Transition Metal Complexes with Sulfur Ligands, 134[+]

Synthesis of the Tetradentate Thioether Amine and Thioether Thiolate Ligands ′tpS$_2$(NH$_2$)$_2$′ and ′tpS$_4$′-H$_2$ and Some Representative Six-Coordinate Ruthenium and Osmium Complexes [′tpS$_2$(NH$_2$)$_2$′ = 1,2-Bis(2-aminophenylthio)phenylene; ′tpS$_4$′$^{2-}$ = 1,2-Bis(2-mercaptophenylthio)phenylene(2–)]

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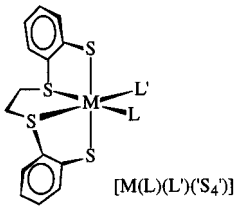
Dedicated to Professor Bernt Krebs on the occassion of his 60th birthday

Keywords: Cleavage reactions / C–S cleavage / Ligand synthesis / Osmium / Ruthenium / S ligands

In search of a tetradentate thioether thiolate ligand that is more stable toward reductive C–S bond cleavage than the parent ligand ′S$_4$′-H$_2$ [′S$_4$′-H$_2$ = 1,2-bis(2-mercaptophenylthio)ethane], the novel tris-phenylene ligand ′tpS$_4$′-H$_2$ (**3**) [′tpS$_4$′-H$_2$ = 1,2-bis(2-mercaptophenylthio)phenylene] was synthesized via the nitro and amine compounds ′tpS$_2$(NO$_2$)$_2$′ (**1**) and ′tpS$_2$(NH$_2$)$_2$′ (**2**). The coordination of ′tpS$_4$′$^{2-}$ to ruthenium centers resulted in the formation of six-coordinate [Ru(L)(PR$_3$)(′tpS$_4$′)] complexes (R = Et, L = PEt$_3$ **4**; R = Ph, L = PPh$_3$ **5**, CO **6**, DMSO **7**). The X-ray structure analyses of **4** and **6** revealed that the thiolate donors occupy trans positions; consequently the ′tpS$_4$′$^{2-}$ ligand coordinates in the same way as the ′S$_4$′$^{2-}$ ligand. The stability of the ′tpS$_4$′$^{2-}$ ligand toward reductive C–S cleavage reactions was shown by the synthesis of [Os(PEt$_3$)$_2$(′tpS$_4$′)] (**8**). In contrast to [Os(PEt$_3$)$_2$(′S$_4$′)], **8** is stable for unlimited periods of time. The X-ray structure analysis of [Ru(Cl)$_2$(PPh$_3$)(′tpS$_2$(NH$_2$)$_2$′)] (**9**) demonstrates that the potentially tetradentate ligand ′tpS$_2$(NH$_2$)$_2$′ coordinates in **9** through three donors leaving one NH$_2$ donor dangling.

The tetradentate thioether thiolate ligand ‘S$_4$’−H$_2$ [= 1,2-bis(2-mercaptophenylthio)ethane] exhibits a rich coordination chemistry. It binds to numerous transition metals, e.g. Fe, Ru, Os, Cr, Mo, W, Ni, and the resulting [M(′S$_4$′)] complex fragments are able to coordinate a large variety of coligands to give six-coordinate complexes of the type [M(L)(L′)(′S$_4$′)].[1]



[M(L)(L')('S4')]

The coligands L or L′ range from hard ligands such as halides or oxide to soft ligands such as CO or phosphanes. The coligands also include a large number of biologically relevant small species, for example, N$_2$H$_2$, N$_2$H$_3$, N$_2$H$_4$, NH$_3$, NO$^+$, NO, NH$_2$O, H$_2$, H$^-$, CH$_3^-$, CH$_3$CO$^-$, H$_2$S, or S$_2$. The activation or stabilization and the reactivity of these small species is strongly influenced by the [M(′S$_4$′)] cores. In some of these reactions, the ′S$_4$′$^{2-}$ ligand appears to behave as a ′spectator′ ligand only, yielding a robust [M(′S$_4$′)] core, although in all reactions involving protons, the Brønsted basicity of the thiolate donors has been shown to be pivotal.[1b,1g,2,3] In other reactions, the ′S$_4$′$^{2-}$ ligand can experience severe changes. Coordination of the ′S$_4$′$^{2-}$ ligand to very electron-rich metal centers and UV irradiation or treatment of [M(′S$_4$′)] complexes with strongly reducing reagents frequently causes the reductive elimination of the C$_2$H$_4$ bridge as ethylene. For example, the reaction of ′S$_4$′$^{2-}$ with [MoCl$_2$(PMe$_3$)$_4$] gives the Mo^{IV} complex [Mo(PMe$_3$)$_2$(S$_2$C$_6$H$_4$)$_2$] and C$_2$H$_4$,[4] [Os(PEt$_3$)$_2$(′S$_4$′)] readily releases C$_2$H$_4$ to give [Os(PEt$_3$)$_2$(S$_2$C$_6$H$_4$)$_2$],[1e] UV irradiation of [Ru(CO)(PCy$_3$)(′S$_4$′)] yields [Ru(PCy$_3$)(S$_2$C$_6$H$_4$)$_2$] and C$_2$H$_4$,[5] and the reduction of [Fe(CO)$_2$(′S$_4$′)] by metallic sodium gives the Fe^{II} complex [Fe(S$_2$C$_6$H$_4$)$_2$]$^{2-}$ and C$_2$H$_4$.[6] The partial cleavage of S−C bonds is observed when [Ru(PPh$_3$)$_2$(′S$_4$′)] is treated with NO.[7] In this case, [Ru(NO)(PPh$_3$)(S$_2$C$_6$H$_4$)(CH$_2$=CH−SC$_6$H$_4$S)] forms, which contains a vinyl thioether thiolate ligand. All these reactions represent the reversal of the ′S$_4$′$^{2-}$ formation, which is synthesized via template alkylation of S$_2$C$_6$H$_4^{2-}$ by 1,2-C$_2$H$_4$Br$_2$.[1a] The ′S$_4$′$^{2-}$ cleavage reactions are usually unwanted. They can be traced back to the π acidity of the thioether donor functions and the partial occupation of antibonding C−S(thioether) σ* orbitals by metal d-electrons.[8] We have now tried to synthesize a ligand which

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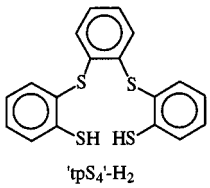
maintains the donor functions and coordination pattern of the $'S_4'^{2-}$ ligand, but is stable toward strong reducing reagents and photolysis. For this purpose, the C_2H_4 bridge in $'S_4'^{2-}$ has been replaced by an *o*-phenylene bridge. In order to clearly distinguish the target from the parent ligand and for indicating the presence of the phenylene entities, we use the acronym $'tpS_4'$-H_2.

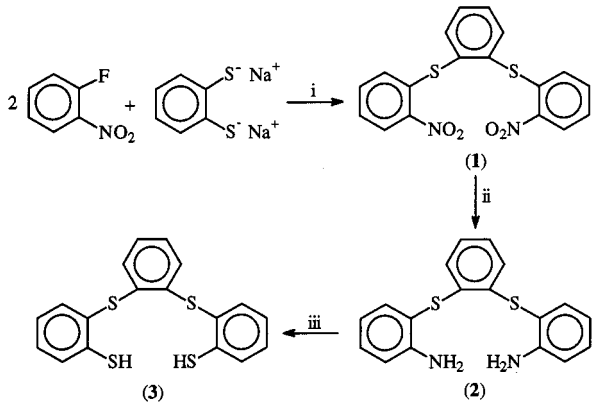


'tpS$_4$'-H$_2$

In orienting experiments, the coordination of $'tpS_4'^{2-}$ to electron-rich Ru^{II} and Os^{II} complexes was tested.

Results

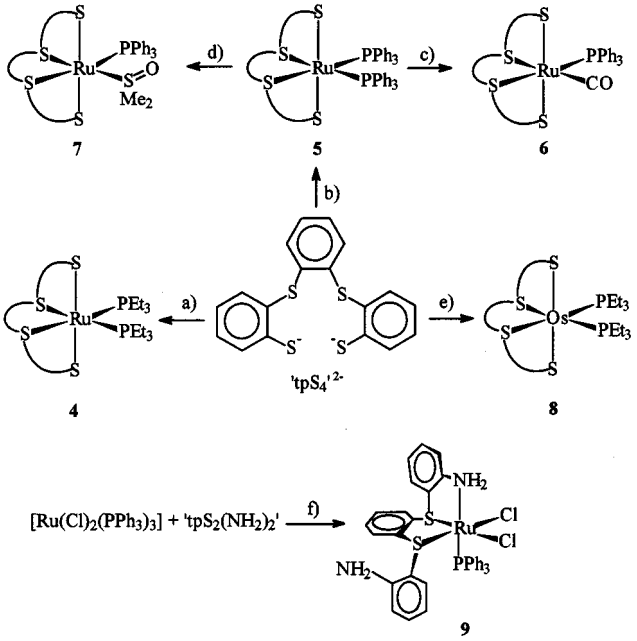
The target ligand $'tpS_4'$-H_2 (**3**) was synthesized by the route given in Scheme 1.



Scheme 1. Synthesis of $'tpS_4'$-H_2; i: MeOH/12 h/reflux; ii: Zn/NH_4Cl/THF/12 h/reflux; iii: 1. $NaNO_2/H_2SO_4/H_2O$/0°C; 2. KSC(S)OEt/H_2O/85°C; 3. KOH/EtOH/12 h/reflux; 4. HCl/H_2O, 5. LiOMe/Niac$_2$ · 4 H_2O, 6. HCl

Nucleophilic substitution of fluorine in 1,2-C_6H_4(F)-(NO_2)[9] by the thiolate functions of $Na_2S_2C_6H_4$ yielded the tris-phenylene nitro compound $'tpS_2(NO_2)_2'$ (**1**) in practically quantitative yield. Reduction of the nitro groups in **1** by Zn/NH_4Cl[10] gave the diamine-dithioether $'tpS_2(NH_2)_2'$ (**2**). Diazotisation of the NH_2 groups of **2** and subsequent reaction of the resulting bis-diazonium salt with KSC(S)(OEt), hydrolysis and acidification[11] yielded a brown oil containing $'tpS_4'$-H_2 (**3**) and a mixture of other compounds. Purification of this brown oil proved difficult. After many unsuccessful attempts applying conventional techniques, isolation of pure $'tpS_4'$-H_2 (**3**) was finally achieved by coordination to Ni^{II} salts and subsequent hydrolysis of the resulting nickel complex. Treatment of the brown oil with LiOMe and Niac$_2$ · 4 H_2O yielded a red-brown microcrystalline solid which was analyzed as $[Ni('tpS_4')]_2$ · THF · 0.5 MeOH. Hydrolysis with hydrochloric acid gave a colorless analytically pure oil of $'tpS_4'$-H_2 (**3**). The compounds **1**, **2**, and **3** were characterized by elemental analysis and spectroscopic methods. The molecular structures of **1** and **2** were determined by X-ray diffraction.

Scheme 2 summarizes the syntheses of ruthenium and osmium complexes which were obtained with $'tpS_4'^{2-}$. In one experiment also the coordination of $'tpS_2(NH_2)_2'$ (**2**) was investigated.



Scheme 2. Synthesis of $'tpS_4'^{2-}$ ruthenium and osmium complexes and of $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$; (a) $[Ru(Cl)_2(DMSO)_4]$/PEt_3/MeOH/1 h reflux; (b) $[RuCl_2(PPh_3)_3]$/THF/4 h at room temperature/5 min reflux; (c) CH_2Cl_2/CO/12 h/room temperature; (d) DMSO/5 min at 40°C; (e) $OsCl_3$ · **x** H_2O/PEt_3/MeOH/2 h reflux; (f) THF/1 h reflux

The reaction of dianionic $'tpS_4'^{2-}$, which was routinely obtained from $'tpS_4'$-H_2 (**3**) and NaOMe or BuLi, with $[Ru(Cl)_2(DMSO)_4]$ in the presence of excess PEt_3 yielded $[Ru(PEt_3)_2('tpS_4')]$ (**4**). Heating to reflux was necessary in order to drive the reaction to completeness. Treatment of $[RuCl_2(PPh_3)_3]$ with $'tpS_4'$-Li_2 in boiling THF gave $[Ru(PPh_3)_2('tpS_4')]$ (**5**). Complex **5** shows that also two sterically demanding phosphanes can bind to the $[Ru('tpS_4')]$ fragment. One PPh_3 ligand in **5** is labile and readily exchanges for CO at ambient temperatures to give $[Ru(CO)(PPh_3)('tpS_4')]$ (**6**). The PPh_3 ligand also exchanges for DMSO at slightly elevated temperature (40°C) to give $[Ru(DMSO)(PPh_3)('tpS_4')]$ (**7**). The DMSO ligand in **7** is also labile. ^{1}H-NMR spectra of **7** in [D_6]DMSO show only one DMSO signal at $\delta = 2.57$ indicating exchange of coordinated DMSO and [D_6]DMSO solvent molecules, which is rapid on the NMR time-scale.

A critical test for the inertness of $'tpS_4'^{2-}$ toward C−S cleavage reactions was its reaction with $OsCl_3$ · **x** H_2O in the presence of excess PEt_3. It yielded, although in low yield, $[Os(PEt_3)_2('tpS_4')]$ (**8**). Subsequent NMR spectroscopic investigations showed that **8** is stable in solution for unlimited periods of time and contrasts $[Os(PEt_3)_2('S_4')]$

which rapidly releases C_2H_4 to give $[Os(PEt_3)_2(S_2C_6H_4)_2]$.[1e]

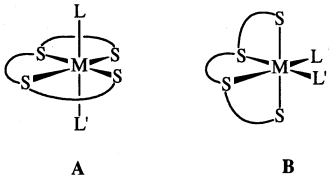
The comparison of the reactions b) and f) in Scheme 2 shows that $'tpS_2(NH_2)_2'$ (**2**) has poorer coordinating capabilities than $'tpS_4'^{2-}$ (**3**). Even after prolonged heating to reflux, the THF mixture of $RuCl_2(PPh_3)_3$ and $'tpS_2(NH_2)_2'$ yielded exclusively $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**) in which the potentially tetradentate $'tpS_2(NH_2)_2'$ (**2**) utilizes only three of its four donor functions.

Characterization of the Compounds and Complexes

All compounds were characterized by elemental analysis and spectroscopic methods, the molecular structures of $'tpS_2(NO_2)_2'$ (**1**), $'tpS_2(NH_2)_2'$ (**2**), $[Ru(PEt_3)_2('tpS_4')]$ (**4**), $[Ru(CO)(PPh_3)('tpS_4')]$ (**6**), and $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**) were also determined by X-ray diffraction.

Characteristic IR absorptions of the nitro compound **1** are ν(NO) bands of the asymmetric and symmetric ν(NO) vibrations at 1511, 1333, and 1303 cm^{-1}. The $'tpS_4'$-H_2 ligand (**3**) exhibits a medium intensity ν(SH) band at 2526 cm^{-1}. All $[M('tpS_4')]$ complexes show a nearly identical IR pattern for the $[M('tpS_4')]$ cores. Strong ν(CO) (1965 cm^{-1}) and ν(SO) (1087 cm^{-1}) bands are suited to readily identify $[Ru(CO)(PPh_3)('tpS_4')]$ (**6**) and $[Ru(DMSO)(PPh_3)('tpS_4')]$ (**7**). The ν(SO) band of **7** indicates *S*-bound DMSO.[12a]

A major concern was the coordination mode of the $'tpS_4'^{2-}$ ligand and the question whether, despite of the rigid phenylene bridge, $[M('tpS_4')]$ cores assume the same helical configuration as $[M('S_4')]$ cores. Formulas A and B schematically show the two potential configurations of $[M('tpS_4')]$ cores.



The X-ray structure analysis of **4** and **6** revealed that configuration B is assumed. When the $[M('tpS_4')]$ cores bind two different coligands L and L′ also ^{13}C-NMR spectra allow to distinguish between A and B.

Identical coligands L = L′ result in any case either in C_{2v} (formula A) or in C_2 symmetrical structures (formula B). When L ≠ L′, formula A exhibits (approximately) C_S symmetry, formula B, however, C_1 symmetry. Consequently, in complexes assuming the structure B, all aromatic C atoms are chemically non equivalent. The ^{13}C-NMR spectrum of $[Ru(CO)(PPh_3)('tpS_4')]$ (**6**) exhibits 22 aromatic ^{13}C signals and thus allows to unambiguously assign structure B. In contrast, the ^{13}C-NMR spectrum of **4** exhibits only 9 aromatic ^{13}C signals which do not allow to distinguish between structures A and B.

The coordination of $'tpS_2(NH_2)_2'$ (**2**) in $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**) leaving one amino donor dangling could be concluded from the ^1H-NMR spectrum of **9**. The protons of the uncoordinated NH_2 group give rise to a singlet, while the protons of the coordinated NH_2 group give rise to two doublets, because the NH protons are nonequivalent in C_1-symmetrical **9**. In addition, only the uncoordinated NH_2 group shows H^+/D^+ exchange with D_2O.

The molecular structures of $'tpS_2(NO_2)_2'$ (**1**), $'tpS_2(NH_2)_2'$ (**2**) $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**), $[Ru(PEt_3)_2('tpS_4')] \cdot 0.5\ Et_2O$ (**4** · 0.5 Et_2O), and $[Ru(CO)(PPh_3)('tpS_4')] \cdot CH_2Cl_2$ (**6** · CH_2Cl_2) are depicted in Figure 1. Table 1 lists selected distances and angles.

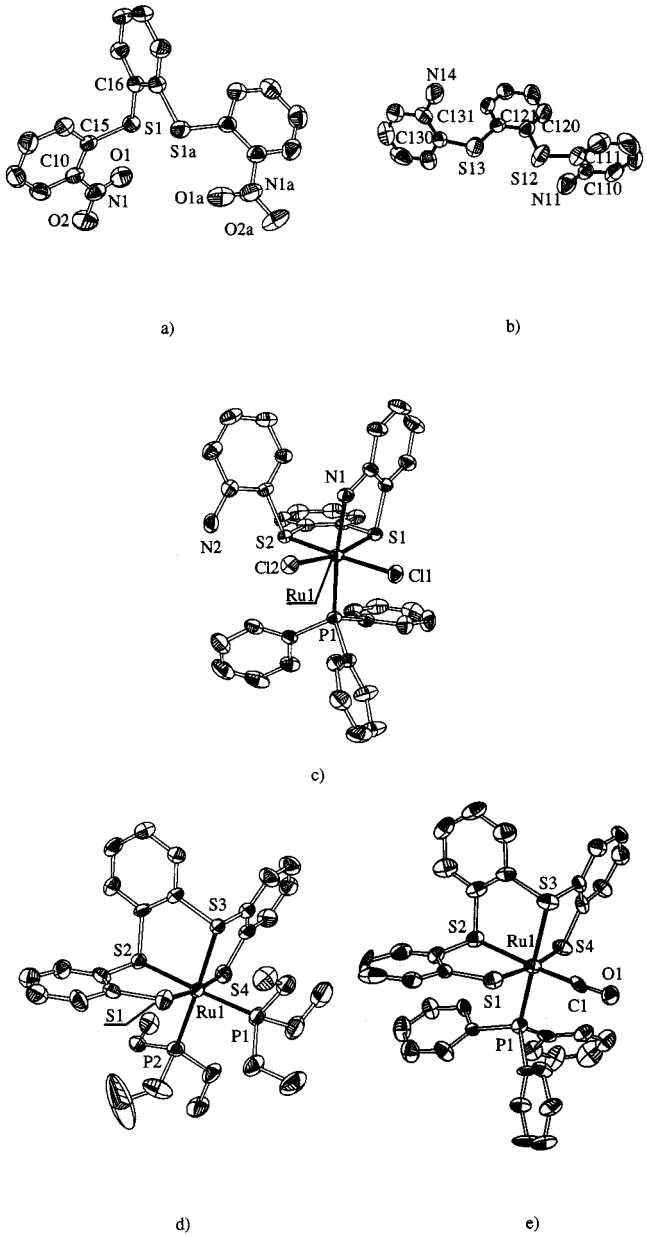


Figure 1. Molecular structures of (a) $'tpS_2(NO_2)_2'$ (**1**), (b) $'tpS_2(NH_2)_2'$ (**2**), (c) $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**), (d) $[Ru(PEt_3)_2('tpS_4')] \cdot 0.5\ Et_2O$ (**4** · 0.5 Et_2O), and (e) $[Ru(CO)(PPh_3)('tpS_4')] \cdot CH_2Cl_2$ (**6** · CH_2Cl_2) (50% probability ellipsoids, H atoms and solvent molecules omitted)

The compound $'tpS_2(NO_2)_2'$ (**1**) exhibits crystallographically imposed C_2 symmetry and shows that the two thioether S atoms lead to a helical preorganization of the three

Table 1. Selected distances [pm] and angles [°] of 'tpS$_2$(NO$_2$)$_2$' (**1**), 'tpS$_2$(NH$_2$)$_2$' (**2**), [Ru(Cl)$_2$(PPh$_3$)('tpS$_2$(NH$_2$)$_2$')] (**9**), [Ru(PEt$_3$)$_2$('tpS$_4$')] · 0.5 Et$_2$O (**4** · 0.5 Et$_2$O), and [Ru(CO)(PPh$_3$)('tpS$_4$')] · CH$_2$Cl$_2$ (**6** · CH$_2$Cl$_2$)

1			**2**		
S1−C15	177.7(2)	S12−C111	177.0(5)	S22−C211	177.8(5)
S1−C16	178.5(2)	S12−C120	177.1(4)	S22−C220	177.4(4)
N1−C10	145.8(3)	N11−C110	137.9(5)	N21−C210	136.8(5)
N1−O1	122.4(2)	−	−	−	−
N1−O2	123.3(2)	−	−	−	−
C15−S1−C16	100.93(8)	C111−S12−C120	103.1(2)	C211−S22−C220	104.1(2)
C15−C10−N1	120.7(2)	C111−C110−N11	122.9(6)	C211−C210−N21	122.6(6)
O1−N1−O2	122.7(2)				

9			**4** · 0.5 Et$_2$O	**6** · CH$_2$Cl$_2$
Ru1−Cl1	243.8(2)	Ru1−S1	239.2(3)	241.5(3)
Ru1−Cl2	242.9(2)	Ru1−S2	236.1(2)	241.8(3)
Ru1−S1	227.9(1)	Ru1−S3	234.3(2)	238.6(3)
Ru1−S2	228.9(1)	Ru1−S4	239.0(3)	238.2(3)
Ru1−N1	216.3(3)	Ru1−P1	233.0(3)	233.8(3)
Ru1−P1	230.6(1)	Ru1−P2	234.1(3)	−
−	−	Ru1−C1	−	179.5(11)
S1−Ru1−S2	88.54(5)	S1−Ru1−S4	173.2(1)	172.4(1)
Cl1−Ru1−S1	91.97(5)	S2−Ru1−S3	86.81(8)	86.4(1)
Cl2−Ru1−S2	88.59(5)	P1−Ru1−P2	94.2(1)	−
−	−	P1−Ru1−C1	−	90.2(3)
N1−Ru1−P1	173.4(1)	S1−Ru1−P1	90.9(1)	−
−	−	S1−Ru1−C1	−	95.9(3)

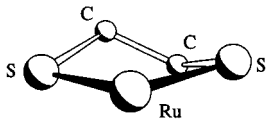
phenylene units as found in **4** and **6**. The NO_2 groups bind approximately coplanar to the phenylene rings. Distances and angles show no anomalies.

The thioetheramine compound 'tpS$_2$(NH$_2$)$_2$' crystallizes with 2 independent molecules per asymmetric unit, having practically identical distances and angles. The thioether distances and angles compare with those of **1**, and **2** is also characterized by well-approximated C_2 symmetry.

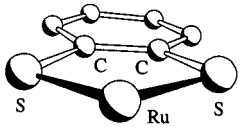
The metal centers of all three ruthenium complexes exhibit pseudo-octahedral coordination. The molecular structure of **9** unambiguously shows that one NH_2 group remains uncoordinated. Distances and angles of **9** lie in the same range as found in other Ru^{II} thioether ammine complexes, for example, [Ru(Br)(PPh$_3$)('Bz$_2$S$_2$N$_2$H$_2$')]Br ('Bz$_2$S$_2$N$_2$H$_2$' = 1,10-dibenzyl-2,3,8,9-dibenzo-1,10-dithia-4,7-diazadecane).[12b]

The 'tpS$_4$'$^{2-}$ ligand in **4** and **6** coordinates in the same helical configuration as the 'S$_4$'$^{2-}$ ligand in analogous [Ru('S$_4$')] complexes. As a result, the thiolate donors assume trans positions. Also worth being noted is that the distances of **4** and **6** are virtually identical to those found in the analogous [Ru(PR$_3$)$_2$('S$_4$')][1d] or [Ru(L)(PR$_3$)('S$_4$')] complexes (L = Cl, I).[13] For example, C_2-symmetrical [Ru(P*n*Bu$_3$)$_2$('S$_4$')] exhibits Ru−S(thiolate) [239.8(2) pm] and Ru−S(thioether) [236.8(2) pm] distances.[1d] This suggests that the small difference in the Ru−S(thioether) distances of **4** [236.1(2) pm; 234.3(2) pm] is due to crystal packing effects. It is further noted that the differences either in the Ru−S(thiolate) or the Ru−S(thioether) distances of C_1-symmetrical **6** remain very small and are certainly due to coligand effects.

The only significant difference between [Ru('S$_4$')] and [Ru('tpS$_4$')] cores thus is the central five-membered chelate ring formed by the metal, the two thioether donors and the C_2H_4 or C_6H_4 bridge. In [Ru('S$_4$')] cores, this chelate ring invariably assumes the chair conformation C, in both [Ru('tpS$_4$')] complexes it is found to be virtually planar (D). The deviation of the two phenylene C atoms from the plane defined by the Ru and the two S atoms is only 7(1) pm and 12(1) pm in **4** · 0.5 Et$_2$O and 7(1) and 11(1) pm in **6** · CH$_2$Cl$_2$ respectively.



C



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Concluding Discussion

Aim of this work was the synthesis of a tetradentate thioether thiolate ligand which shows a coordination chemistry as rich as that of the 'S$_4$'$^{2-}$ ligand but is stable toward the reductive elimination of the C_2 bridge connecting the $C_6H_4S_2$ units. The new ligand 'tpS$_4$'$^{2-}$ coordinates to metal centers in six-coordinate complexes in the same way as the 'S$_4$'$^{2-}$ ligand. The resulting [M('tpS$_4$')] cores exhibit two *trans*-positioned thiolate donors and two *cis* positions which can be occupied by ligands such as PEt$_3$, PPh$_3$, CO,

or DMSO. Orienting experiments indicate that, for example, $[Ru(PPh_3)_2('tpS_4')]$ shows a PPh_3 substitution chemistry similar to that of $[Ru(PPh_3)_2('S_4')]$. X-ray structure analyses further demonstrate that the RuS_4 distances and core angles remain invariant when the C_2H_4 bridge in $[Ru('S_4')]$ is replaced by a phenylene bridge in $[Ru('tpS_4')]$. The only and significant difference of $[Ru('S_4')]$ and $[Ru('tpS_4')]$ fragments is the central $[RuS_2C_2]$ chelate ring, which is virtually planar in $[Ru('tpS_4')]$, but exhibits a chair conformation in $[Ru('S_4')]$. The stability of the $'tpS_4'^{2-}$ ligand toward reductive cleavage could be demonstrated by the synthesis of $[Os(PEt_3)_2('tpS_4')]$ (**8**). Complex **8** is stable in solution for unlimited periods of time and thus contrasts $[Os(PEt_3)_2('S_4')]$ which readily eliminates ethylene.

Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. − Spectra were recorded with the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated): Perkin Elmer 983, 1620 FT IR, and 16PC FT-IR. − NMR: Jeol FT-JNM-GX 270, EX 270, and Lambda LA 400 with the protio-solvent signal used as a reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) related to tetramethylsilane (^1H, $^{13}C\{^1H\}$ NMR) or 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR). Spectra were recorded at 25°C. − Mass spectra: Varian MAT 212 and Jeol MSTATION 700 spectrometers. − Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. − $[RuCl_2(DMSO)_4]$,[14] $[RuCl_2(PPh_3)_3]$,[15] and *o*-benzenedithiol ($'S_2'$-H_2)[16] were prepared as described in the literature, potassiumethylxanthogenate, 1-fluoro-2-nitrobenzene, LiOMe, and *n*BuLi (2.5 M in *n*-hexane) were purchased from Aldrich.

$'tpS_2(NO_2)_2'$ (1): A red-orange solution containing NaOMe (2.70 g, 50 mmol), $'S_2'$-H_2 (3 mL, 23.7 mmol), and 1-fluoro-2-nitrobenzene (5 mL, 47.4 mmol) in MeOH (100 mL) was heated under reflux for 20 h. A bright yellow solid precipitated that was separated, washed with MeOH (100 mL) and H_2O (150 mL), and dried in vacuo. Yield: 9.00 g of **1** (99%). − $C_{18}H_{12}N_2O_4S_2$, **1** (384.42): calcd. C 56.24, H 3.15, N 7.29, S 16.68; found C 56.41, H 3.12, N 7.33, S 16.28. − IR (KBr): $\tilde{\nu}$ = 1511, 1333, 1303 cm^{-1} ν(NO). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 8.20 (m, 2 H, C_6H_4), 7.70−7.20 (m, 8 H, C_6H_4), 6.90 (m, 2 H, C_6H_4). − $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 137.52, 137.10, 136.55, 133.57, 131.15, 129.39, 129.35, 125.96, 125.78 [C(aryl)]. − EI MS (70 eV); *m/z*: 385 $['tpS_2(NO_2)_2']^+$.

$'tpS_2(NH_2)_2'$ (2): A yellow-grey suspension of **1** (6.0 g, 15.6 mmol), zinc powder (15.4 g, 235.5 mmol), and NH_4Cl (8.0 g, 149.6 mmol) in THF (120 mL) was heated under reflux for 20 h yielding a grey suspension. The grey solid was filtered off and washed with hot THF (100 mL), the colorless filtrate was concentrated to dryness. The remaining oily residue was recrystallized from hot EtOH (20 mL) yielding white crystals that were washed with EtOH (15 mL) and dried in vacuo. Yield: 4.00 g of **2** (79%). − $C_{18}H_{16}N_2S_2$, **2** (324.46): calcd. C 66.63, H 4.97, N 8.63, S 19.76; found C 66.67, H 5.21, N 8.65, S 19.37. − IR (KBr): $\tilde{\nu}$ = 3448, 3360 cm^{-1} ν(NH). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.45 (m, 2 H, C_6H_4), 7.25 (m, 2 H, C_6H_4), 6.95 (m, 2 H, C_6H_4), 6.80−6.70 (m, 6 H, C_6H_4), 4.35 (s, 4 H, NH_2). − $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 149.32, 137.25, 135.49, 131.42, 128.01, 126.73, 118.94, 115.69, 114.69 [C(aryl)]. − FD MS (CH_2Cl_2); *m/z*: 324 $['tpS_2(NH_2)_2']^+$.

Synthesis of Crude $'tpS_4'$-H_2 (3): At 0°C, $'tpS_2(NH_2)_2'$ (**2**) (3.0 g, 18.5 mmol) was suspended in a mixture of H_2SO_4 (2.2 g, 22.4 mmol) and H_2O (35 mL). After addition of ice (12 g), a solution of $NaNO_2$ (1.34 g, 19.4 mmol) in H_2O (12 mL) was added dropwise to the suspension. The resulting yellow suspension was stirred for 1 h at 0°C and subsequently added slowly to a hot solution (85°C) of KSC(S)OEt (12.0 g, 74.9 mmol) in H_2O (30 mL), whereupon a red oil separated. The mixture was stirred for 45 min at 85°C, cooled to room temperature, and extracted with CH_2Cl_2 (150 mL). The CH_2Cl_2 extract was evaporated in vacuo. The remaining red oil was dissolved in EtOH (50 mL), solid KOH (6.0 g) was added, and the mixture was heated under reflux for 12 h. Evaporation of the solvent yielded a yellow residue which was suspended in H_2O (100 mL) and extracted with CH_2Cl_2 (75 mL). To the remaining aqueous solution hydrochloric acid was added until pH = 1 was reached and an orange oil separated. The oil was extracted from the aqueous phase with CH_2Cl_2 (125 mL), and the CH_2Cl_2 extract was dried with Na_2SO_4. Removal of CH_2Cl_2 yielded a brown oil. Yield: 1.5 g of **3** (46%). − IR (Film): $\tilde{\nu}$ = 2526 cm^{-1} (SH). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.40 (m, 2 H, C_6H_4), 7.30 (m, 2 H, C_6H_4), 7.35−6.95 (m, 8 H, C_6H_4), 4.20 (s, 2 H, S*H*). − $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 137.43, 135.94, 134.54, 131.42, 130.67, 130.04, 129.32, 128.05, 126.71 [C(aryl)]. − FD MS (CH_2Cl_2); *m/z*: 358 $['tpS_4'$-$H_2]^+$.

Purification of Crude $'tpS_4'$-H_2 (3)

$[Ni('tpS_4')]_2$: The brown oil containing crude $'tpS_4'$-H_2 (1.5 g, 4.2 mmol) was dissolved in THF (40mL). LiOMe (8.4 mL, 8.4 mmol of a 1 M solution in MeOH) was added and stirred for 1 h. Removal of the THF yielded a yellow brown solid which turned into a white powder upon digestion with CH_2Cl_2 (150 mL). After drying, the white powder was characterized as $Li_2'tpS_4'$ by ^1H- and ^{13}C-NMR spectroscopy. − $Li_2'tpS_4'$ (330 mg, 0.89 mmol) in 20 mL of THF and $Niac_2 \cdot 4\ H_2O$ (222 mg, 0.89 mmol) in 20 mL MeOH were combined and stirred for 12 h. A microcrystalline red brown solid resulted which was separated, washed with MeOH (20 mL), THF (50 mL), Et_2O (20 mL), and dried in vacuo. It analyzed as $[Ni('tpS_4')]_2 \cdot THF \cdot 0.5\ MeOH$. Yield: 290mg (70%). − $C_{40.5}H_{34}O_{1.5}S_8Ni_2$ (918.60): calcd. C 52.95, H 3.74, S 27.92; found C 52.98, H 3.64, S 27.93.

$'tpS_4'$-H_2 (3): A red brown suspension of $[Ni('tpS_4')]_2 \cdot THF \cdot 0.5$ MeOH (280 mg, 0.30 mmol) in CH_2Cl_2 (15 mL) was combined with concentrated aqueous hydrochlorid acid (10 mL) and stirred for 1 h. A colorless CH_2Cl_2 and a light-green aqueous phase formed. The CH_2Cl_2 phase was separated, dried with Na_2SO_4, and concentrated to dryness, yielding a colorless oil of **3**. Yield: 120 mg of **3** (56%).− $C_{18}H_{14}S_4$, **3** (358.55): calcd. C 60.30, H 3.94, S 35.77; found C 60.51, H 3.99, S 35.47.

$[Ru(PEt_3)_2('tpS_4')]$ (4): A yellow suspension of $'tpS_4'$-H_2 (**3**) (120 mg, 0.33 mmol), NaOMe (38 mg, 0.7 mmol), and $[Ru(Cl)_2(DMSO)_4]$ (161 mg, 0.33 mmol) in MeOH (10 mL) was combined with PEt_3 (0.23 mL, 1.69 mmol) and heated under reflux for 1 h. After cooling to room temperature, the precipitated yellow solid was separated, washed with MeOH (10 mL) and Et_2O (10 mL), dried in vacuo for 5 min, and redissolved in CH_2Cl_2 (5 mL). The yellow CH_2Cl_2 solution was layered with MeOH (15 mL) and stored at room temperature. In the course of 4 d, yellow crystals precipitated that were separated, washed with MeOH (10 mL) and Et_2O (10 mL), and dried in vacuo. Yield: 100 mg of **4** · 0.5 CH_2Cl_2 (41%). − $C_{30.5}H_{43}ClP_2RuS_4$, **4** · 0.5 CH_2Cl_2 (736.41): calcd. C 49.75, H 5.89, S 17.42; found C 49.70, H 6.26, S 17.13. − IR (KBr):

$\tilde{\nu}$ = 1086 cm^{-1} δ(PCH). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.90 (m, 2 H, C_6H_4), 7.75 (m, 2 H, C_6H_4), 7.30 (m, 2 H, C_6H_4), 7.20 (m, 2 H, C_6H_4), 6.90−6.70 (m, 4 H, C_6H_4), 1.85 (m, 12 H, PCH_2), 1.05 (m, 18 H, CH_3). − $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 159.02, 138.48, 136.66, 132.00, 131.58, 130.10, 129.68, 128.81, 121.06 [C(aryl)], 19.23 (vt, PCH_2CH_3), 8.49 (PCH_2CH_3). − $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = 18.5 (s). − FD MS (CH_2Cl_2, ^{102}Ru); *m/z*: 694 $[Ru(PEt_3)_2('tpS_4')]^+$.

[Ru(PPh$_3$)$_2$('tpS$_4$')] (5): A yellow solution of 'tpS$_4$'-H$_2$ (**3**) (102 mg, 0.28 mmol) in THF (15 mL) was combined with *n*BuLi (0.23 mL, 0.58 mmol) at −78°C and subsequently warmed to room temperature. Addition of $[Ru(Cl)_2(PPh_3)_3]$ (281 mg, 0.28 mmol) resulted in an orange solution which was stirred for 4 h at room temperature, heated to reflux for 5 min, and cooled to room temperature. Yellow microcrystals precipitated which were separated, washed with THF (20 mL) and Et_2O (10 mL), dried in vacuo for 5 min, and redissolved in CH_2Cl_2 (15 mL). The yellow CH_2Cl_2 solution was filtered, THF (50 mL) was added to the filtrate, and the mixture was reduced in volume to 10 mL. The precipitated yellow microcrystals were separated, washed with THF (20 mL), MeOH (20 mL), and Et_2O (20 mL), and dried in vacuo. Yield: 145 mg of **5** · 0.25 CH_2Cl_2 (51%). − $C_{54.25}H_{42.5}Cl_{0.5}P_2RuS_4$, **5** · 0.25 CH_2Cl_2 (1003.44): calcd. C 64.94, H 4.27, S 12.78; found C 65.18, H 4.42, S 12.55. − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.60 (m, 2 H, C_6H_4), 7.30 (m, 14 H, C_6H_4), 7.25 (m, 6 H, C_6H_4), 7.15 (m, 2 H, C_6H_4), 7.05 (m, 14 H, C_6H_4), 6.85 (m, 2 H, C_6H_4), 6.60 (m, 2 H, C_6H_4). − $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2): δ = 157.70, 138.50, 137.35, 135.20, 131.45, 130.90, 129.80, 129.60, 129.40, 128.95, 128.25, 121.40 [C(aryl)]. − $^{31}P\{^1H\}$ NMR (109.38, CD_2Cl_2) δ = 27.0 (s). − FD MS (CH_2Cl_2, ^{102}Ru); *m/z*: 982 $[Ru(PPh_3)_2('tpS_4')]^+$.

[Ru(CO)(PPh$_3$)('tpS$_4$')] (6): CO gas was bubbled through a yellow suspension of $[Ru(PPh_3)_2('tpS_4')]$ (**5**) (147 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) for 3 h. A yellow solution resulted which was stirred for another 12 h under CO, reduced in volume to 3 mL, and layered with MeOH (50 mL). In the course of 3 d, yellow crystals precipitated which were separated, washed with MeOH (20 mL) and Et_2O (10 mL), and dried in vacuo. Yield: 85 mg of **6** (73%). − $C_{37}H_{27}OPRuS_4$, **6** (747.90): calcd. C 59.42, H 3.64, S 17.15; found C 59.43, H 3.80, S 16.83. − IR (KBr): $\tilde{\nu}$ = 1964 cm^{-1} (CO). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.90 (m, 1 H, C_6H_4), 7.75 (m, 1 H, C_6H_4), 7.60 (m, 7 H, C_6H_4), 7.35 (m, 10 H, C_6H_4), 7.20 (m, 2 H, C_6H_4), 7.10−6.85 (m, 4 H, C_6H_4), 6.70 (m, 1 H, C_6H_4), 6.55 (m, 1 H, C_6H_4). − $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ = 200.81 (d, *C*O); 155.89 (d), 155.28, 138.57 (d), 136.20 (d), 135.36 (d), 134.45 (d), 134.07, 133.09, 132.93 (d), 132.80, 132.62, 131.86, 131.80 (d), 130.83, 130.52 (t), 130.30, 130.19, 129.81, 129.15, 128.16 (d), 122.60, 122.01 [C(aryl)]. − $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ = 38.98 (s). − FD MS (CH_2Cl_2, ^{102}Ru); *m/z*: 748 $[Ru(CO)(PPh_3)('tpS_4')]^+$.

[Ru(DMSO)(PPh$_3$)('tpS$_4$')] (7): $[Ru(PPh_3)_2('tpS_4')]$ (**5**) (170 mg, 0.17 mmol) was dissolved in warm DMSO (6 mL, 40°C) and the resulting yellow solution was cooled to room temperature. After addition of MeOH (45 mL), a yellow solid precipitated which was separated, washed with MeOH (50 mL) and Et_2O (20 mL), and dried in vacuo. Yield: 105 mg of **7** (77%). − $C_{38}H_{33}OPRuS_5$, **7** (798.02): calcd. C 57.19, H 4.17, S 20.09; found C 57.12, H 4.10, S 20.01. − IR (KBr): $\tilde{\nu}$ = 1087 cm^{-1} (SO). − ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.95 (m, 1 H, C_6H_4), 7.80−7.50 (m, 9 H, C_6H_4), 7.40−7.15 (m, 11 H, C_6H_4), 7.10−6.95 (m, 2 H, C_6H_4), 6.90−6.70 (m, 3 H, C_6H_4), 6.50 (m, 1 H, C_6H_4), 3.00 (s, 3 H, CH_3), 2.70 (s, 3 H, CH_3). − $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2): δ = 157.20 (d), 155.03, 137.79 (t), 135.25, 135.00 (d), 134.62, 132.36, 132.20, 132.10, 131.84, 131.44, 130.95, 130.79, 130.47, 130.12, 129.92, 129.54, 129.14, 128.93, 128.75, 127.40 (d), 122.17, 121.63 [C(aryl)],

Table 2. Selected crystallographic data of $'tpS_2(NO_2)_2'$ (**1**), $'tpS_2(NH_2)_2'$ (**2**), $[Ru(Cl)_2(PPh_3)('tpS_2(NH_2)_2')]$ (**9**), $[Ru(PEt_3)_2('tpS_4')]$ · 0.5 Et_2O (**4** · 0.5 Et_2O), and $[Ru(CO)(PPh_3)('tpS_4')]$ · CH_2Cl_2 (**6** · CH_2Cl_2)

Compound	**1**	**2**	**9**	**4** · 0.5 Et_2O	**6** · CH_2Cl_2
formula	$C_{18}H_{12}N_2O_4S_2$	$C_{18}H_{16}N_2S_2$	$C_{36}H_{31}Cl_2N_2PRuS_2$	$C_{32}H_{47}O_{0.5}P_2RuS_4$	$C_{38}H_{29}Cl_2OPRuS_4$
M_r[g/mol]	384.42	324.45	758.69	1461.89	832.79
crystal size [mm]	0.6 × 0.5 × 0.4	0.40 × 0.30 × 0.25	0.6 × 0.6 × 0.6	0.7 × 0.5 × 0.4	0.5 × 0.4 × 0.2
F(000)	792	680	1544	3048	1688
space group	*Pccn*	*P*−1	$P2_1/n$	$Pna2_1$	$P2_1/c$
crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic
a [pm]	2210.3(12)	1101.9(3)	940.8(6)	3073.7(4)	1802.3(5)
b [pm]	518.6(3)	1105.4(3)	1877.4(6)	1511.0(2)	1142.6(5)
c [pm]	1481.0(4)	1519.1(5)	1866.7(6)	1491.8(2)	1888.3(4)
α [°]	90	109.65(2)	90	90	90
β [°]	90	105.88(2)	98.62(4)	90	110.70(2)
γ [°]	90	90.22(2)	90	90	90
V [nm^3]	1.698(1)	1.6667(8)	3.260(3)	6.929(2)	3.638(2)
Z	4	4	4	8	4
$D_{calcd.}$ [g/cm^3]	1.504	1.293	1.546	1.401	1.521
μ [mm^{-1}]	0.341	0.317	0.852	0.808	0.882
diffractometer	Nicolet R3m/V	Nicolet R3m/V	Siemens P4	Siemens P4	Siemens P4
radiation [pm]	Mo-K_α (λ = 71.073)	Mo-K_α (λ = 71.073)	Mo-K_α (λ = 71.073)	Mo-K_α (λ = 71.073)	Mo-K_α (λ = 71.073)
temperature [K]	293	298	200	200	200
scan technique	ω scan	ω scan	ω scan	ω scan	ω scan
$2\Theta_{range}$ [°]	3−54	3−54	4−54	4−55	4−52
scan speed [°/min]	3.0−15.0	10	3.0−30.0	3.0−30.0	30.0 (fixed)
meas. reflections	3847	8111	9382	9870	8666
indep. reflections	1825	7272	7105	8870	7132
R_{int} [%]	3.85	7.53	5.42	4.21	13.12
obs. reflections	1271	1270	5499	6068	2190
σ criterion	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
*R*1; *wR*2 [%]	3.70; 9.59	3.95; 7.76	3.59; 12.56	5.70; 16.41	6.38; 15.32
ref. parameters	142	397	521	726	424
abs. struct. param.[19]	−	−	−	−0.03(5)	−

49.78, 44.52 (SCH_3). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = 34.8 (s).

[Os(PEt$_3$)$_2$('tpS$_4$')] (8): A solution of 'tpS$_4$'-H$_2$ (**3**) (190 mg, 0.53 mmol) and LiOMe (40 mg, 1.06 mmol) in THF (20 mL) was stirred for 1 h. Removal of the solvent yielded a yellow residue. It was dissolved in MeOH (20 mL) and combined with $OsCl_3 \cdot$ **x** H_2O (158 mg, 0.53 mmol) and PEt_3 (1.60 mL, 11.8 mmol). The resulting yellow-brown solution was heated under reflux for 2 h, cooled to room temperature, reduced in volume to 10 mL, and Et_2O (10 mL) was added. A yellow solid precipitated, which was separated, washed with MeOH (15 mL), Et_2O (5 mL), and H_2O (10 mL), and dried in vacuo. Yield: 20 mg of **8** · 2 H_2O (5%). – $C_{30}H_{46}O_2OsP_2S_4$, **8** · 2 H_2O (819.08): calcd. C 43.99, H 5.66, S 15.66; found C 44.27, H 5.53, S 15.63. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.90 (m, 2 H, C_6H_4), 7.85 (m, 2 H, C_6H_4), 7.20 (m, 4 H, C_6H_4), 6.85 (m, 2 H, C_6H_4), 6.55 (m, 2 H, C_6H_4), 1.95 (m, 12 H, PCH_2), 1.00 (m, 18 H, CH_2CH_3). – $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2): δ = 158.98 (d), 139.35, 137.75, 131.54, 131.29, 130.02, 129.90, 129.62, 128.99, 121.26 [C(aryl)], 18.95 (vq, PCH_2CH_3), 8.51 (PCH_2CH_3). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = –25.0 (s). – FD MS (CH_2Cl_2, ^{192}Os); *m/z*: 784 [Os(PEt$_3$)$_2$('tpS$_4$')]$^+$.

[Ru(Cl)$_2$(PPh$_3$)('tpS$_2$(NH$_2$)$_2$')] (9): 'tpS$_2$(NH$_2$)$_2$' (**2**) (168 mg, 0.52 mmol) was added to a brown solution of [Ru(Cl)$_2$(PPh$_3$)$_3$] (495 mg, 0.52 mmol) in THF (25 mL). An orange solution formed which was heated under reflux for 1 h, cooled to room temperature, and reduced in volume to 15 mL. Yellow microcrystals precipitated which were separated, washed with THF (15 mL) and Et_2O (25 mL), and dried in vacuo. Yield: 330 mg of **9** · THF (76%). – $C_{40}H_{39}Cl_2N_2OPRuS_2$, **9** · THF (759.93): calcd. C 57.83, H 4.73, N 3.37, S 7.72; found C 57.90, H 4.64, N 3.37, S 7.45. – IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1} δ(NH). – ^1H NMR (269.6 MHz, $CDCl_3$): δ = 7.85 (m, 7 H, C_6H_5), 7.15 (m, 1 H, C_6H_4), 7.40–7.05 (m,13 H, C_6H_4), 7.00 (m, 1 H, C_6H_4), 6.75 (m, 1 H, C_6H_4), 6.00 (m, 1 H, N*H*), 5.95 (m, 1 H, C_6H_4), 5.00 (s, 2 H, N*H*), 4.80 (m, 1 H, C_6H_4), 4.50 (m, 1 H, N*H*). – $^{13}C\{^1H\}$ NMR (67.7 MHz, $CDCl_3$): δ = 148.03, 144.16, 142.12, 139.86, 138.60, 135.90, 135.24, 134.50 (d), 133.38, 132.09, 131.56, 131.50, 131.24, 130.86, 130.45, 129.83, 129.02, 128.22 (d), 119.31, 119.11, 119.03 [C(aryl)]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = 43.5 (s). – FD MS (CH_2Cl_2, ^{102}Ru); *m/z*: 721 [Ru(Cl)(PPh$_3$)('tpS$_2$(NH$_2$)$_2$') – 2 H]$^+$.

X-ray Structure Analyses of 'tpS$_2$(NO$_2$)$_2$' (1), 'tpS$_2$(NH$_2$)$_2$' (2), [Ru(Cl)$_2$(PPh$_3$)('tpS$_2$(NH$_2$)$_2$')] (9), [Ru(PEt$_3$)$_2$('tpS$_4$')] · 0.5 Et$_2$O (4 · 0.5 Et$_2$O), and [Ru(CO)(PPh$_3$)('tpS$_4$')] · CH$_2$Cl$_2$ (6 · CH$_2$Cl$_2$): Yellow cubes of **1** crystallized from a hot saturated solution of **1** in THF upon cooling to room temperature, colorless cubes of **2** from a satured $CHCl_3$ solution. Orange cubes of **9** formed in the course of 7 d, when a saturated CH_2Cl_2 solution of **9** was stored at room temperature. Yellow plates of **4** and **6** were grown by layering CH_2Cl_2 solutions of **4** and **6** with Et_2O and MeOH, respectively, at room temperature. In the case of **4**, spontaneous separation of racemic **4** occured. Both independent molecules present in the asymmetric unit of **4** · 0.5 Et_2O represent the same enantiomer. Distances and angles of the two independent molecules differ only marginally. Suitable single crystals were sealed under N_2 in glass capillaries. Data were corrected for Lorentz and polarization effects, no absorption correction. The structures were solved by direct methods (SHELXTL 5.03[17]). Full-matrix least-squares refinement was carried out on F^2 (SHELXTL 5.03). All non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms of **1**, **2**, and **9** were taken from the difference Fourier map and were either refined isotropically (**1**, **9**) or kept fixed with a common isotropic displacement parameter (**2**). In the case of **4** and **6** the hydrogen atoms were geometrically positioned with isotropic displacement parameters fixed at 1.5 times *U*(eq) of the preceding carbon atom. In the case of **2** and **4**, there are two crystallographically independent molecules per asymmetric unit. Selected crystallographic data are summarized in Table 2.[18]

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC-102376 (**1**), -102377 (**2**), -102378 (**4**), -102379 (**6**), -102380 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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