses one of the two S-bonded sulfoxides. In diluted solutions the dissociation equilibrium is almost completely shifted toward the aqua species **3** (δ 3.58), but it can be partially reversed to the parent compound (δ 3.53) in the presence of excess free dmso. In the absence of added dmso, the ratio of free to S-bonded sulfoxide (3:1 for **2a**) is constant with time, suggesting that no further loss of dmso occurs. We observed, however, that the peak of **3** slowly decreases with time, while two new resonances of different intensity increase correspondingly at δ 3.59 (assigned to species **4**, major product) and at δ 3.57 (assigned to **5**). This second process is completed within approximately 48 h. Since, from integration, both new species bear only one dmso-*S*, the main process can safely be attributed to the dissociation of a chloride from **3** forming the *cis*-(diaqua) species *mer,cis*-[$RhCl_3(H_2O)_2$(dmso-*S*)] **4**. The minor resonance is assigned to the monocationic species *cis,fac*-[$RhCl_2(H_2O)_3$(dmso-*S*)]$^+$, obtained from **4** upon further dissociation of a chloride. In agreement with this assignment, the signal of **5** decreases upon addition of free chloride (as NaCl), while the signals of **4** and **3** increase correspondingly. Owing to the higher *trans* effect of Cl compared to H_2O, dissociation of one of the two *trans* chlorides in **4** to give *cis,fac*-[$RhCl_2(H_2O)_3$(dmso-*S*)]$^+$ **5** should be favoured over the dissociation of a chloride *trans* to water and formation of the isomer *trans,mer*-[$RhCl_2(H_2O)_3$(dmso-*S*)]$^+$. As for the ruthenium analogue,[1] the rate of chloride dissociation increases with pH; for example, the rate of formation of **4** and **5** from **2a′** is approximately twice that from an equimolar solution of **2a**, the pH of which is lowered by the presence of the proton-containing cation. The ^1H NMR spectrum of a freshly prepared aqueous solution of *mer,cis*-[$RhCl_3$(dmso-*S*)$_2$(dmso-*O*)] **1a** is rather complicated, with at least five resonances in addition to free dmso at δ 2.71. A study of the time dependence of the spectrum allowed us to distinguish between the signals of **1a** and those of its aqua derivatives. As observed in $CDCl_3$,[7,14] the NMR pattern of **1a** in D_2O is characterized by three peaks of equal intensity, two in the region of S-bonded dmso (δ 3.59 and 3.41) and one in that of O-bonded dmso (δ 2.90). In agreement with previous assignments,[7] the lowest-field resonance can be attributed to the two equivalent methyl groups of the dmso-*S* *trans* to dmso-*O*. This pattern can be detected only for a short time (30 min), since the O-bonded dmso is quite labile and is

---

* A very slow partial thermal isomerization of **2b′** to [NEt_4][*trans*-$RhCl_4$(dmso-*S*)$_2$] **2a′** was also observed in light-protected chloroform solution. An equilibrium mixture of **2b′** to **2a′** (3:1) was reached after two weeks at room temperature.



Scheme 1 Proposed mechanism for the thermal and photochemical isomerization paths connecting **2a** and **2b**



Scheme 2 Chemical behaviour in aqueous solution of compounds **1** and **2**

Table 4 ^1H NMR chemical shifts (δ) in aqueous solution for compounds **1**–**9**

Compound	*S*-bonded dmso	*O*-bonded dmso
1a	3.59,[a] 3.41[b]	2.90
2a	3.53	
2b	3.48	
3	3.58	
4	3.59	
5	3.57	
6	3.61,[a] 3.45[b]	
7	3.54	
8	3.55	2.99
9	3.58	2.84

[a] Protons *trans* to either dmso-*O* or H_2O. [b] Proton *trans* to chloride.

Table 5 ^{13}C NMR chemical shifts (δ) in aqueous solution for compounds **1**–**7** and **9**

Compound	*S*-bonded dmso	*O*-bonded dmso
1a		
2a	44.4	
2b	45.1	
3	47.2	
4	46.5	
5	45.0	
6	47.4, 44.0	
7	45.8	
9	46.3	39.8

rapidly replaced by a water molecule. The peak for free dmso increases correspondingly, together with two peaks of equal intensity at δ 3.61 and 3.45, assigned to the equivalent methyl groups of the two inequivalent *cis* dmso-*S* ligands in the aqua species *mer,cis*-$[RhCl_3(H_2O)(dmso\text{-}S)_2]$ **6**.*

As already reported,[8] complex **6** could occasionally be isolated during the synthesis of **1a**, thus unambiguously confirming its assignment by NMR spectroscopy. By analogy with **1a**, we assigned the lowest-field resonance of **6** to the dmso-

---

* No peaks attributable to the all S-bonded isomer *mer*-$[RhCl_3(dmso\text{-}S)_3]$, which is observed in aprotic solvents, are seen in D_2O. This suggests that either this isomer is not formed in water or, where it is formed, dissociation of one of the two *trans* S-bonded dmso ligands occurs immediately, giving rise to the spectral pattern of **6**.

S trans to H_2O. The only other species that would be expected to give two resonances in that region of the spectrum is *fac,cis*-$[RhCl_3(H_2O)(\text{dmso-}S)_2]$ where the two equivalent dmso-*S* ligands have inequivalent methyl groups. However, a *mer* to *fac* isomerization of the chlorides during dmso-*O* dissociation would be expected to be accompanied by a significant variation in the visible spectrum,[27] which was not observed. This isomerization could be definitely ruled out on the basis of the further evolution of **6** with time. In fact, the signals of **6** are slowly partially replaced by peaks of **4** and **5** and by a new signal at δ 3.54 (compound **7**) which, from integration, corresponds to two equivalent dmso-*S* molecules. Equilibrium is reached in approximately 48 h (**6**:**4**:**5**:**7** ≈ 2:2:1:1). Compound **7** is presumed to be the cationic species *trans,cis,cis*-$[RhCl_2(H_2O)_2(\text{dmso-}S)_2]^+$, and this assignment was unambiguously confirmed by the evolution (as assigned from ^1H and ^{13}C NMR spectra) of the cationic complex *trans,cis,cis*-$[RhCl_2(\text{dmso-}S)_2(\text{dmso-}O)_2]^+$ **8**.[5] In fact, the original signals of **8** at δ 3.55 (dmso-*S*) and 2.99 (dmso-*O*) are replaced in a few hours by two equally intense resonances at δ 2.71 (free dmso) and 3.54 (**7**), upon complete dissociation of the two O-bonded dmso molecules. In further agreement with the assignment of **7**, addition of chloride to an aged solution of **8** leads slowly to the formation of **6** and **4** at the expense of **7**. Therefore, the two main products **4** and **7** derive from **6** according to the two parallel reactions: dissociation of the dmso-*S trans* to a chloride leads to **4** (and consequently to **5**), while dissociation of the chloride *trans* to dmso-*S* leads to **7**. The same behaviour was observed when **6** was used as starting material.

The chemical behaviour of *cis*-$[RhCl_4(\text{dmso-}S)_2]^-$ was studied using pure $[NEt_4]$[*cis*-$RhCl_4(\text{dmso-}S)_2$] **2b′**. In addition to the signal for the cation, a fresh solution of **2b′** gives a sharp singlet at δ 3.48 integrating for two dmso-*S* ligands. This resonance slowly decreases with time and is gradually replaced by those of **6** indicating that, in agreement with dmso-*S* having a greater *trans* effect than Cl, dissociation of a chloride *trans* to dmso-*S* is the first step. As was reported above for **1a**, the concentration of **6** reaches a maximum after approximately three hours and then slowly decreases in favour of **4**, **5** and **7**, until the equilibrium mixture is reached. No signals corresponding to an anionic species derived from **2b** upon dissociation of a dmso-*S* ligand could be observed.

Upon dissolution in water, **1b** immediately loses one of the two *trans* S-bonded sulfoxides to give the monoaqua derivative *mer,trans*-$[RhCl_3(H_2O)(\text{dmso-}S)(\text{dmso-}O)]$ **9**, as indicated by three singlets of equal intensity at δ 2.71 (free dmso), 2.84 (O-bonded dmso) and 3.58 (S-bonded dmso). No signals for the parent compound could be observed, even after the minimum amount of time required for recording an NMR spectrum (3–5 min). Compound **9** slowly evolves in time according to two parallel reactions, that is O/S linkage isomerization yielding **6** (and therefore **4**, **5** and **7**) and dissociation of the O-bonded dmso yielding **4**. Equilibrium is reached after approximately 72 h. We observed that in every case the dissociation of the dmso molecule *trans* to chloride becomes significantly faster in the presence of light, the process being complete after a few hours in solutions exposed to the diffused light of the laboratory. Accordingly, in the presence of light **4** is the main product from each species.

Conclusion

The synthesis and structural characterization of *cis*-$[RhCl_4(\text{dmso-}S)_2]^-$ adds a further contribution to the elucidation of the chemistry of $[RhCl_n(\text{dmso})_{6-n}]^{3-n}$ (n = 1–5) compounds. The greater thermodynamic stability of the new *cis* isomer compared to the *trans* one reflects a definite trend already observed in the case of the neutral isomers **1a** and **1b** and is in agreement with the nature of the Rh–dmso-*S* bond. Also, in this case, the reverse *cis* to *trans* isomerization of the two S-bonded sulfoxides is promoted by visible light.

The chemical behaviour of complexes **1** and **2** in aqueous solution is mainly determined by the *trans* effect of dmso-*S* and is influenced by the presence of light and by the pH. Some common features can be summarized as follows: Dissociation of the ligand *trans* to an S-bonded dmso is always the first step. This is very fast (seconds) when the leaving ligand is a dmso-*S* (*i.e.* in **1b** and **2a**), slower (minutes) for dmso-*O* (*i.e.* in **1a**) and markedly slower (hours) for chloride (*i.e.* in **2b**). This first step can be followed by further slow dissociation of dmso and/or chloride to give neutral and monocationic derivatives, the former process being promoted by light and the second by an increase in pH. It should be noted that the new anionic isomer **2b** behaves quite differently compared to **2a**, particularly in light-protected solutions.

The dissociation chemistry of complexes **1b** and **2a** in aqueous solution is qualitatively very similar to that observed for the corresponding isostructural Ru^{III} derivatives *mer,trans*-$[RuCl_3(\text{dmso-}S)_2(\text{dmso-}O)]$ and $[H(\text{dmso})_2]$[*trans*-$RuCl_4(\text{dmso-}S)_2$], even though neither the effect of visible light on the dissociation of dmso nor the formation of cationic species has been detected for ruthenium.[1] This reinforces our hypothesis that rhodium(III) dimethyl sulfoxide compounds can be useful in understanding the chemical behaviour of the analogous Ru^{III} derivatives, with the obvious limitations that the substitution kinetics can be different and rhodium complexes are less likely to undergo reduction processes than complexes of ruthenium.

Experimental

Materials.—Analytical grade dimethyl sulfoxide (C. Erba) and solvents (Baker) were used without further purification for synthetic purposes. $RhCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey. Deuteriated solvents for NMR spectroscopy were purchased from Aldrich and Cambridge Isotope Laboratories.

Physical Measurements.—Electronic absorption spectra were recorded in stoppered quartz cells with a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer equipped with a thermostat. Unless otherwise stated, spectra were recorded immediately after dissolution of the complexes. Solid-state infrared spectra (Nujol) were obtained on a Perkin-Elmer 983G spectrometer, and ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100.5 MHz, respectively, on a JEOL EX400 FT instrument. All spectra were run at room temperature with tetramethylsilane as an internal reference for $CDCl_3$ solutions and sodium 4,4-dimethyl-4-silapentane-1-sulfonate for D_2O solutions. Elemental analyses were performed by the Dipartimento Scienze Chimiche, Università di Trieste.

Syntheses.—The complexes *mer,cis*-$[RhCl_3(\text{dmso-}S)_2(\text{dmso-}O)]$ **1a**, *mer,trans*-$[RhCl_3(\text{dmso-}S)_2(\text{dmso-}O)]$ **1b** and $[H(\text{dmso})_2]$[*trans*-$RhCl_4(\text{dmso-}S)_2$] **2a** were synthesized according to the methods reported in refs. 7, 8 and 9, respectively.

[Hdmso][*trans*-$RhCl_4(\text{dmso-}S)_2$]. This complex was isolated as red crystals from the mother-liquor in the recrystallization of **2b** from either warm acetone or methanol (Found: C, 14.9; H, 3.95; S, 19.6. $C_6H_{19}Cl_4O_3RhS_3$ requires C, 15.00; H, 4.00; S, 20.05%); $\lambda_{max}(H_2O)$ 418.5(sh) (220), 490 nm (sh, br) (55 $dm^3\ mol^{-1}\ cm^{-1}$); λ_{max}(dmso) 420(sh) (250), 510 nm (sh, br) (45 $dm^3\ mol^{-1}\ cm^{-1}$); $\tilde{\nu}_{max}/cm^{-1}$ 1131s (SO in dmso-*S*), 863s (SO in Hdmso), 420m (Rh–S), 345s (Rh–Cl); $\delta_H(D_2O)$, 3.58 (6 H, s, dmso-*S*) and 2.71 (12 H, s, free dmso).

$[H(\text{dmso})_2]$[*cis*-$RhCl_4(\text{dmso-}S)_2$] **2b**. Complex **2b** was obtained either by isomerization of **2a** in warm dmso (*i*) or, more conveniently, by warming $RhCl_3 \cdot 3H_2O$ in dmso–HCl mixtures (*ii*). In each procedure the product cocrystallized with variable amounts of **2a**, ranging from a minimum of 5 to a maximum of 15%.

(*i*) Complex **2a** (0.3 g, 0.53 mmol) was dissolved in dmso (1 cm^3) and warmed to *ca.* 100 °C for 10 min, until a clear deep orange solution was obtained. The product precipitated as pale orange needles upon addition of acetone (3 cm^3) to the cooled solution which was filtered off, washed with cold acetone and diethyl ether and vacuum dried (yield 0.24 g, 80%).

(*ii*) Rhodium chloride trihydrate (0.25 g, 0.95 mmol) was dissolved in a mixture of dmso (1.5 cm^3) and conc. HCl (0.2 cm^3). The mixture was warmed to *ca.* 100 °C for 30 min, until a clear orange solution was obtained. The product separated as pale orange microcrystals from the cooled solution upon addition of acetone (5 cm^3). It was filtered off, washed with cold acetone and diethyl ether and vacuum dried at room temperature (0.45 g, 85%) (Found: C, 17.1; H, 4.35; S, 22.2. $C_8H_{25}Cl_4O_4RhS_4$ requires C, 17.20; H, 4.50; S, 22.95%); $\tilde{\nu}_{max}/cm^{-1}$ 1155s (SO), $\{O\cdots H\cdots O$ in $[H(dmso)_2]^+\}$, 425m (Rh–S), 342s and 327m (Rh–Cl), 750 (br).

Recrystallization of the product from warm acetone yielded pale orange crystals of **2b** together with red prisms of [Hdmso][*trans*-$RhCl_4$(dmso-*S*)$_2$] (identified by ^1H NMR). When the recrystallization was carried out in refluxing methanol, orange crystals of **1a** were obtained together with crystals of **2b** and [Hdmso][*trans*-$RhCl_4$(dmso-*S*)$_2$].

[NEt_4][*cis*-$RhCl_4$(dmso-*S*)$_2$] **2b′**. Complex **2b** (0.25 g, 0.45 mmol) and NEt_4Cl (0.15 g, 0.9 mmol) were dissolved in the minimum amount of water (*ca.* 1 cm^3). The solution was rapidly extracted four times with CH_2Cl_2 (5 cm^3). The organic phase, kept in an ice-bath and protected from light in order to limit isomerization, was dehydrated over anhydrous Na_2SO_4 and then reduced to 3 cm^3 at room temperature. Some diethyl ether (*ca.* 2 cm^3) was added and the solution was stored in the refrigerator. The first crop of product that precipitated within a few hours was mainly orange-red crystals of the less soluble isomer [NEt_4][*trans*-$RhCl_4$(dmso-*S*)$_2$] **2a′**. A second crop of light orange crystals of the *cis* isomer **2b′** was obtained from the mother-liquor after *ca.* 2 d. When necessary, separation of the two isomers, based upon the colour of the crystals, could be performed quite easily under a microscope (yield 0.12 g, 50%) (Found: C, 26.9; H, 6.05; N, 2.55; S, 12.1. $C_{12}H_{32}Cl_4NO_2RhS_2$ requires C, 27.15; H, 6.05; N, 2.65; S, 12.05%); $\tilde{\nu}_{max}/cm^{-1}$ 1140s (SO), 421m (Rh–S), 346s and 326m (Rh–Cl); $\delta_H(D_2O)$ 3.48 (12 H, s, dmso-*S*), 3.24 (8 H, q, $CH_3C\mathit{H}_2$) and 1.25 (12 H, t, $C\mathit{H}_3CH_2$); $\delta_H(CDCl_3)$ 3.52 (12 H, s, dmso-*S*), 3.39 (8 H, q, $CH_3C\mathit{H}_2$) and 1.36 (12 H, t, $C\mathit{H}_3CH_2$); $\delta_C(CDCl_3)$ 52.9 ($CH_3C\mathit{H}_2$), 43.0 (dmso-*S*) and 7.9 ($C\mathit{H}_3CH_2$).

[NEt_4][*trans*-$RhCl_4$(dmso-*S*)$_2$] **2a′**. For comparison, a pure sample of **2a′** was obtained upon reaction of **1a** (0.2 g, 0.45 mmol) with NEt_4Cl (0.15 g. 0.9 mmol) according to the procedure of ref. 7* (yield 0.17 g, 70%) (Found: C, 27.0; H, 5.95; N, 2.60; S, 12.0. $C_{12}H_{32}Cl_4NO_2RhS_2$ requires C, 27.15; H, 6.05; N, 2.65; S, 12.05%) $\tilde{\nu}_{max}/cm^{-1}$ 1139s (SO), 418m (Rh–S), 349s and 334s (Rh–Cl); $\delta_H(CDCl_3)$ 3.56 (12 H, s, dmso-*S*), 3.39 (8 H, q, $CH_3C\mathit{H}_2$) and 1.36 (12 H, t, $C\mathit{H}_3CH_2$); $\delta_C(CDCl_3)$ 52.9 ($CH_3C\mathit{H}_2$), 42.7 (dmso-*S*) and 7.9 ($C\mathit{H}_3CH_2$).

Crystal Structure Determination.—Crystals of **2b′** were obtained according to the synthetic procedure reported above.

Crystal data. $C_{12}H_{32}Cl_4NO_2RhS_2$, M = 531.24, monoclinic, $a = 10.500(4)$, $b = 17.054(3)$, $c = 13.304(5)$ Å, $\beta = 114.19(2)°$, $U = 2173(1)$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1088$. Crystal dimensions 0.5 × 0.5 × 0.6 mm, μ(Mo-Kα) = 14.60 cm^{-1}.

Data collection and processing. CAD-4 diffractometer, ω–2θ mode with ω scan width = $0.8 + 0.35 \tan\theta$, ω scan speed 1–20° min^{-1}, graphite-monochromated Mo-Kα radiation; 15 231 reflections measured ($2.0 \leqslant \theta \leqslant 28.0°$, $\pm h, k, l$), 4076 unique with $I > 3\sigma(I)$ after empirical absorption correction (maximum, minimum transmission factors = 0.999, 0.950).

Structure analysis and refinement. The structure was solved by the heavy-atom method. Hydrogen atoms were located at calculated positions and not refined, with thermal parameters of $1.3B_{eq}$ of the bonded carbon atom. The structure was refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic. The weighting scheme $w = 1/[1 + \sigma(|F_o|)^2 + (0.02|F_o|)^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final $R = \Sigma||F_o| - F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ values are 0.042, 0.052, goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$ of 0.95, with m = number of observed reflections, n = number of variables (199). Atomic scattering factors and anomalous dispersion terms were those of the program package MOLEN,[28] used for the determination.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Support of this work by the Italian Ministero dell' Universitá e della Ricerca Scientifica e Tecnologica (40% grant) is gratefully acknowledged. We thank Mr. P. de Baseggio and Dr. Cebulec for technical assistance.

References

1 E. Alessio, G. Balducci, M. Calligaris, G. Costa, W. M. Attia and G. Mestroni, *Inorg. Chem.*, 1991, **30**, 609.
2 E. Alessio, G. Balducci, A. Lutman, G. Mestroni, M. Calligaris and W. M. Attia, *Inorg. Chim. Acta*, 1993, **203**, 205.
3 G. Sava, S. Pacor, G. Mestroni and E. Alessio, *Anti-Cancer Drugs*, 1992, **3**, 25.
4 G. Mestroni, E. Alessio, G. Sava, S. Pacor and M. Coluccia, in *Metal Complexes in Cancer Chemotherapy*, ed. B. K. Keppler, VCH, Weinheim, 1993, pp. 157–185.
5 M. Calligaris, P. Faleschini and E. Alessio, *Acta Crystallogr., Sect. C*, 1991, **47**, 747.
6 V. I. Sokol and M. A. Porai-Koshits, *Sov. J. Coord. Chem.* (*Engl. Transl.*), 1975, **1**, 476.
7 B. R. James and R. H. Morris, *Can. J. Chem.*, 1980, **58**, 399.
8 E. Alessio, P. Faleschini, A. Sessanta o Santi, G. Mestroni and M. Calligaris, *Inorg. Chem.*, 1993, **32**, 5756.
9 H. B. Henbest and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 1974, 607.
10 V. I. Sokol, N. D. Rubstova and A. Y. Gribernyuk, *J. Struct. Chem.* (*Engl. Transl.*), 1974, **15**, 296.
11 B. R. James, R. H. Morris, F. W. B. Einstein and A. Willis, *J. Chem. Soc., Chem. Commun.*, 1980, 31.
12 S. N. Gamage, R. H. Morris, S. J. Rettig, D. C. Thackray, I. S. Thorburn and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1987, 894.
13 S. N. Gamage, B. R. James, S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1988, **66**, 1123.
14 J. R. Barnes, P. L. Goggin and R. J. Goodfellow, *J. Chem. Res.*, 1979, (*M*) 1610; (*S*) 118.
15 Y. M. Y. Haddad, H. B. Henbest and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 1974, 592.
16 B. R. James, R. H. Morris and P. Kvintovics, *Can. J. Chem.*, 1986, **64**, 897.
17 P. S. Cartwright, R. D. Gillard, E. R. J. Sillanpaa and J. Valkonen, *Polyhedron*, 1988, **7**, 2143.
18 O. V. Rudnitskaya, I. V. Miroshnichenko, A. I. Stash and N. M. Sinitsyn, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1993, **38**, 1101.

---

* The reaction between **1a** and NEt_4Cl was followed by ^1H NMR spectroscopy in $CDCl_3$ at room temperature. As expected from the reactivity of **1a**, the product is the *cis* isomer **2b′**. In light-protected samples, the amount of **2a′** in equilibrium with **2b′** increases very slowly with time (see text). Heating the reaction mixture to reflux, as required in ref. 7, induces a fast equilibration of the two isomers. The considerably lower solubility of **2a′** compared to **2b′** allows selective precipitation of the *trans* isomer. By running the reaction at room temperature in a carefully light-protected flask, we have been able to isolate pure samples of **2b′** in high yield; the procedure is however scarcely reproducible since the product is often contaminated by various amounts of the *trans* isomer.

19 E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P. Faleschini and W. M. Attia, *Inorg. Chim. Acta*, 1990, **177**, 255.

20 J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 115.

21 P. Faleschini, Ph.D. Thesis, University of Trieste, 1993.

22 W. J. J. Smeets, A. L. Spek, F. G. M. Niele, C. F. Martens and R. J. M. Nolte, *Acta Crystallogr., Sect. C*, 1987, **43**, 2330.

23 F. D. Rochon, P. C. Kong and R. Melanson, *Can. J. Chem.*, 1983, **61**, 1823.

24 S. N. Gamage, R. H. Morris, S. J. Rettig and B. R. James, *J. Organomet. Chem.*, 1986, **309**, C59.

25 E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava and S. Zorzet, *Inorg. Chem.*, 1988, **27**, 4099.

26 M. Henn, E. Alessio, G. Mestroni, M. Calligaris and W. M. Attia, *Inorg. Chim. Acta*, 1991, **187**, 39.

27 J. Chatt, G. J. Leigh, A. P. Storace, D. A. Squire and B. J. Starkey, *J. Chem. Soc. A*, 1971, 899.

28 MOLEN, An Interactive Intelligent System for Crystal Structure Analysis, Enraf-Nonius, Delft, 1990.

Received 9th December 1993; Paper 3/07291F