Reactions of Secondary Dithioxamides with $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$: The Role of Steric Hindrance on Amidic Nitrogen in Determining the Reaction Products

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The reactions of secondary dithioxamides H_2R_2DTO **1**–**11** [R = methyl **1**, ethyl **2**, *n*-propyl **3**, *n*-butyl **4**, isoamyl **5**, benzyl **6**, *p*-tolyl **7**, (*R*)-1-phenylethyl **8**, (*R*,*S*)-1-phenylethyl **9**, isopropyl **10**, cyclohexyl **11**] with the chloride-bridge dimer $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ complex readily afforded either bimetallic ruthenium complexes of formula $[(\eta^6\text{-}p\text{-cymene})RuCl_2](\mu\text{-}R_2DTO)$ (R = methyl **12a**, R = ethyl, **12b**, R = *n*-propyl **12c**; R = *n*-butyl **12d**; R = isoamyl **12e**; R = benzyl **12f**; R = *p*-tolyl **12g**) or mononuclear "piano stool" geometry ion pairs $\{(\eta^6\text{-}p\text{-cymene})RuCl(H_2R_2DTO)^+,(Cl^-)$ κ-*S*,*S*′ Ru} [R = (*R*)-1-phenylethyl, **13a**; R = (*R*,*S*)-1-phenylethyl, **13b**; R = isopropyl, **13c**; R = cyclohexyl, **13d**]. The driving force of the reactions was the bulkiness of the R groups attached to dithioxamides, leading respectively from primary and aromatic *N*-bonded carbons to neutral bimetallic species **12a**–**g**, or from secondary *N*-bonded carbons to monometallic **13a**–**d** species. These latter compounds could be easily dehydrohalogenated to give neutral "piano stool" complexes $[(\eta^6\text{-}p\text{-cymene})RuCl(HR_2DTO)$ κ-*S*,*S*′ Ru] [R = (*R*)-1-phenylethyl **14a**; R = (*R*,*S*)-1-phenylethyl **14b**; R = isopropyl **14c**; R = cyclohexyl **14d**]. All complexes were characterised in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **12f** was also characterised by mass spectrometry, and **12g** by solid state X-ray crystallography.

Introduction

Dimeric $[(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)]_2$ species provide an ideal way of entering the synthesis of η^6-monoarene "three legged piano stool" ruthenium complexes, where the η^6-coordinated arene are the "bench", and the other ligands "the legs" of the stool.[1] However, when the $[(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)]_2$ chloride-bridge dimers are reacted under particular experimental conditions with binucleating chelate ligands, binuclear complexes of the type $[(\mu\text{-L-L})\{RuCl_2(\eta^6\text{-arene})\}_2]$ can be also obtained.[2] Mononuclear η^6-arene ruthenium complexes revealed themselves as effective enantioselective catalysts in a number of asymmetric organic transformations when ruthenium is itself presented as a stereogenic centre or ligands are chiral species such as BINAP[3] or aminophosphanyl-phosphinite.[4]

We have previously reported that the platinum complexes [Pt(PN)Cl(HR_2DTO) κ-*S*,*S*′ Pt] (PN = 2-diphenylphosphanyl-pyridine. HR_2DTO^- = alkyl-substituted dithioxamidato) react with the ruthenium dimer $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ giving rise to heterobimetallic "piano stool" ruthenium complexes:[5]

In complex **I** (Figure 1), the ruthenium is a stereogenic centre since the three legs of the stool are different. The stereochemistry of **I** remains ambiguous if one considers only the configuration of the ruthenium centre; thus, we have proposed that the best way to describe the asymmetry of **I** is to consider the Ru−Pt axis as an unprecedented element of chirality. As a matter of fact, the reactivity of [Pt(PN)Cl(HR_2DTO) κ-*S*,*S*′ Pt] type compounds opens the way to a new class of organometallic complexes. When these square planar complexes containing *S*,*S*′-coordinated

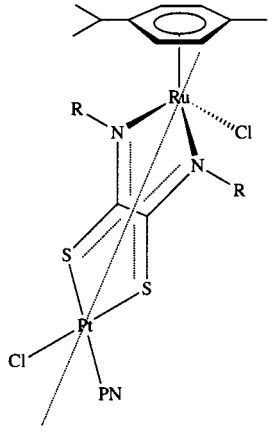

Figure 1. [Pt(PN)Cl(μ-R_2DTO)Ru(*p*-cymene)Cl, κ-*S*,*S*′ Pt, κ-*N*,*N*′ Ru] **I**

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dithioxamides are forced to chelate by the unusual *N,N′*-coordination mode with a second prochiral metal fragment such as $[Ru(\eta^6\text{-}p\text{-cymene})Cl]^+$, new binuclear species exhibiting very interesting stereochemical features are formed. Starting from this point, we found it interesting to see how un-coordinated secondary dithioxamides react with the ruthenium dimer $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$. The coordination chemistry of secondary dithioxamides ligands is very rich; the multi-site donor nature of the two nitrogen and two sulfur atoms, their respective hard and soft character, the possibility of modulating electronic and geometrical properties by loss of one or two protons, and finally, the dicompartmental rigid structure of the dianionic rubeanate ligand have been largely exploited to form complexes of different coordination type, geometries, and nuclearity.[6] The organometallic chemistry of these ligands, on the contrary, has hitherto been rather unexplored: only one report has appeared in the last few years,[7] even though the alkyl groups of secondary dithioxamides could be usefully exploited as molecular probes or as electronic, steric, and enantioselective tools for modelling peculiar properties of the molecules.

The present paper stems from a systematic study devoted to the synthesis of η^6-arene-ruthenium(II) complexes containing dithioxamides: the aim of the research is to investigate the stereochemical effect of R groups in [RHNSC−CSNHR] or [RHNSC−CSNHR′] molecules in determining the possible stereoselective synthesis of half-sandwich molecules like **I**. In the following we report results concerning the reactions $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ with a series of disubstituted dithioxamides bearing alkyl substituents of varying molecular complexity.

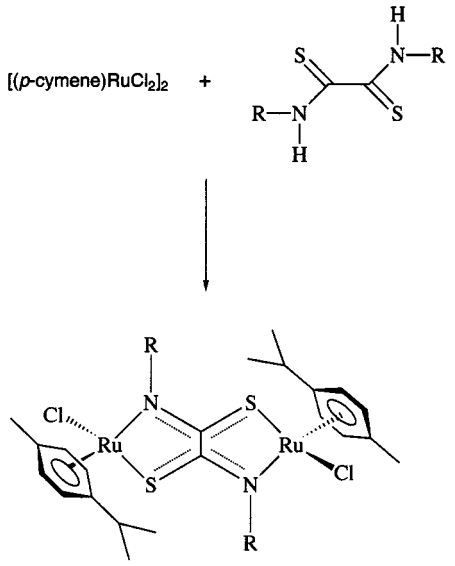
Results and Discussion

Structurally, the ligands [RHNSC−CSNHR] used in the present study can be divided into three families, according to the nature of the carbon bonded to the amidic nitrogens: i) primary [R = methyl (**1**), ethyl (**2**), *n*-propyl (**3**), *n*-butyl (**4**), isoamyl (**5**), and benzyl (**6**); ii) aromatic [*p*-tolyl (**7**)]; and iii) secondary [(*R*)-1-phenylethyl (**8**), (*R*,*S*)-1-phenylethyl (**9**), isopropyl (**10**), and cyclohexyl (**11**)].

The reactions of ligands **1**−**7** with $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ in chloroform lead to the bimetallic complexes **12a**−**g** in high yields (Scheme 1).

In these compounds the two ruthenium atoms are connected by a dianionic rubeanate frame in an NS−NS binucleating mode, which is the usual coordination mode observed in many other inorganic bi- and polymetallic complexes.[8]

^{1}H NMR spectra of compounds **12a**−**g** show cymene ring protons as four doublets and methyl groups of the isopropyl moiety of cymene as two doublets. $^{13}C\{^1H\}$ NMR spectra, in turn, show four resonances corresponding to CH carbons of cymene ring, and two featuring cymene isopropyl CH_3 carbons (see Exp. Sect.). These spectral patterns are observed since ruthenium atoms are stereogenic, hence



Scheme 1. Reactions of $[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ with the ligands **1**−**7**

the plane perpendicular to the *p*-cymene and passing through the quaternary phenyl carbons C^1 and C^4 is not a symmetry plane. Consequently, the methyl protons of the isopropyl group and the aromatic protons (H^2 and H^6) in the *ortho* position with respect to the same group, as well as H^3 and H^5, are diastereotopic. At the same time NCH_2−R protons in **12a**−**g** are diastereotopic, and appear in the ^{1}H NMR spectra as an ABC_n (n = 0, 1, 2, 3) spin systems. As explained previously, pseudo-octahedral ruthenium atoms are both stereogenic since they are surrounded by four different ligands, hence two diastereomers could have been formed in which the two ruthenium atoms could have equal or opposite configurations. However, we have observed that the reaction is totally diastereoselective and an X ray analysis of **12f** (Figure 2 and Table 1) revealed that only the compound with ruthenium atoms in the opposite configuration is formed.

Compounds **12a**−**g** are highly symmetric *meso* molecules, due to the presence of a centre of inversion in the middle of the central C−C bond of the rubeanate frame. We attempted to destroy this centre of inversion by three distinct strategies: i) metathesis of one of the two chlorides on ruthenium atoms; ii) use of a dithioxamide bearing an optically pure substituent on nitrogens; iii) use of an unsymmetrically disubstituted dithioxamide. This latter procedure is under investigation, since some additional problems concerning stereoselectivity arose that are not yet fully understood. As far as the metathesis of the chloride ligand, our attempt to change only one chloride with iodide failed. Consequently, we have used the enantiopure homochiral dithioxamide **8** to get into asymmetric ruthenium dimers of the type **12a**−**g** by depletion of the inversion centre. This ligand however, as well as **9**−**11**, undergoes a different reaction leading to the monomeric "piano stool" type complexes **13a**−**d** (Scheme 2).

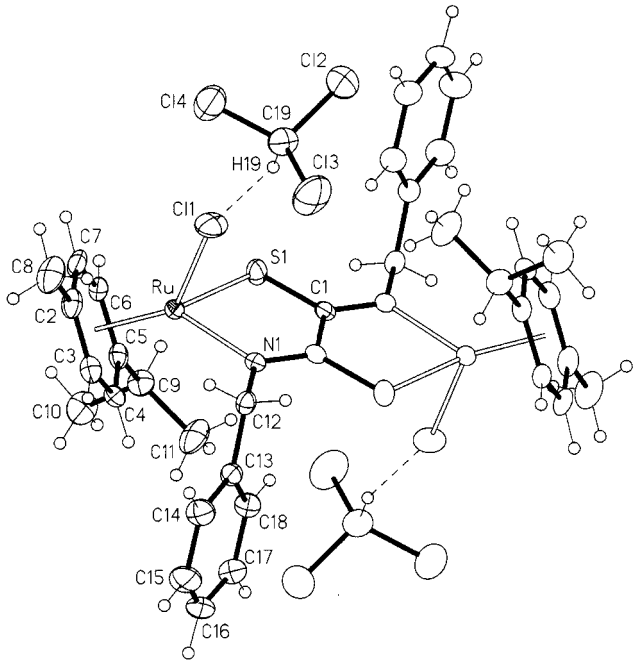
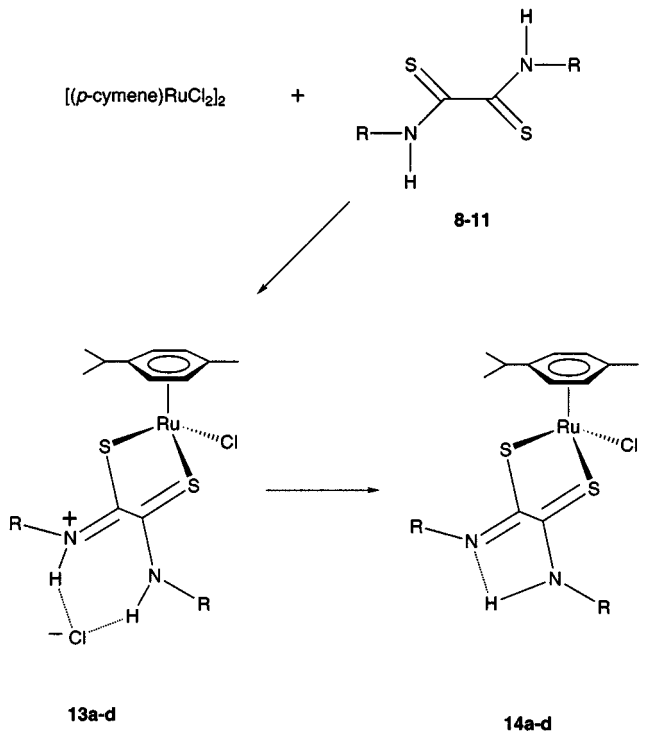


Figure 2. View of the whole molecule of **12f·2CHCl₃** at a crystallographic inversion centre, showing the labelling scheme of its half independent moiety. Thermal ellipsoids are drown at 30% probability, while hydrogen size is arbitrary

Table 1. Crystallographic data for **12f·2CHCl₃**

empirical formula	$C_{36}H_{42}Cl_2N_2Ru_2S_2 \cdot 2\ CHCl_3$
formula mass	1078.66
crystal dimensions	0.30 × 0.25 × 0.18 mm
crystal colour and form	yellow, prismatic
crystal system	triclinic
space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	a = 9.515(1) Å
	b = 10.195(1) Å
	c = 12.391(2) Å
	α = 77.88(1)°
	β = 78.13(1)°
	γ = 71.64(1)°
V	1102.7(2) Å^3
Z	1
F(000)	542
$\rho_{calcd.}$	1.624 g/cm^3
μ	1.294 mm^{-1}
λ (graphite-monochromated)	0.71073 Å (Mo-K_α)
2θ range	3−50°
number of data collected (2θ − ω)	4597
number of data independent	3572 ($R_{int.}$ = 0.0232)
number of data refined	2222 [$F \geq 4\ \sigma(F)$]
number of variables	238
R[a]	0.0418/0.0725
(refined/all data)	
Rw[b] (refined/all data)	0.0493/0.1100
GOF[c] (refined/all data)	0.69/0.69
Max. diff. peak and hole	0.49/−0.48 eÅ^{-3}
Max. and mean shift/esd	0.002/0.001

[a] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R_w\ [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.



Scheme 2. Reactions of [(η⁶-*p*-cymene)RuCl(μ-Cl)]₂ with the ligands **8−11**

The N−H proton resonances at δ ≈ 13 in **13a−d** suggest that amidic nitrogens are engaged in an =N−H···Cl⁻···H−N= interaction.[6] This proves that the dithioxamide molecules are linked to ruthenium through sulfur atoms. Considering this and the absence of structural data, the geometry of **13a−d** compounds seems to be defined. Mass spectrum of **13a** shows a low intensity but significant peak at M^+ = 634, characterised by the usual ruthenium isotopomers pattern. More intense peaks observed in the spectrum are attributable to HCl, *p*-cymene, and 1-phenylethyldithioxamide. Compounds **13a−d** are tight contact ion pairs, extensively associated (Beer's law holds in the range 5 × 10^{-5} to 6 × 10^{-6} M), in which the steric repulsion between amidic hydrogens requires a torsion angle between the two NCS moieties in the neutral dithioxamide ligand. In fact, the co-planarity of the thioamide groups in an *S*,*S*′-coordinated neutral disubstituted dithioxamide would require a nonbonded H···H distance of ca. 1.4 Å between the amide protons. It may be emphasised that extremely short nonbonded H···H distances have been reported in the range 1.71−1.74 Å.[9]

A series of crystal structures performed on different metal complexes (copper, zinc, bismuth, and tin) containing neutral dithioxamides coordinated in the *S*,*S*′-mode, and having different geometrical environments (square-planar, tetrahedral, octahedral, bipyramidal) have appeared in the literature.[10] In all of them, in the solid state, a torsion angle between the two NCS fragments of about 40° was measured, which, being independent from both the metal and its geometrical environment, can be taken as a characteristic of any neutral *S*,*S*′-coordinated dithioxamides. In spite of

their chemical unequivalence, only one set of NMR signals for the dithioxamide alkyl groups of **13a−d** has been observed; as previously suggested, in the NMR time scale, fast HCl-mediated exchange should be responsible for the alkyl averaging.[11] Compounds **13a−d** can be easily dehydrohalogenated to give neutral rubeanate complexes **14a−d** in a pure form, by means of double phase reaction on a chromatographic column (see Exp. Sect.). HCl can also be removed from **13a−d** ion pairs by means of classical Brønsted bases such as alkylamines, and can be easily added to **14a−d** neutral complexes to restore the ion pairs **13a−d**. This easy and reversible protonation further supports *S*,*S*′ coordination in **14a−d**, as well as in **13a−d**. Complexes **13a** and **14a** are optically pure chiral molecules of C_1 symmetry; therefore in these species, RNCS fragments are diastereotopic, and accordingly two sets of signals appear in the NMR spectra. These complexes present optically pure chiral chelate ligands bonded to the metal by sulfur atoms. It is worth mentioning that in recent years new chiral auxiliaries appearing in the literature have attracted increasing interest and have found applications in synthetic organic chemistry.[12] Several different chiral chelates including diphosphane,[13] diamine,[14] diimine,[15] dithiol ligands,[16] and "mixed" chelates, e.g., S−N[17,18] and P−N[18] combinations, have been incorporated into the catalyst precursors and successfully employed in enantioselective synthesis (up to 90% enantiomeric excess often reported).

Compounds **13b** and **14b** were obtained from a dithioxamide, prepared by racemic phenylethylamine; the diastereoisomeric mixture was not separated, but characterised in solution by NMR spectra subtraction procedure. The reaction of $[(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)]_2$ with **9** produces a mixture containing 50% of the racemate (*R*,*R*) and (*S*,*S*) and 50% of the two (*R*,*S*) and (*S*,*R*) *meso* forms. The NMR spectra of the (*R*,*R*) and (*S*,*S*) racemate is of course equal to that of the optical pure (*R*,*R*) enantiomer **13a**; thus by subtraction of the **13a** spectrum from that of the mixture, the spectrum of the two **13b** *meso* forms of C_s symmetry can be obtained. The diastereoisomers **13b** give rise to perfectly superimposable ^1H and ^{13}C NMR spectra which, owing to the internal reflection plane, show a single set of NMR signals; the two *meso* forms depict an interesting example of stereogenic achirotopic ruthenium centre.[19]

The different reactivity towards ruthenium(*p*-cymene)dichloro dimer of benzyl dithioxamide with respect to 1-phenylethyldithioxamide is rather surprising: a striking change in the reaction products and in the coordination mode of the ligands follows a small change in the molecular complexity of R substituents on nitrogen. This probably means that the *N*,S binucleation is a more favourable coordination mode of dithioxamide ligands towards the organoruthenium fragment $[(arene)RuCl]^+$: a better 'hard/soft' interaction and less steric hindrance should be achieved when only one alkyl substituent interacts with *p*-cymene ring. Vice versa is true when the ligands have sterically hindered amidic nitrogens, the *S*,*S*′ *cis*-chelation should be easier and mononuclear "piano stool" complexes formed preferentially. Actually, dithioxamide ligands other than **6**, **8**, and **9** were designed to verify if the steric hindrance on nitrogen could be responsible for the different reaction paths. Thus, we prepared **1**, **2**, **3**, **4**, and **5** where R = $-CH_2-R'$ (R′ = H, methyl, ethyl, propyl, isobutyl) at the scope of varying the molecular complexity of R′ while leaving the structure of the carbon attached to nitrogen unchanged. Alternatively, **10** and **11** were prepared to increase steric hindrance on the carbon directly attached to nitrogen, and **7** was prepared because the aromatic carbon on nitrogen is part of a flat structure, which does not have three-dimensional hindrance. The analysis of the reaction products confirms that the bulk on the nitrogen-bonded carbon is the structural property of secondary dithioxamides that leads to the synthesis of piano stool complexes **13a−d** rather than to the binuclear compounds **12a−g**.

Conclusions

Secondary dithioxamides *N*-substituted with substituents of various complexity were reacted with ruthenium(*p*-cymene)dichloro dimer. Binuclear $[(p\text{-cymene})ClRu]_2$ (μ-$R_2N_2S_2H_2$ κ-*N*,*S* Ru κ-*N*′,*S*′ Ru′) were synthesized when R = methyl, ethyl, *n*-propyl, *n*-butyl, isoamyl, *p*-tolyl. Mononuclear "piano stool" complexes $\{Ru(p\text{-cymene})Cl(H_2R_2N_2S_2C_2)^+, Cl^-\}$ and $[Ru(p\text{-cymene})Cl(H_2R_2N_2S_2C_2)]$ were obtained when R = cyclohexyl, isopropyl, 1-phenylethyl.

These results suggest that the bulk on the nitrogen-bonded carbon is the structural property of secondary dithioxamides that leads to the synthesis of piano stool complexes rather than to the binuclear compounds. This observation opens interesting perspectives; in fact, unsymmetrically disubstituted dithioxamides [RHNSC−CSNHR′] properly designed could provide binuclear as well as "piano stool" mononuclear chiral diastereomers. Furthermore, the tuning of steric effects, both on nitrogen substituents and on η^6-arene "stools", could promote stereoselective synthesis of "piano stool" type $[(\eta^6\text{-arene})Ru(HDTO)Cl]$ complexes.

Molecular Structure of $[(\eta^6\text{-}p\text{-Cymene})RuCl]_2$(μ-*N*,*N*′-dibenzyl-dithioxamidato κ-*N*,*S* Ru κ-*N*′,*S*′ Ru′)·2$CHCl_3$ (12f·2$CHCl_3$)

The complex consists of two $[(\eta^6\text{-}p\text{-cymene})RuCl]^+$ units *N*,*S*-bis-chelated by a planar bridge [(*N*,*N*′-dibenzyl-dithioxamidato)]$^{2-}$. The compound co-crystallises with solvent molecules (ratio 1:2) interacting with the chloride of the ruthenium moieties: H(19)···Cl(1) 2.407(9) Å, C(19)···Cl(1) 3.327(9) Å, C(19)−H(19)···Cl(1) 160.5(9)°. The observed decay of the diffraction data is due to the crystal packing deterioration due to loss of co-crystallised $CHCl_3$. In the solid state the middle point of the NSC−CSN is both a crystallographic and molecular inversion centre; thus the asymmetric unit contains only half complex moiety H-bonded to a chloroform molecule, as shown in Figure 2.

By considering the (η⁶-*p*-cymene) ligand as a unique coordination site represented by the centre of the benzene ring (Xcym in Table 2), the ruthenium geometry might be described as a significantly distorted tetrahedron. This deformation as evidenced by the space-filling model is mainly due to the metal d orbitals orientation (that is octahedral); these develop bonds toward ligands: the "three legs of the stool" are nearly 90° mutually oriented. The Ru−Ccym bond lengths shift from 2.170(7) for C(4) to 2.256(6) Å for C(2) with the average value 2.198(8) Å; the metal distance from the benzene centre is 1.685(6) Å. The ruthenium coordination geometry is the same as that of [(η⁶-*p*-cymene)RuCl(μ-bis(2-hydroxypropyl)-DTO)Pt(2-diphenylphosphanyl-pyridine)Cl] reported in our previous work[5] on DTO chirality, where ruthenium and platinum are *N*,*N*′- and *S*,*S*′-chelated, respectively. The difference arises from the *N*,*N*′-ditolyl-dithioxamidato, which undergoes *S*,*N*-chelation in order to better distribute the steric hindrance between tolyl substituents and *p*-cymene on two ruthenium centres. This arrangement, similar to an already reported *SN* coordination,[20] causes the C_i symmetry of the binuclear complex (if the tetrahedral ruthenium atom is a chiral centre, then the whole molecule is a *meso* form) and the formation of the observed centrosymmetric crystal packing in the solid state. The coordination through the bigger sulfur atom causes a slight elongation of the Ru−N bond with respect to the mean 2.06(1) Å value reported for the *N*,*N*-chelation.[21]

Table 2. Selected interatomic distances (Å) and angles (deg) for **12f·2CHCl₃**

Ru−Cl(1)	2.418(2)	Ru−S(1)	2.357(2)
Ru−N(1)	2.105(6)	Ru−Xcym	1.685(6)
Ru−C(2)	2.256(6)	Ru−C(3)	2.222(8)
Ru−C(4)	2.170(7)	Ru−C(5)	2.175(7)
Ru−C(6)	2.174(7)	Ru−C(7)	2.188(6)
C(2)−C(3)	1.39(1)	C(2)−C(7)	1.40(1)
C(2)−C(8)	1.52(1)	C(3)−C(4)	1.425(9)
C(4)−C(5)	1.41(1)	C(5)−C(6)	1.42(1)
C(5)−C(9)	1.52(1)	C(6)−C(7)	1.409(9)
C(9)−C(10)	1.52(1)	C(9)−C(11)	1.53(1)
S(1)−C(1)	1.724(7)	C(1)−C(1′)	1.46(1)
N(1)−C(1′)	1.314(7)	N(1)−C(12)	1.46(1)
C(12)−C(13)	1.49(1)		
N(1)−Ru−Xcym	133.7(3)	S(1)−Ru−Xcym	127.9(3)
Cl(1)−Ru−Xcym	126.3(3)	S(1)−Ru−N(1)	81.2(2)
Cl(1)−Ru−N(1)	83.3(2)	Cl(1)−Ru−S(1)	88.23(8)
C(7)−C(2)−C(8)	121.0(7)	C(3)−C(2)−C(8)	120.7(7)
C(3)−C(2)−C(7)	118.2(7)	C(2)−C(3)−C(4)	121.2(7)
C(3)−C(4)−C(5)	120.9(7)	C(4)−C(5)−C(9)	122.7(7)
C(4)−C(5)−C(6)	117.2(7)	C(6)−C(5)−C(9)	120.0(6)
C(5)−C(6)−C(7)	121.0(6)	C(2)−C(7)−C(6)	121.4(7)
C(5)−C(9)−C(11)	113.4(7)	C(5)−C(9)−C(10)	111.0(7)
C(10)−C(9)−C(11)	110.8(7)	Ru−N(1)−C(1′)	122.1(5)
Ru−S(1)−C(1)	100.3(2)	S(1)−C(1)−N(1′)	123.9(5)
S(1)−C(1)−C(1′)	118.2(5)	C(1)−C(1′)−N(1)	117.9(6)
C(12)−N(1)−C(1′)	118.5(6)	Ru−N(1)−C(12)	118.9(4)
N(1)−C(12)−C(13)	114.2(6)		

The DTO bridge exhibits a flat arrangement, observed in all the known complexes of the bis-chelating dithioxamide derivatives. The Ru atom is 0.116(1) Å out of the mean plane of the perfectly planar NSC−CSN fragment, in whose respect the tolyl substituent is disposed orthogonally [dihedral angle 81.5(2)°, torsion angle C(1′)−NCH₂−C_{phen} −92.7(8)°] to minimise the hindrance with the ruthenium bonded *p*-cymene. The C(1)−C(1′) distance of 1.46(1) Å is evidence of the large conjugation on the whole NSC−CSN system, as compared with the tilted conformation of the mono-chelate neutral *S*,*S*′-coordinated complexes with the C−C distance over 1.5 Å.[21]

Experimental Section

General Remarks: ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded, at 298 K, on a Bruker ARX-300 spectrometer equipped with a broad-band probe operating at 300.13 and 75.46 MHz, respectively [δ (ppm) relative to Me_4Si, *J*(Hz)]. Electronic impact (EI) mass spectra were recorded with a Finnigan MAT 90 reverse-geometry double-focusing mass spectrometer. Sample was introduced into the EI source by a heated direct inlet probe. Ion source conditions: ionisation energy 70 eV; acceleration voltage 5 kV; temperature 220 °C.

The reagents are commercially available products used as purchased. Solvents were freshly distilled from sodium wire under a nitrogen atmosphere.

The dithioxamides **1**, **5**, **6**, **8**, **9**, **10**, **11**,[26] **7**,[27] and the starting complex [(η⁶-*p*-cymene)$RuCl_2$]$_2$ [28] were prepared according to known procedures. Compounds **2**, **3**, and **4**, already known,[26] were prepared with the following improved procedure: $H_4N_2C_2S_2$ (1 g, 8.32 mmol) was suspended in 50 mL of water and six fold excess (49.9 mmol) of the corresponding amine was added to the mixture. On stirring, yellow micro crystals of the product separated in a highly pure form.

[Ru(*p*-Cy)Cl]₂(μ-Me₂DTO) (12a): To a solution of [(η⁶-*p*-cymene)$RuCl_2$]$_2$ (612.4 mg, 1 mmol) in chloroform (100 mL), was added ligand **1** (148.2 mg, 1 mmol) and the mixture allowed to stand for 0.5 h at room temperature. After this time, the solution was concentrated to 10 mL and petroleum ether 40−60 (about 100 mL) added. A red brown solid precipitated, which was dissolved in the minimum amount of chloroform and purified by chromatography on silica with chloroform as eluent. The pure product was finally obtained by precipitation adding petroleum ether 40−60 (about 100 mL) to concentrated portions (about 10 mL) of eluates. Yield: 516 mg, 75%. ^{1}H NMR ($CDCl_3$): δ = 1.16, 1.23 [2 d, $^3J_{H,H}$ = 6.7 Hz, 6 H each, $CH(CH_3)_2$, cymene], 2.18 (s, 6 H, CH_3, cymene), 2.81 [seven lines, 2 H, $^3J_{H,H}$ = 6.7 Hz, $CH(CH_3)_2$, cymene], 3.88 (s, 6 H, NCH_3), 5.06, 5.18, 5.26, 5.42, (4 d, 2 H each, $^3J_{H,H}$ = 5.9 Hz, $H^{2,3,5,6}$, cymene). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.8 (s, CH_3, cymene), 22.0, 22.7 [2 s, $CH(CH_3)_2$, cymene], 30.9 [s, $CH(CH_3)_2$, cymene], 50.6 (s, NCH_3), 81.3, 81.8, 85.6, 85.8, (4 s, $C^{2,3,5,6}$, cymene), 99.9, 104.2, (2 s, $C^{1,4}$, cymene), 188.7 (s, CS). $C_{24}H_{34}Cl_2N_2Ru_2S_2$ (687.72): calcd. C 41.92, H 4.98, N 4.07, S 9.32, Cl 10.31; found C 41.40, H 4.92, N 4.00, S 9.40, Cl 10.24.

[Ru(*p*-Cy)Cl]₂(μ-Et₂DTO) (12b): This reddish compound was obtained as described for **12a** by using **2** (176.3 mg, 1 mmol) in place of **1**. Yield: 501 mg, 70%. ^{1}H NMR ($CDCl_3$): δ = 1.14, 1.23 [2 d, 6 H each, $^3J_{H,H}$ = 6.6 Hz, $CH(CH_3)_2$, cymene], 1.47 (t, 6 H, $^3J_{H,H}$ = 6.6 Hz, NCH_2CH_3), 2.20 (s, 6 H, CH_3, cymene), 2.81 [seven lines, 2 H, $^3J_{H,H}$ = 6.6 Hz, $CH(CH_3)_2$, cymene], 4.08, 4.57 (2 dq, 2 H each, $^2J_{H,H}$ = 13.6 Hz, $^3J_{H,H}$ = 7.0 Hz, NCH_2CH_3),

4.99, 5.14, 5.31, 5.40, (4 d, 2 H each, $^3J_{H,H}$ = 6.6 Hz, $H^{2,3,5,6}$, cymene). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.9 (s, NCH_2CH_3), 18.5 (s, CH_3, cymene), 21.8, 22.8 [2 s, $CH(CH_3)_2$, cymene], 30.7 [s, $CHCH_3)_2$, cymene], 58.3 (s, NCH_2CH_3), 80.4, 81.7, 85.1, 86.5, (4 s, $C^{2,3,5,6}$, cymene), 100.0, 104.5 (2 s, $C^{1,4}$, cymene), 188.3 (s, CS). $C_{26}H_{38}Cl_2N_2Ru_2S_2$ (715.77): calcd. C 43.63, H 5.35, N 3.91, S 8.96, Cl 9.91; found C 43.41, H 5.38, N 3.82, S 8.98, Cl 9.70.

[Ru(*p*-Cy)Cl]$_2$(μ-*n*Pr$_2$DTO) (12c): This compound was obtained as a reddish powder from [(η^6-*p*, cymene)$RuCl_2]_2$ (612.4 mg, 1 mmol) and **3** (204.3 mg, 1 mmol) following the procedure reported for **12a**. Yield: 521 mg, 70%. ^1H NMR ($CDCl_3$): δ = 1.14, 1.23 [2 d, 6 H each, $^3J_{H,H}$ = 6.6 Hz, $CH(CH_3)_2$, cymene], 1.22 (t, 6 H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_3$), 1.52÷1.96 (m, 4 H, $NCH_2CH_2CH_3$), 2.19 (s, 6 H, CH_3, cymene), 2.81 [seven lines, 2 H, $^3J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$, cymene], 3.91, 4.46, (2 m, 2 H each, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 6.0 Hz, $NCH_2CH_2CH_3$), 4.97, 5.13, 5.28, 5.38 (4 d, 2 H each, $^3J_{H,H}$ = 6.8 Hz, $H^{2,3,5,6}$, cymene). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 12.0 (s, $NCH_2CH_2CH_3$), 18.6 (s, CH_3, cymene), 22.7, 22.8 [2 s, $CH(CH_3)_2$, cymene], 20.1 (s, $NCH_2CH_2CH_3$), 30.7 [s, $CH(CH_3)_2$, cymene], 65.7 (s, $NCH_2CH_2CH_3$), 80.5, 81.5, 85.5, 86.5 (4 s, $C^{2,3,5,6}$, cymene), 100.0, 105.0 (2 s, $C^{1,4}$, cymene), 189.0 (s, CS). $C_{28}H_{42}Cl_2N_2Ru_2S_2$ (743.82): calcd. C 45.21, H 5.69, N 3.77, S 8.62, Cl 9.53; found C 45.35, H 5.71, N 3.65, S 8.53, Cl 9.38.

[Ru$_2$(*p*-Cy)$_2$Cl$_2$](μ-*n*Bu$_2$DTO) (12d): This reddish compound was prepared as described for **12a** by using **4** (232.4 mg, 1 mmol) in place of **1**. Yield: 540 mg, 70%. ^1H NMR ($CDCl_3$): δ = 1.04 (t, 6 H, $^3J_{H,H}$ = 7.1 Hz, $NCH_2CH_2CH_2CH_3$), 1.14, 1.24 [2 d, 6 H each, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, cymene], 1.42÷2.19 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 2.20 (s, 6 H, CH_3, cymene), 2.81 [seven lines, 2 H, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, cymene], 3.98, 4.52 (2 dt, 2 H each, $^2J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 6.9 Hz, $NCH_2CH_2CH_2CH_3$), 4.98, 5.13, 5.30, 5.39, (4 d, 2 H each, $^3J_{H,H}$ = 5.5 Hz, $H^{2,3,5,6}$, cymene). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.0 (s, $NCH_2CH_2CH_2CH_3$), 18.7 (s, CH_3, cymene), 21.0 (s, $NCH_2CH_2CH_2CH_3$), 22.7, 21.9 [2 s, $CH(CH_3)_2$, cymene], 28.5 (s, $NCH_2CH_2CH_2CH_3$), 30.7 [s, $CH(CH_3)_2$, cymene], 69.9 (s, $NCH_2CH_2CH_2CH_3$), 80.4, 81.6, 84.9, 86.7, (4 s, $C^{2,3,5,6}$, cymene), 99.9, 104.6 (2 s, $C^{1,4}$, cymene), 189.9 (CS). $C_{30}H_{46}Cl_2N_2Ru_2S_2$ (771.8): calcd. C 46.68, H 6.01, N 3.63, S 8.31, Cl 9.19; found C 46.69, H 6.11, N 3.48, S 8.24, Cl 9.10.

[Ru(*p*-Cy)Cl]$_2$(μ-Isoamyl$_2$DTO) (12e): This reddish compound was prepared as described for **12a** by using **5** (260.5 mg, 1 mmol) in place of **1**. Yield: 600 mg, 70%. ^1H NMR ($CDCl_3$): δ = 1.03 [d, 6 H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH(CH_3)_2$], 1.15, 1.25 [2 d, 6 H each,, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, cymene], 1.62−2.19 [m, 6 H, $NCH_2CH_2CH(CH_3)_2$], 2.19 (s, 6 H, CH_3, cymene), 2.82 [seven lines, $^3J_{H,H}$ = 6.9, 2 H, $CH(CH_3)_2$, cymene], 4.03, 4.50 [2 dt, 2 H each, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 5.9 Hz, $NCH_2CH_2CH(CH_3)_2$], 4.99, 5.21, 5.31, 5.40 (4 d, 2 H each, $^3J_{H,H}$ = 5.6 Hz, $H^{2,3,5,6}$, cymene). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.7 (s, CH_3, cymene), 22.0, 22.7 [2 s, $CH(CH_3)_2$, cymene], 22.7 [s, $NCH_2CH_2CH(CH_3)_2$], 27.2 [s, $NCH_2CH_2CH(CH_3)_2$], 34.7 [s, $CH(CH_3)_2$, cymene], 34.8 [s, $NCH_2CH_2CH(CH_3)_2$], 62.8 [s, $NCH_2CH_2CH(CH_3)_2$], 80.2, 81.2, 84.7, 86.9, (4 s, $C^{2,3,5,6}$, cymene), 99.7, 104.5 (2 s, $C^{1,4}$, cymene), 188.0 (CS). $C_{32}H_{50}Cl_2N_2Ru_2S_2$ (799.93): calcd. C 48.05, H 6.30, N 3.50, S 8.02, Cl 8.86; found C 48.10, H 6.40, N 3.40, S 8.00, Cl 8.81.

[Ru(*p*-Cy)Cl]$_2$(μ-Benzyl$_2$DTO) (12f): This reddish compound was prepared as described for **12a** by using **6** (324.5 mg, 1 mmol) in place of **1**. Yield: 588 mg, 70%. ^1H NMR ($CDCl_3$): δ = 1.14, 1.33 [2d, 3 H each, $^3J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$, cymene], 2.10 (s, 3 H, CH_3, cymene), 2.68 [seven lines, 1 H, $^3J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$, cymene], 4.20, 4.50 (2 d, 2 H each, $^2J_{H,H}$ = 14.7 Hz $NCH_2C_6H_5$), 4.65, 4.71, 5.17, 5.21, (4d, 1 H each, $^3J_{H,H}$ = 5.5 Hz, $H^{2,3,5,6}$, cymene), 7.37 (m, 3 H, $H^{m,p}$ of $NCH_2C_6H_5$), 7.51 (d, 2 H, $^3J_{H,H}$ = 7.6 Hz, $H_o$of $NCH_2C_6H_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.4 (s, CH_3, cymene), 21.6, 22.3 [2 s, $CH(CH_3)_2$, cymene], 30.7 [s, $CH(CH_3)_2$, cymene], 66.3 (s, $NCH_2C_6H_5$), 79.7, 82.0, 83.3, 83.8, (4 s, $C^{2,3,5,6}$, cymene), 99.4, 105.0 (2 s, $C^{1,4}$, cymene), 128.1−129.1 (CH^{Ph} of $NCH_2C_6H_5$), 133.9 (s, C_{quat} of $NCH_2C_6H_5$), 187.2 (s, CS). $C_{36}H_{42}Cl_2N_2Ru_2S_2$ (839.91): calcd. C 51.48, H 5.04, N 3.34, S 7.63, Cl 8.44; found C 51.43, H 5.10, N 3.32, S 7.60, Cl 8.20.

[Ru(*p*-Cy)Cl]$_2$(μ-*p*-Tolyl$_2$DTO) (12g): This reddish compound was prepared as described for **12a** by using **7** (324.5 mg, 1 mmol) in place of **1**. Yield: 588 mg, 70%. ^1H NMR ($CDCl_3$): δ = 1.07, 1.10 [2 d, 6 H each, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, cymene], 2.05 (s, 6 H, CH_3, cymene), 2.42 (s, 6 H, $NC_6H_5CH_3$), 2.61 [seven lines, 2 H, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, cymene], 4.60, 4.76, 4.79, 5.01 (4 d, 2 H each, $^3J_{H,H}$ = 5.7 Hz, $H^{2,3,5,6}$, cymene), 7.25 (2 d, 4 H, $^3J_{H,H}$ = 8.4 Hz, H_m of $NC_6H_4CH_3$), 7.44 (m, 4 H, H_o of $NC_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.7 (s, CH_3, cymene), 21.3 (s, $NC_6H_5CH_3$), 21.6, 22.9 (2 s, $CH(CH_3)_2$, cymene), 30.7 [s, $CH(CH_3)_2$, cymene], 81.4, 81.5, 84.4, 87.5 (4 s, $C^{2,3,5,6}$, cymene), 100.9, 103.7 (2 s, $C^{1,4}$, cymene), 123.4, 129.5 (2 s, CH_{Ph} of $NC_6H_5CH_3$), 135.7, 152.9 (2 s, C_{quat} of $NC_6H_5CH_3$), 192.4 (s, CS). $C_{36}H_{42}Cl_2N_2Ru_2S_2$ (839.91): calcd. C 51.48, H 5.04, N 3.34, S 7.63, Cl 8.44; found C 51.35, H 5.09, N 3.28, S 7.65, Cl 8.32.

Complex {[Ru(*p*-Cy)Cl(H$_2$-(R)-1-phenylethyl$_2$DTO)]$^+$, (Cl^-)} (13a): To a solution of $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (612.4 mg, 1 mmol) dissolved in chloroform (100 mL), was added **8** (657.0 mg, 2 mmol), and the mixture allowed to stand for 0.5 h at room temperature. After this time the solution was concentrated to a small volume (about 10 mL), and petroleum ether 40−60 (100 mL) was added. Complex **13a** precipitated as a brown powder. Yield: 622 mg, 98% − ^1H NMR ($CDCl_3$): δ = 1.13, 1.16 [2 d, 3 H each, $^3J_{H,H}$ = 7.0 Hz, $CH(CH_3)_2$, cymene], 1.89, 1.93 [2 d, 3 H each, $^3J_{H,H}$ = 7.0 Hz, $NHCH(CH_3)Ph$], 2.19 (s, 3 H, CH_3, cymene), 2.62 [seven lines, 1 H, $^3J_{H,H}$ = 7.0 Hz, $CH(CH_3)_2$, cymene], 5.26, 5.41 [2 q, 1 H each, $^3J_{H,H}$ = 7.0 Hz, $NHCH(CH_3)Ph$], 5.39, 5.45, 5.51, 5.56, (4 d, 1 H each, $^3J_{H,H}$ = 5.9 Hz, $H^{2,3,5,6}$, cymene), 7.34 [m, 6 H, $H_{m,p}$ of $NHCH(CH_3)Ph$], 7.56, 7.61 [2 d, 4 H, $^3J_{H,H}$ = 7.0 Hz, H_o of $NHCH(CH_3)Ph$], 13.3 [br. s, 2 H, $NHCH(CH_3)Ph$]. $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ = 18.7 (s, CH_3, cymene), 21.5, 22.4 [2 s, $NHCH(CH_3)Ph$], 22.2, 22.5 [2 s, $CH(CH_3)_2$, cymene], 31.2 [s, $CH(CH_3)_2$, cymene], 60.5, 61.0 [2 s, $NHCH(CH_3)Ph$], 86.5, 86.7, 87.4, 87.8 (4 s, $C^{2,3,5,6}$, cymene), 104.3, 107.7 (2 s, $C^{1,4}$, cymene), 127.4−128.8 [CH_{Ph} of $NHCH(CH_3)Ph$], 139.8, 140.4 [2 s, C_{quat} $NHCH(CH_3)Ph$], 186.9, 187.1 (2 s, CS). $C_{28}H_{34}Cl_2N_2RuS_2$ (634.69): calcd. C 52.99, H 5.40, N 4.41, S 10.10, Cl 11.17; found C 52.88, H 5.52, N 4.45, S 10.05, Cl 11.12.

{Ru(*p*-Cy)Cl(H$_2$-(*R*,S)-1-phenylethyl$_2$DTO)$^+$, (Cl^-)} (13b): This brown compound was prepared as described for **13a** by using **9** (657.0 mg, 2 mmol) in place of **8**. Yield: 609 mg, 96%. ^1H NMR ($CDCl_3$): δ = 1.08 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, $CH(CH_3)_2$, cymene], 1.93 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, $NHCH(CH_3)Ph$], 2.13 (s, 3 H, CH_3, cymene), 2.52 [seven lines, 1 H, $^3J_{H,H}$ = 7.0 Hz, $CH(CH_3)_2$, cymene], 5.37, 5.49 (2 d, 2 H each, $^3J_{H,H}$ = 5.9 Hz, $H^{2,3,5,6}$, cymene), $NHCH(CH_3)Ph$ obscured by *p*-cymene ring signals, 7.33 [m, 6 H, $H_{m,p}$ of $NHCH(CH_3)Ph$], 7.58 [d, 4 H, $^3J_{H,H}$ = 7.0 Hz, H_o $NHCH(CH_3)Ph$], 13.4 [br. s, 2 H, $NHCH(CH_3)Ph$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.4 (s, CH_3, cymene), 21.6 and 22.3 [2 s, $CH(CH_3)_2$, cymene], 22.4 (s, $NHCH(CH_3)Ph$], 30.7 [s, $CH(CH_3)_2$, cymene], 60.6 [s, $NHCH(CH_3)Ph$], 79.7, 83.3 (2s, $C^{2,3,5,6}$, cymene), 99.4, 105.0 (2 s, $C^{1,4}$, cymene), 128.58 −140.19 (aromatic carbons of $NHCH(CH_3)Ph$), 185.8 (s, CS). − $RuC_{28}H_{34}N_2S_2Cl_2$ (634.69):

calcd. C 52.99, H 5.40, N 4.41, S 10.10, Cl 11.17; found C 52.87, H 5.53, N 4.44, S 10.07, Cl 11.15.

{Ru(*p*-Cy)Cl(H_2-*i*Pr_2DTO)$^+$, (Cl^-)} (13c): This brown compound was prepared as described for **13a** by using **10** (408.6 mg, 2 mmol) in place of **8**. The reaction product was a diastereoisomer mixture analysed without purification. Yield: 490 mg, 96%. ^{1}H NMR ($CDCl_3$): δ = 1.24 [d, 6 H, $^3J_{H,H}$ = 6.9 Hz, CH(CH_3)$_2$, cymene], 1.24 [d, 12 H, $^3J_{H,H}$ = 6.9 Hz, NHCH(CH_3)$_2$], 5.64, 5.49 (2 d, 2 H each, $^3J_{H,H}$ = 6.0 Hz, $H^{2,3,5,6}$, cymene), 2.26 (s, 3 H, CH_3, cymene), 2.81 [seven lines, 1 H, $^3J_{H,H}$ = 6.9 Hz, C*H*(CH$_3$)$_2$, cymene], 12.6 [br. s, 2 H, N*H*CH(CH$_3$)$_2$], 4.17 [seven lines, $^3J_{H,H}$ = 6.9 Hz, 2 H, NHC*H*(CH$_3$)$_2$], − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.6 (s, CH_3, cymene), 22.2 [s, CH(*C*H$_3$)$_2$, cymene], 24.6, 24.8 [2 s, NHCH(*C*H$_3$)$_2$], 31.0 [s, *C*H(CH$_3$)$_2$, cymene], 59.9 [s, NH*C*H(CH$_3$)$_2$], 86.1, 87.0 (2 s, $C^{2,3,5,6}$, cymene), 103.9, 107.1 (2 s, $C^{1,4}$, cymene), 184.4 (s, *C*S). − $RuC_{18}H_{30}N_2S_2Cl_2$ (510.55): calcd. C 42.35, H 5.92, N 5.49, S 12.56, Cl 13.89; found C 42.27, H 5.98, N 5.45, S 12.55, Cl 13.90.

{Ru(*p*-Cy)Cl[H_2-(cyclohexyl)$_2$DTO]$^+$ (Cl^-)} (13d): This brown compound was prepared as described for **13a** by using **11** (569.0 mg, 2 mmol) in place of **8**. Yield: 567 mg, 95%. ^{1}H NMR ($CDCl_3$): δ = 1.28 [d, 6 H, $^3J_{H,H}$ = 6.7 Hz, CH(CH_3)$_2$, cymene], 1.86 (m, 20 H, CH_2 of NHC_6H_{11}), 2.29 (s, 3 H, CH_3, cymene), 2.84 [seven lines, 1 H, $^3J_{H,H}$ = 6.7 Hz, C*H*(CH$_3$)$_2$, cymene], 4.21 (m, 2 H, CH of NHC_6H_{11}), 5.50, 5.66 (2d, 2 H each, $^3J_{H,H}$ = 5.9 Hz, $H^{2,3,5,6}$, cymene), 12.6 (br. s, 2 H, N*H*C_6H_{11}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.9 (s, CH_3, cymene), 22.5 [s, CH(*C*H$_3$)$_2$, cymene], 24.8, 25.0, 25.1, 30.0, 30.1 (5 s, CH_2 of NHC_6H_{11}), 31.3 [s, *C*H(CH$_3$)$_2$, cymene], 60.3 (s, CH of NHC_6H_{11}), 86.3, 87.3 (2 s, $C^{2,3,5,6}$, cymene), 104.1, 107.5, (2 s, $C^{1,4}$, cymene), 184.8 (s, *C*S). − $RuC_{24}H_{38}N_2S_2Cl_2$ (590.68): calcd. C 48.80, H 6.48, N 4.74, S 10.86, Cl 12.00; found C 48.84, H 6.55, N 4.71, S 10.80, Cl 12.04.

Ru(*p*-Cy)Cl[H-(*R*)-1-(phenylethyl)$_2$DTO] (14a): A solution of **13a** (634.7 mg, 1 mmol) dissolved in about 15 mL of chloroform was purified by column chromatography. During chromatography, owing to HCl loss, the brown solution turned yellow. The yellow eluate was concentrated to a small volume (about 10 mL), and then petroleum ether/diethyl ether (boiling range 40−60 °C) was added (about 100 mL). The complex precipitated as yellow powder. Yields: 425 mg, 71%. ^{1}H NMR ($CDCl_3$): δ = 1.21, 1.22 [2 d, 3 H each, $^3J_{H,H}$ = 7.0 Hz, CH(CH_3)$_2$, cymene], 1.56 and 1.58 [2 d, 3 H each, $^3J_{H,H}$ = 7.0 Hz, NHCH(CH_3)Ph], 2.25 (s, 3 H, CH_3, cymene), 2.79 [seven lines, 1 H, $^3J_{H,H}$ = 7.0 Hz, C*H*(CH$_3$)$_2$, cymene], 5.2 [NHC*H*(CH$_3$)Ph partially obscured by *p*-cymene ring signals], 5.36 (m, 4 H, $H^{2,3,5,6}$, cymene), 7.35 [m, 10 H, $H_{o,m,p}$ of NHCH(CH$_3$)Ph], − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.6 (s, CH_3, cymene), 21.0, 22.4 [2s, NHCH(*C*H$_3$)Ph], 22.4 and 22.5 [2 s, (CH*C*H$_3$)$_2$, cymene], 30.9 [s, *C*H(CH$_3$)$_2$, cymene], 55.8, 58.0 [2 s, NH*C*H(CH$_3$)Ph], 84.5, 84.6, 85.7, 85.8 (4 s, $C^{2,3,5,6}$, cymene), 101.6, 104.7 (2 s, $C^{1,4}$, cymene), 126.61−143.08 [C_{Ph} of NHCH(CH$_3$)Ph], 177.9, 181.0 (2 s, *C*S). − $RuC_{28}H_{33}N_2S_2Cl$ (598.23): calcd. C 56.22, H 5.56, N 4.68, S 10.72, Cl 5.93; found C 56.25, H 5.55, N 4.72, S 10.80, Cl 5.85.

Ru(*p*-Cy)Cl[H-(*R*,S)-1-(phenylethyl)$_2$DTO] (14b): This compound was obtained by following the procedure reported for **14a**, starting from complex **13b** (634.7 mg, 1 mmol). Yields: 425 mg, 71%. ^{1}H NMR ($CDCl_3$): δ = 1.12 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, CH(CH_3)$_2$, cymene], 1.59 [d, 6 H, $^3J_{H,H}$ = 7.0 Hz, NHCH(CH_3)Ph], 2.21 (s, 3 H, CH_3, cymene), 2.66 [seven lines, 1 H, $^3J_{H,H}$ = 7.0 Hz, C*H*(CH$_3$)$_2$, cymene], ≈ 5.3 [m, NHC*H*(CH$_3$)Ph partially obscured by *p*-cymene ring signals], 5.36 (m, 4 H, $H^{2,3,5,6}$, cymene), 7.3 [m, 10 H, $H_{o,m,p}$ of NHCH(CH$_3$)Ph]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.5 (s, CH_3, cymene), 20.9, 22.4 [2 s, NHCH(*C*H$_3$)Ph], 22.4 [s, CH(*C*H$_3$)$_2$], 30.8 [s, *C*H(CH$_3$)$_2$, cymene], 57.9 [s, NH*C*H(CH$_3$)Ph], 84.6, 85.5, (2 s, $C^{2,3,5,6}$, cymene), 101.6, 104.7 (2 s, $C^{1,4}$, cymene), 128.4−143.3 [aromatic carbons of NHCH(CH$_3$)Ph], 179.6 (1s, *C*S). − $RuC_{28}H_{33}N_2S_2Cl$ (598.23): calcd. C 56.22, H 5.56, N 4.68, S 10.72, Cl 5.93; found C 56.23, H 5.57, N 4.70, S 10.82, Cl 5.83.

[Ru(*p*-Cy)Cl(H−*i*Pr_2DTO)] (14c): This compound was obtained following the procedure reported for **14a**, starting from **13c** (510.5 mg, 1 mmol). Yields: 379 mg, 80%. ^{1}H NMR ($CDCl_3$): δ = 1.24 [d, 6 H, $^3J_{H,H}$ = 6.8 Hz, CH(CH_3)$_2$, cymene], 1.25 [d, 12 H, $^3J_{H,H}$ = 5.8 Hz, NCH(CH_3)$_2$], 2.24 (s, 3 H, CH_3, cymene), 2.85 [seven lines, 1 H, $^3J_{H,H}$ = 6.8 Hz, C*H*(CH$_3$)$_2$, cymene], 4.36 [seven lines, 2 H, $^3J_{H,H}$ = 5.8 Hz, NC*H*(CH$_3$)$_2$], 5.30, 5.47 (2 d, 2 H each, $^3J_{H,H}$ = 5.8 Hz, $H^{2,3,5,6}$, cymene). − $RuC_{18}H_{29}N_2S_2Cl$ (474.09): calcd. C 45.60, H 6.17, N 5.91, S 13.52, Cl 7.48; found C 45.52, H 6.27, N 5.90, S 13.48, Cl 7.55.

{Ru(*p*-Cy)Cl[H−(cyclohexyl)$_2$DTO]} (14d): This compound was obtained following the procedure reported for **14a**, starting from complex **13d** (590.7 mg, 1 mmol). Yields: 432 mg, 78%. ^{1}H NMR ($CDCl_3$): δ = 1.25 [d, 6 H, $^3J_{H,H}$ = 6.9 Hz, CH(CH_3)$_2$, cymene], 1.25−2.02 (m, 20 H, CH_2 of $NHCC_6H_{11}$), 2.23 (s, 3 H, CH_3, cymene), 2.84 [seven lines, 1 H, $^3J_{H,H}$ = 6.90 Hz, C*H*(CH$_3$)$_2$, cymene], 4.04 (m, 2 H, CH of $NHCC_6H_{11}$), 5.30, 5.45 (2 d, 2 H each, $^3J_{H,H}$ = 6.3 Hz, $H^{2,3,5,6}$, cymene). ^{13}C {^{1}H} NMR ($CDCl_3$): δ = 18.4 (s, CH_3, cymene), 22.2 [s, CH(*C*H$_3$)$_2$, cymene], 24.2, 24.4, 25.3, 31.2, 31.5, (5 s, CH_2 of $NHCC_6H_{11}$), 30.6 [s, *C*H(CH$_3$)$_2$, cymene], 57.2 (s, CH of $NHCC_6H_{11}$), 85.2, 84.0 (2 s, $C^{2,3,5,6}$, cymene), 104.1, 101.1 (2 s, $C^{1,4}$, cymene), 177.4 (s, *C*S). − $RuC_{24}H_{37}N_2S_2Cl$ (554.22): calcd. C 52.01, H 6.73, N 5.05, S 11.57, Cl 6.40; found C 52.07, H 6.75, N 5.01, S 11.51, Cl 6.47.

Single-Crystal X-ray Diffraction Studies of 12f: Suitable crystals of the complex **12f** (with R = R′ = benzyl) were obtained by slow evaporation of solvent from a chloroform/MeOH (1:1) solution. Diffraction data were collected on a Siemens R3m/V automatic four-circle diffractometer. Lattice parameters were obtained from least-squares refinement of the setting angles of 30 reflections within 15 ≤ 2θ ≤ 30° range. A summary of the crystallographic data and the structure refinement is reported in Table 1. A significant crystal deterioration was evidenced by the measurement of three standard reflections, monitored every 97 measurements. When the standard intensities decreased below 40% of the starting values, a new crystal was mounted to complete data collection (one third of the whole data). The reflection intensities were evaluated by a learnt-profile procedure[22] among 2θ shells, and then corrected for Lorentz-polarization effects. The data of each set were scaled on the standard intensities separately, while an inter-scaling factor was included and refined in the last least-square model recycling. No account was taken for absorption and extinction effects.

The structure was resolved by standard methods with the SHELXTL-PLUS system[23] and subsequently completed by a combination of least-squares technique and Fourier Syntheses. All non-hydrogen atoms were refined anisotropically. Whilst the final difference Fourier maps showed several hydrogen positions, the H atoms were placed in calculated positions (d_{X-H} = 0.960 Å) and included in the refinement among the "riding model" method with a unique common refined thermal isotropic displacement parameter [U_{iso} = 0.064(6) Å^2]. The refinement was carried out by the full-matrix least-squares technique, minimising the function $\Sigma w(|F_o| - |F_c|)^2$. In the last difference Fourier map, obtained with

the final weighting scheme $w^{-1} = [\sigma^2(F) + 0.0023*(F)^2]$, the minimum and maximum density residuals were −0.48 and 0.49 eÅ^{-3}, respectively. Neutral-atom scattering factors and anomalous dispersion corrections come from ref.[24]

All calculations were performed using the SHELXTL-PLUS system. The final geometrical calculations and drawings were carried out with the PARST program[25] and the XP utility of the Siemens package, respectively. Selected bond lengths and bond angles are reported in Table 2. By considering that the complex **12f** is placed at a crystallographic inversion centre, Figure 2 shows the atom-labelling scheme of the asymmetric moiety, which represents half a molecule.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 164512. Copies of the data can be obtained free of charge on applicaton to The Director, CCDC, 12 Union Road,m Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk

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