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Synthesis and Reactivity of (Thioamido S-oxide)(diene)rhodium(I) Complexes. X-ray Structure of Rh(I)[(*p*-Tol)(*p*-TolN)C=S=O](NBD)

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Abstract

Monoanionic amidosulphines $[R(R'N)C{=}S{=}O]^-$ are coordinated to rhodium diolefine centres in the N,O-chelate bonding mode as shown by an X-ray structure determination of Rh(I)[(*p*-Tol)(*p*-TolN)-CSO](NBD); triclinic space group $P\bar{1}$ with $Z = 4$ and $a = 9.314(2)$, $b = 10.379(2)$, $c = 23.170(3)$ Å, $\alpha = 75.23(1)°$, $\beta = 75.83(1)°$, $\gamma = 65.37(2)°$. The structure was solved to $R = 0.042$ for 7625 observed reflections. The (thioamido S-oxide)(diene)rhodium(I) complexes show fluxional behaviour in solution (proton and ^{13}C NMR spectrometry), involving either rotation of the diolefine through a tetrahedral transition state, or the formation of a five-coordinate rhodium species with the assistance of a solvent molecule as the fifth ligand. Reactions of the (thioamido S-oxide)(diene)rhodium(I) complexes with 1,2-bis(diphenylphosphino)ethane (DPPE) gave dimeric compounds with a chelate bonded amidosulphine and the DPPE ligands bridging between the two Rh(I) centres. Reactions of (thioamido S-oxide)(diene)-rhodium(I) complexes with carbon monoxide gave monomeric 1/1 complexes with the amidosulphine in a chelate bonding mode.

Introduction

In recent years the coordination of heterocumulenic systems, which are isoelectronic with sulphur dioxide, e.g. *N*,*N'*-substituted sulphurdiimines (RNSNR), *N*-sulphinylanilines (RNSO) and sulphines (R_2CSO), has been the subject of extensive research in our laboratory [1–6].

The coordination mode of the NSN and NSO ligands depends on the nature of the metal atom and may involve bonding via the N (Pt(0), Ni(0)) or the S atom (Rh(I) or via the N=S π-bond Pt(0)). Also the coordination of sulphines, R_2CSO, was found to be dependent on the nature of the metal centre. In the case where the atom α to the sulphine carbon is sulphur [7], examples of coordination via the S atom, the C=S π-bond as well as coordination in a pseudo-allylic mode via the S–C=S system, have been isolated and characterized. Moreover, insertions of the metal centre in both the carbon–sulphur bond of R(R'S)CSO and of the carbon–chlorine bond of R(Cl)CSO, resulting in the formation of the metallosulphines R(XM)CSO (X = Cl, R'S), have been observed [6, 7]. These insertion reactions are especially of interest because they create new possibilities for the synthesis of new sulphines at a metal centre [8] according to Scheme 1.

In order to further investigate the influence of the atom α to the sulphine carbon on the coordination mode of sulphines we studied the coordination behaviour of aminosulphines. The striking influence that the introduction of a nitrogen atom α to the sulphine carbon atom exerts on the coordination properties by the sulphine oxygen atom, is demonstrated by the isolation of the first example of η^1-O coordination of an aminosulphine molecule, *i.e.* of Me_2SnCl_2[(Ph)(PhMeN)CSO] [9].

In view of this η^1-O coordination and the fact that aminosulphines have Z configuration at the C=S bond we set out to study whether aminosulphines have in addition to the known coordination modes of the C=S=O entity also the possibility to coordinate in the N,O chelate bonding mode. Since the electron pair in the neutral aminosulphine is strongly delocalized over the N–C=S=O skeleton (see 'Discussion') we reacted the aminosulphine in its deprotonated form, *i.e.* as $[(R')(RN)C{=}S{=}O]^-$. In this paper the coordination of the monoanionic amidosulphines towards rhodium(I) centres is described. Novel Rh(amidosulphine)(diolefine) complexes containing N,O-chelate coordinated amidosulphines have been synthesized. The reactivity of these compounds towards mono- and bidentate ligands has been studied.

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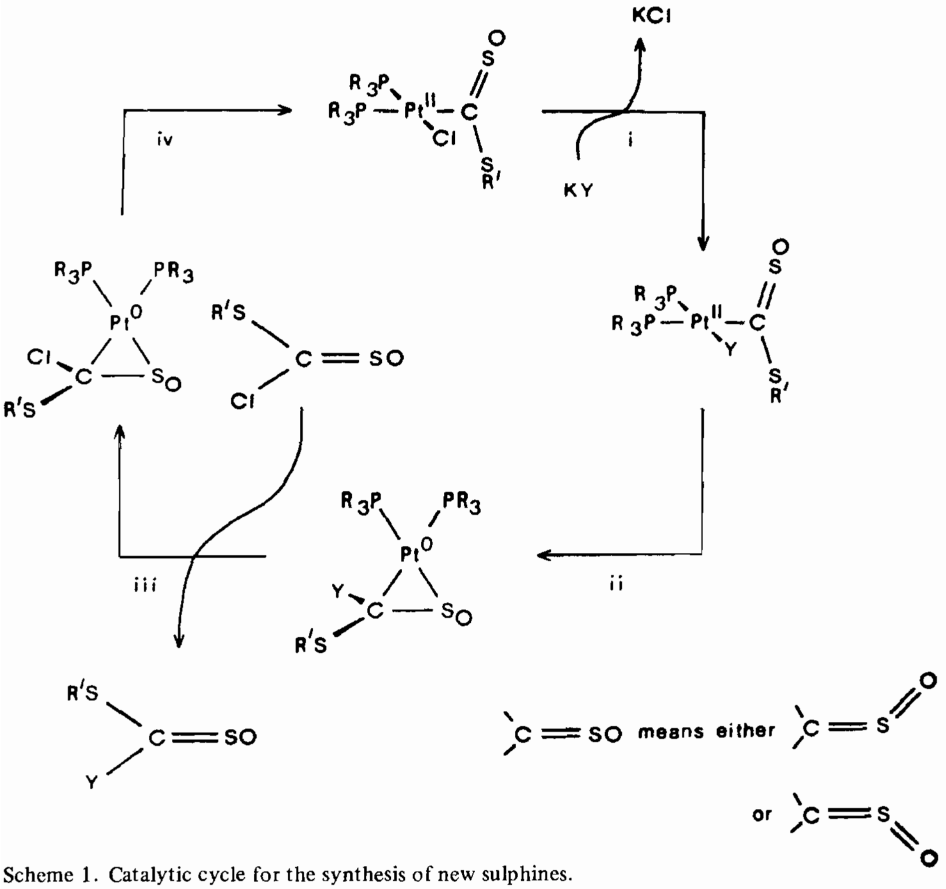

Scheme 1. Catalytic cycle for the synthesis of new sulphines.

Experimental

The ^1H NMR spectra were recorded on a Bruker WM250 and a Varian XL100 12' spectrometer. The ^{13}C NMR spectra were recorded on a Bruker WP80 spectrometer operating at a frequency of 20.1 MHz, or on a Bruker WM250 spectrometer at a frequency of 62.9 MHz. The ^{31}P NMR data were collected on a Varian XL100 15' spectrometer working with a frequency of 40.5 MHz, and a Bruker WP80 spectrometer operating at a frequency of 32.4 MHz. IR data were obtained from a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

The aminosulphines (p-Tol)[(p-Tol)HN]C=S=O and (i-Pr)[(p-Tol)HN]C=S=O were prepared as described in the literature [10–12].

General Syntheses of the (Thioamido S-oxide)(diene)-rhodium(I) Complexes

All reactions were carried out under a nitrogen atmosphere. Solvents were dried before use by distillation over sodium. *ca.* 2 mmol of NaH in paraffin oil (*ca.* 50%) was washed with pentane and the clean NaH then suspended in 20 ml of tetrahydrofuran. Subsequently 1 mmol of the aminosulphine was added, which resulted in precipitation of the amidosulphine salt (15 min). The precipitate was dissolved in THF and the excess of NaH was filtered off. To the resulting solution of the sodium amidosulphine salt 1 mmol of [Rh(diolefine)Cl]$_2$ was added and the NaCl formed filtered off. The resulting filtrate was taken to dryness. The dark-yellow coloured solid residue was extracted with either warm hexane, or cold diethyl ether (0 °C). After evaporation of the hexane or the diethyl ether, a light yellow compound was obtained (85%). Crystals suitable for single crystal X-ray analysis were obtained by recrystallization from hot hexane.

Syntheses of [(Thioamido S-oxide)(1,2-bis(diphenylphosphino)ethane)rhodium(I)]$_2$ Complexes

(Thioamido S-oxide)(diene)rhodium(I) (0.3 mmol) was dissolved in hexane. Subsequently 0.3 mmol of DPPE was added. After stirring the reaction mixture for 16 h the orange–brown precipitate formed was filtered off and then recrystallized from ethyl acetate. Yield 80%.

TABLE I. Elemental Analyses[a] and Molecular Weight Determinations[b]

Compound	No.	%C found(calc.)	%H found(calc.)	%N found(calc.)	%S found(calc.)	%P found(calc.)	Molecular weight
Rh((*p*-Tol)(*p*-TolN)CSO)(NBD)	1	57.98(59.09)	4.95(4.91)	2.99(3.10)	6.85(7.10)	–(–)	425(451)
Rh((*p*-Tol)(i-PrN)CSO)(COD)	2	52.83(53.47)	5.70(5.73)	3.17(3.46)	7.32(7.93)	–(–)	406(403)
Rh((*p*-Tol)(*p*-TolN)CSO)(COD)	3	61.83(59.09)	5.98(5.61)	3.32(3.00)	5.32(6.86)	–(–)	468(467)
Rh((*p*-Tol)(i-PrN)CSO)(NBD)	4[c]	52.07(50.60)	6.11(6.10)	2.95(3.03)	6.28(6.93)	–(–)	445(419)
Rh((*p*-Tol)(*p*-TolN)CSO)(DPPE)	5	61.95(65.00)	5.14(5.05)	1.80(1.85)	4.22(4.23)	8.46(8.18)	1396(757)
Rh((*p*-Tol)(i-PrN)CSO)(DPPE)	6	65.13(62.63)	5.45(5.40)	2.06(1.97)	4.49(4.52)	8.62(8.73)	1296(709)
Rh((*p*-Tol)(*p*-TolN)CSO)$(CO)_2$	7	49.70(49.17)	3.59(3.40)	3.32(3.37)	7.21(7.72)	–(–)	–(–)
Rh((*p*-Tol)(i-PrN)CSO)$(CO)_2$	8	41.89(42.52)	3.88(3.84)	3.87(3.81)	9.02(8.73)	–(–)	–(–)

[a] The analytical data are not completely satisfactory because of slow decomposition of the complexes. [b] Measured by osmometry in $CHCl_3$ [found(calc.)]. [c] The actual stoichiometry is Rh[(*p*-Tol)(i-PrN)CSO][COD]$\cdot CH_2Cl_2$ according to the analytical results.

TABLE II. Crystal Data and Details of the Structure Determination

(a) Crystal data	
Formula	$C_{22}H_{22}NOSRh$
Molecular weight	451.40
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	9.314(2)
b (Å)	10.379(2)
c (Å)	23.170(3)
α (°)	75.23(1)
β (°)	75.83(2)
γ (°)	65.37(2)
V (Å^3)	1944.2(8)
Z	4
D_{calc} (g cm^{-1})	1.542
F(000) electrons	920
μ(Mo Kα) (cm^{-1})	9.8
Crystal size (mm)	0.20 × 0.45 × 0.83
(b) Data collection	
θmin, θmax (°)	2.19, 30
Radiation (Å)	Mo Kα (Zr-filtered), 0.71073
$\omega/2\theta$ scan (°)	0.50 + 0.35 tan θ
Hor., vert. apert., dist to cryst. (mm)	3, 3, 173
Ref. rflns. (e.s.d.)	400 (3%); 040 (3%); 008 (5%)
Data set	h –13:13; k –14:14; l –32:0
Total data, unique data	10990, 10730
Observed data ($I > 2.5\sigma(I)$)	7625
(c) Refinement	
NO, NV, S	7625, 482, 1.02
R, R_w	0.042, 0.062
Weighting scheme	$w = 1/\sigma^2(F)$
Min. and max. resd. des. (e Å^{-3})	1.23, –0.58

Reaction of (Thioamido S-oxide)(diene)rhodium(I) with Triphenylphosphine

(Thioamido S-oxide)(diene)rhodium(I) and either one or two equivalents of PPh_3 were dissolved in $CDCl_3$ in a NMR tube. The NMR spectra were recorded at various temperatures. Attempts to isolate an adduct of the (thioamido S-oxide)rhodium(I) complex and PPh_3 were unsuccessful.

Reaction of (Thioamido S-oxide)(diene)rhodium(I) with Carbon Monoxide

Carbon monoxide was bubbled through a solution of [Rh((*p*-Tol)(*p*-TolN)C=S=O)(diene)] in hexane for about 5 min. No colour change was observed. The solution was stored at –80 °C for 48 h. An orange precipitate was collected by filtration. Elemental analyses of this precipitate indicated a [Rh((*p*-Tol)(*p*-TolN)C=S=O)$(CO)_2$] stoichiometry (see Table I). Yield 80%.

Reaction with ^{13}CO

The (thioamido S-oxide)(diene)rhodium(I) complexes were dissolved in $CDCl_3$ and stirred under a low pressure ^{13}CO atmosphere for 3 h, followed by stirring under nitrogen-^{13}CO atmosphere for 16 h.

X-ray Data Collection and Structure Determination

X-ray data for an orange–brown crystal of $C_{22}H_{22}NOSRh$ mounted on a glass fiber were recorded on an Enraf-Nonius CAD4F diffractometer. Crystal data and numerical details, of the structure determination are given in Table II. See also 'Supplementary Material'. Lattice parameters with standard deviations were determined from the θ-values of 25 reflections ($7 < \theta < 18°$). An analysis [13] of the translation lattice in view of $Z = 4$ did not reveal any symmetry higher than triclinic. Standard deviations in the intensities were increased according to an analysis of the variance of the reference reflections [14]: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.06I)^2$. The reflection set was corrected for Lp, a linear decay of 20% over the 176 h of X-ray exposure time and absorption (DIFABS [15]; min. and max. correction 0.605 and 1.340). The structure was solved by Patterson and Fourier methods with SHELX-84

TABLE III. Positional and Equivalent Isotropic Thermal Parameters for the Non-hydrogen Atoms of $C_{22}H_{22}NOSRh$

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Molecule 1				
Rh(1)	0.03526(3)	0.03412(3)	0.17169(1)	0.0426(1)
S(1)	−0.2070(1)	0.34825(9)	0.16875(5)	0.0579(3)
O(1)	−0.0324(3)	0.2447(2)	0.1805(1)	0.0635(5)
N(1)	−0.1826(3)	0.1102(2)	0.1427(1)	0.0427(5)
C(101)	0.3698(4)	−0.2950(4)	0.1984(2)	0.0572(6)
C(102)	0.2182(4)	−0.2106(4)	0.2402(2)	0.0585(6)
C(103)	0.2250(4)	−0.0613(4)	0.2231(2)	0.0567(6)
C(104)	0.2896(4)	−0.0442(4)	0.1622(2)	0.0534(6)
C(105)	0.3217(4)	−0.1831(3)	0.1411(2)	0.0519(5)
C(106)	0.1500(4)	−0.1675(3)	0.1443(2)	0.0485(5)
C(107)	0.0860(4)	−0.1849(3)	0.2056(2)	0.0514(5)
C(108)	−0.2747(4)	0.2478(3)	0.1429(2)	0.0432(5)
C(109)	−0.4358(3)	0.3243(3)	0.1252(2)	0.0424(5)
C(110)	−0.4720(4)	0.4550(3)	0.0854(2)	0.0521(6)
C(111)	−0.6228(4)	0.5273(3)	0.0693(2)	0.0566(6)
C(112)	−0.7425(4)	0.4720(3)	0.0930(2)	0.0506(5)
C(113)	−0.7062(4)	0.3431(3)	0.1333(2)	0.0539(6)
C(114)	−0.5540(4)	0.2692(3)	0.1489(2)	0.0472(5)
C(115)	−0.9061(4)	0.5507(4)	0.0753(2)	0.0730(6)
C(116)	−0.2209(3)	0.0314(3)	0.1100(1)	0.0379(5)
C(117)	−0.1996(4)	0.0623(3)	0.0476(2)	0.0498(6)
C(118)	−0.2248(4)	−0.0187(4)	0.0147(2)	0.0562(6)
C(119)	−0.2702(4)	−0.1351(3)	0.0445(2)	0.0499(5)
C(120)	−0.2881(4)	−0.1650(3)	0.1060(2)	0.0474(5)
C(121)	−0.2630(4)	−0.0855(3)	0.1394(2)	0.0439(5)
C(122)	−0.2923(5)	−0.2245(4)	0.0074(2)	0.0755(6)
Molecule 2				
Rh(2)	0.21913(4)	0.33288(3)	0.67774(1)	0.0529(1)
S(2)	0.5067(1)	0.0474(1)	0.70085(5)	0.0622(3)
O(2)	0.4203(3)	0.2028(3)	0.7163(1)	0.0680(5)
N(2)	0.2664(3)	0.1530(3)	0.6418(1)	0.0515(5)
C(201)	−0.0757(6)	0.6877(4)	0.6842(3)	0.0921(6)
C(202)	0.0960(5)	0.6273(4)	0.6468(2)	0.0841(6)
C(203)	0.1945(5)	0.5312(4)	0.6972(2)	0.0742(6)
C(204)	0.0952(5)	0.4753(4)	0.7409(2)	0.0699(6)
C(205)	−0.0671(5)	0.5369(4)	0.7180(2)	0.0747(6)
C(206)	−0.0197(5)	0.4561(4)	0.6656(2)	0.0640(6)
C(207)	0.0806(5)	0.5123(4)	0.6213(2)	0.0727(6)
C(208)	0.3901(4)	0.0365(4)	0.6575(2)	0.0498(6)
C(209)	0.4447(4)	−0.1058(4)	0.6397(2)	0.0517(6)
C(210)	0.4806(4)	−0.2311(4)	0.6833(2)	0.0633(6)
C(211)	0.5366(5)	−0.3651(4)	0.6670(2)	0.0737(6)
C(212)	0.5535(5)	−0.3779(4)	0.6065(2)	0.0743(6)
C(213)	0.5166(5)	−0.2539(4)	0.5635(2)	0.0768(6)
C(214)	0.4620(5)	−0.1164(4)	0.5799(2)	0.0680(6)
C(215)	0.6066(6)	−0.5218(5)	0.5896(3)	0.1131(6)
C(216)	0.1546(4)	0.1409(3)	0.6127(2)	0.0489(5)
C(217)	0.0673(4)	0.0551(4)	0.6421(2)	0.0529(6)
C(218)	−0.0492(4)	0.0525(4)	0.6154(2)	0.0623(6)
C(219)	−0.0820(4)	0.1325(4)	0.5596(2)	0.0629(6)
C(220)	0.0060(5)	0.2153(4)	0.5310(2)	0.0716(6)
C(221)	0.1206(4)	0.2232(4)	0.5568(2)	0.0620(6)
C(222)	−0.2119(5)	0.1310(5)	0.5324(2)	0.0877(6)

Numbers in parentheses are e.s.d.s in the least significant digit. $U_{eq} = (1/3)\Sigma\Sigma U_{ij} a_i^* a_j^* a_i \cdot a_j$.

[16] and refined by full-matrix least-squares on F with a locally modified implementation of SHELX76 [17] on an Eclipse S/230 mini-computer. Hydrogen atoms were introduced on calculated positions and refined with fixed geometry (C–H = 1.08 Å) to the carbon atoms they are attached to with one overall isotropic temperature parameter ($U = 0.08$ Å^2). Convergence was reached at $R = 0.042$ for 7625 observed reflections. The refined parameters included all positional and anisotropic thermal parameters for the non-hydrogen atoms. A final difference Fourier map did not show any significant residual features. Positional parameters and equivalent temperature factors for the non-hydrogen atoms are listed in Table III. Scattering factors were taken from Cromer and Mann [18] and anomalous dispersion terms from Cromer and Liberman [19]. Geometrical calculations were done with PLATO [20].

Results and Discussion

(i) Synthesis

Aminosulphines $R^1(R^2R^3N)CSO$ (R^1 = aryl, R^2 = H, R^3 = alkyl, aryl) containing a N–H bond can be easily converted into the corresponding monoanionic amidosulphines according to eqn. 1. The reactions of $[(p\text{-Tol})(p\text{-TolN})C{=}S{=}O]^-$ or $[(p\text{-Tol})(\text{i-PrN})C{=}S{=}O]^-$ with $[Rh(cod)Cl]_2$ or $[Rh(nbd)Cl]_2$ are summarized in eqn. 2.

$$(p\text{-Tol})[R(H)N]C{=}S{=}O + NaH \longrightarrow [(p\text{-Tol})(RN)C{=}S{=}O]^-Na^+ + H_2\uparrow \qquad (1)$$

$$[(p\text{-Tol})(RN)C{=}S{=}O]^-Na^+ + [Rh(diene)Cl]_2 \longrightarrow [Rh[(p\text{-Tol})(RN)C{=}S{=}O](diene)] + NaCl\downarrow \qquad (2)$$

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R = *p*-Tol, diene = norbornadiene 1
R = i-Pr, diene = 1,5-cyclooctadiene 2
R = *p*-Tol, diene = 1,5-cyclooctadiene 3
R = i-Pr, diene = norbornadiene 4

Elemental analyses (Table I) of the olefin complexes pointed to the 1:1 stoichiometry indicated in the equation. Molecular weight determinations in chloroform (Table I) showed that the complexes are monomeric in solution. The infrared frequencies of the sulphine unit of the complexes are in the range of 1000 and 1100 cm^{-1}, see Table IV. These values are very close to the values found for this unit in the uncoordinated, neutral aminosulphines. Since aminosulphines in the free form only exist in the Z-isomeric form [9–11] it seems plausible to assume that in the described complexes the sulphine has likewise the Z configuration around the C=S bond. This assumption was confirmed by a X-ray structure determination of Rh[(*p*-Tol)(*p*-TolN)CSO](NBD).

TABLE IV. Spectral Data

Compound	IR^a	T (K)	δ ^{1}H NMR^b	δ ^{13}C NMR^c				δ ^{31}P NMR^d		
			Olefin	Olefin	J(Rh–C)	δCH$_2$(J(Rh–C)	δCH(J(Rh–C))		J(Rh–P)	J(P–P)
1	1030	343	3.72br	53 coal.	–	50.0(3.7)	60.4(6.1)	–	–	–
	1016	303	3.16;4.20br	56.2;49.6	10.2;12.0	49.1(2.4)	60.1(6.1)	–	–	–
		223	3.16;4.28	56.4;49.5	9.8;13.4	50.2(–)	60.8(–)	–	–	–
2	1020	343	4.34br	80.6;72.0v.br	–	31.2(coal)	–	–	–	–
	1001	303	4.06;4.88	80.6;72.0br	–	32.7;29.9	–	–	–	–
		223	3.70;5.02	80.6;72.0	12.2;14.6	34.1;29.7	–	–	–	–
3	1037	373	–	76.8	coal.	30.1 –	–	–	–	–
	1016	343	3.32;4.68	80.3;73.2	12.2;14.6	31.1;29.1	–	–	–	–
		303	3.30;4.70	80.3;73.2	13.4;14.6	31.1;29.1	–	–	–	–
		223	3.28;4.72	–	–	–	–	–	–	–
4	1030	343	4.07	51 coal.	–	49.8(2.5)	61.3(–)	–	–	–
	1019	303	4.10br	54.9;47.2br	–	49.0(2.4)	60.8(6.1)	–	–	–
		223	3.86;4.36	55.4;46.5	9.8;11.0	50.0(–)	61.5(6.1)	–	–	–
5	1025 996	g	–	–	–	–	–	58.3(d)	131.5	–
6	1024 996	g	–	–	–	–	–	57.6(d)	133.4	–
7	1032	313	–	(CO)^e 184.8dd	68^f	–	–	–	–	–
	1015			183.5dd	73	–	–	–	–	–
8	1035	243	–	(CO)^e 185.5dd	71	–	–	–	–	–
	1019			184.2dd	67	–	–	–	–	–
Intermediates^h		223	–	–	–	–	–	75.8(dd)2x	197.3	49
								66.8	169.9	
								62.1(dd)2x	150.2	20
								58.7	122.2	

[a] In cm^{-1}. [b] In d$_8$-toluene, δ ppm form TMS internal standard. [c] In d$_8$-toluene, δ ppm from TMS internal standard. [d] In CDCl$_3$, δ ppm from 85% H$_3$PO$_4$ external standard. [e] ^{13}C enriched carbonyl complexes were used for obtaining these data. [f] J(CC) = 9.8 Hz. [g] The spectra showed no temperature dependent behaviour. [h] *In situ* generated intermediates from Rh[(p-Tol)(p-TolN)CSO](NBD) and DPPE with a molar ratio Rh:DPPE of 1:1 (see text). br, broad; v.br, very broad; coal., coalesced signal; d, doublet; dd, doublet of doublets.

*(ii) Molecular Geometry of Rh[(p-Tol)(p-TolN)-CSO](NBD) (1)**

The triclinic unit cell contains four molecules of the title compound separated with normal van der Waals contacts except for two hydrogen bond-like interactions [21] [C(113)–H(114)···O(1):H(114)···O(1) = 2.382(5) Å; C(121)–H(122)···O(2):H(122)···O(2) = 2.469(6) Å]. The two crystallographically independent molecules show only minor differences in their geometry (Table V). A view of one of the molecules with the adopted numbering is given in Fig. 1. Figure 1 shows the molecular geometry of the Rh[(p-Tol)(p-TolN)CSO](NBD) while Table V gives relevant bond lengths and angles. The complex has a square planar configuration. The rhodium atom is bonded to the two olefinic bonds of the diene, the nitrogen and the oxygen atom of the bidentate coordinated amidosulphine (Rh–O 2.057(2) [2.056(2)] Å; Rh–N 2.062(3) [2.075(3)] Å).

The structure of Rh[(p-Tol)(p-TolN)C=S=O](NBD) is unique because it contains the first example of a coordinated anionic aminosulphine. The N,O-chelate coordination causes small changes in bond lengths and angles in the NCSO part of the amidosulphine ligand as compared with the uncoordinated, neutral aminosulphine thioacetanilid S-oxide [22]. Both the S–O (1.576(3) [1.565(3)] *vs.* 1.50 Å) and the S–C (1.701(4) [1.702(4)] *vs.* 1.64 Å) bond distances have increased on coordination of the amidosulphine to rhodium as compared with these values in the neutral, uncoordinated aminosulphine [22]. The differences in the S=O (1.576(3) [1.565(3)] *vs.* 1.547(3) Å), C–N (1.325(4) [1.319(5)] *vs.* 1.328(4) Å), C=S (1.701(4) [1.702(4)] *vs.* 1.689(3) Å) between the N,O-chelate bonded (anionic) amido-

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*Bond lengths and bond angles which are first mentioned point to the first independent molecule in the unit cell, while the values between square brackets point to the second independent molecule in the unit cell.

TABLE V. Selected Bond Angles and Distances for Rh[(*p*-Tol)(*p*-TolN)CSO][NBD]

Molecule 1				Molecule 2			
Bond distances (Å)		Angles (°)		Bond distances (Å)		Angles (°)	
Within rhodium coordination				Within rhodium coordination			
Rh(1)–O(1)	2.057(2)	O(1)–Rh(1)–N(1)	83.5(1)	Rh(2)–O(2)	2.056(3)	O(2)–Rh(2)–N(2)	83.6(1)
Rh(1)–N(1)	2.062(3)	O(1)–Rh(1)–C(103)	98.6(1)	Rh(2)–N(2)	2.075(3)	O(2)–Rh(2)–C(203)	97.9(2)
Rh(1)–C(103)	2.120(4)	O(1)–Rh(1)–C(104)	102.6(1)	Rh(2)–C(203)	2.126(4)	O(2)–Rh(2)–C(204)	100.5(1)
Rh(1)–C(104)	2.134(4)	O(1)–Rh(1)–C(106)	164.7(1)	Rh(2)–C(204)	2.124(4)	O(2)–Rh(2)–C(206)	162.6(1)
Rh(1)–C(106)	2.099(3)	O(1)–Rh(1)–C(107)	153.5(1)	Rh(2)–C(206)	2.101(5)	O(2)–Rh(2)–C(207)	155.3(2)
Rh(1)–C(107)	2.094(3)	N(1)–Rh(1)–C(103)	165.0(1)	Rh(2)–C(207)	2.103(4)	N(2)–Rh(2)–C(203)	168.4(1)
		N(1)–Rh(1)–C(104)	156.0(1)			N(2)–Rh(2)–C(204)	153.3(1)
		N(1)–Rh(1)–C(106)	102.0(1)			N(2)–Rh(2)–C(206)	101.6(1)
		N(1)–Rh(1)–C(107)	105.1(1)			N(2)–Rh(2)–C(207)	106.8(1)
Within the norbornadiene				Within the norbornadiene			
C(101)–C(102)	1.559(6)	C(102)–C(101)–C(105)	93.3(3)	C(201)–C(202)	1.570(8)	C(202)–C(201)–C(205)	92.9(3)
C(102)–C(103)	1.523(6)	C(101)–C(102)–C(103)	100.7(3)	C(202)–C(203)	1.539(6)	C(201)–C(202)–C(203)	101.3(4)
C(103)–C(104)	1.389(6)	C(102)–C(103)–C(104)	106.8(3)	C(203)–C(204)	1.381(7)	C(202)–C(203)–C(204)	106.6(4)
C(104)–C(105)	1.528(5)	C(103)–C(104)–C(105)	106.3(3)	C(204)–C(205)	1.546(7)	C(203)–C(204)–C(205)	106.3(4)
C(105)–C(106)	1.524(6)	C(104)–C(105)–C(106)	99.5(3)	C(205)–C(206)	1.524(6)	C(204)–C(205)–C(206)	99.6(3)
C(106)–C(107)	1.396(6)	C(105)–C(106)–C(107)	106.3(4)	C(206)–C(207)	1.396(7)	C(205)–C(206)–C(207)	106.4(4)
C(102)–C(107)	1.527(6)	C(102)–C(107)–C(106)	106.5(4)	C(202)–C(207)	1.529(6)	C(202)–C(207)–C(206)	106.3(4)
C(101)–C(105)	1.544(6)	C(101)–C(102)–C(107)	101.2(3)	C(201)–C(205)	1.540(6)	C(201)–C(202)–C(207)	100.3(4)
		C(103)–C(102)–C(107)	99.2(3)			C(203)–C(202)–C(207)	99.9(3)
		C(101)–C(105)–C(104)	100.9(3)			C(201)–C(205)–C(204)	101.9(4)
		C(101)–C(105)–C(106)	101.8(3)			C(201)–C(205)–C(206)	101.3(4)
Within the sulphine				Within the sulphine			
S(1)–O(1)	1.576(3)	O(1)–S(1)–C(108)	104.7(2)	S(2)–O(2)	1.565(3)	O(2)–S(2)–C(208)	104.8(2)
S(1)–C(108)	1.701(4)	Rh(1)–O(1)–S(1)	116.0(2)	S(2)–C(208)	1.702(4)	Rh(2)–O(2)–S(2)	116.2(2)
N(1)–C(108)	1.325(4)	S(1)–C(108)–N(1)	117.7(3)	N(2)–C(208)	1.319(5)	S(2)–C(208)–N(2)	118.4(3)
N(1)–C(116)	1.436(4)	Rh(1)–N(1)–C(108)	117.7(2)	N(2)–C(216)	1.431(5)	Rh(2)–N(2)–C(208)	116.7(3)
C(108)–C(109)	1.481(5)	Rh(1)–N(1)–C(116)	122.3(2)	C(208)–C(209)	1.481(6)	Rh(2)–N(2)–C(216)	122.8(2)
C(109)–C(110)	1.392(5)	C(108)–N(1)–C(116)	118.4(3)	C(209)–C(210)	1.399(6)	C(208)–N(2)–C(216)	119.0(3)
C(109)–C(114)	1.382(5)	N(1)–C(108)–C(109)	126.9(3)	C(209)–C(214)	1.383(6)	N(2)–C(208)–C(209)	126.9(4)
C(110)–C(111)	1.382(6)	S(1)–C(108)–C(109)	115.3(2)	C(210)–C(211)	1.384(6)	S(2)–C(208)–C(209)	114.6(3)
C(111)–C(112)	1.395(6)	C(108)–C(109)–C(110)	120.5(3)	C(211)–C(212)	1.406(6)	C(208)–C(209)–C(210)	120.2(4)
C(112)–C(113)	1.384(5)	C(108)–C(109)–C(114)	120.7(3)	C(212)–C(213)	1.383(6)	C(208)–C(209)–C(214)	120.5(4)
C(112)–C(115)	1.502(6)	N(1)–C(116)–C(117)	119.5(3)	C(212)–C(215)	1.489(6)	N(2)–C(216)–C(217)	120.7(4)
C(113)–C(114)	1.390(6)	N(1)–C(116)–C(121)	121.2(3)	C(213)–C(214)	1.420(6)	N(2)–C(216)–C(221)	120.9(3)
C(116)–C(117)	1.382(5)			C(216)–C(217)	1.393(6)		
C(116)–C(121)	1.391(5)			C(216)–C(221)	1.385(6)		
C(117)–C(118)	1.386(6)			C(217)–C(218)	1.387(6)		
C(118)–C(119)	1.405(6)			C(218)–C(219)	1.374(6)		
C(119)–C(120)	1.362(6)			C(219)–C(220)	1.371(6)		
C(119)–C(122)	1.515(6)			C(219)–C(222)	1.502(7)		
C(120)–C(121)	1.382(5)			C(220)–C(221)	1.383(7)		

Torsion angles (°)		Torsion angles (°)	
S(1)–C(108)–C(109)–C(110)	51.7(5)	S(2)–C(208)–C(209)–C(210)	50.0(5)
C(108)–N(1)–C(116)–C(117)	69.5(4)	C(208)–N(2)–C(216)–C(217)	61.8(5)
C(109)–C(108)–N(1)–C(116)	15.3(6)	C(209)–C(208)–N(2)–C(216)	10.9(6)
O(1)–S(1)–C(108)–C(109)	−176.9(3)	O(2)–S(2)–C(208)–C(209)	−177.1(3)
S(1)–C(108)–N(1)–C(116)	−167.4(2)	S(2)–C(208)–N(2)–C(216)	−171.3(3)
Rh(1)–N(1)–C(108)–S(1)	−1.5(4)	Rh(2)–N(2)–C(208)–S(2)	−4.5(4)
N(1)–C(108)–S(1)–O(1)	5.6(4)	N(2)–C(208)–S(2)–O(2)	4.9(4)
C(108)–S(1)–O(1)–Rh(1)	−7.1(2)	C(208)–S(2)–O(2)–Rh(2)	−3.2(2)
S(1)–O(1)–Rh(1)–N(1)	5.6(1)	S(2)–O(2)–Rh(2)–N(2)	1.1(2)
O(1)–Rh(1)–N(1)–C(108)	−2.2(3)	O(2)–Rh(2)–N(2)–C(208)	2.0(3)

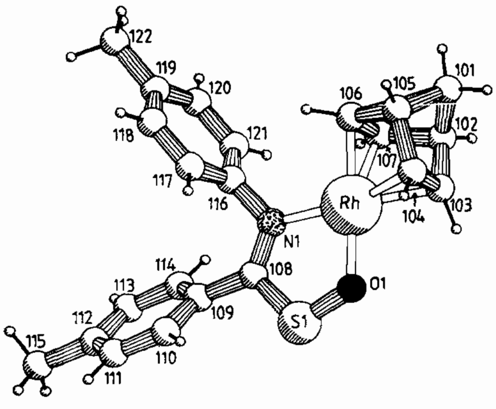

Fig. 1. PLUTO drawing [20] of one of the two crystallographically independent molecules with adopted atom numbering.

sulphine ligand in Rh[(*p*-Tol)(*p*-TolN)C=S=O](NBD) and the η^1-O bonded (neutral) aminosulphine ligand in Me_2SnCl_2[(Ph)(PhMeN)C=S=O] are minimal [23]. The fact that only small changes have been found in the S=O bond lengths of both the N,O-chelate bonded amidosulphine and the η^1-O bonded aminosulphine is in line with the expectation that both coordination modes involve orbitals which are mainly located on the oxygen atom (*vide infra*).

Earlier studies have shown that on π-coordination of the C=S bond of sulphines to Pt^0 as in $Pt(PPh_3)_2$-(fluorene-9-sulphoxide) causes a considerable bond lengthening whereas the S=O bond lengths remained largely unaffected by this coordination [1].

The sulphine nitrogen and carbon atoms in Rh[*p*-Tol)(*p*-TolN)C=S=O](NBD) are almost sp^2 hybridised as can be seen from the torsion angles C(109)–C(108)–N(1)–C(116) = 15.3(6) [10.9(6)]° and Rh(1)–N(1)–C(108)–C(109) = –178.8(3) [–177.8(3)]° together with the angles around the nitrogen atom: Rh(1)–N(1)–C(108) = 117.7(2) [116.7(3)]°, Rh(1)–N(1)–C(116) = 122.3(2) [122.8(2)]° and C(108)–N(1)–C(116) = 118.4(3) [119.0(3)]°, the sum of which is close to 360°. The same sp^2 hybridization of the nitrogen atom is observed in the η^1-O coordinated aminosulphine in the tin complex Me_2SnCl_2[(Ph)(PhMeN)CSO] [23]. The rhodium atom in Rh[(*p*-Tol)(*p*-TolN)C=S=O](NBD) lies in the same plane as the sulphine unit as shown in Fig. 1. The O(1)–Rh(1)–N(1) angle is 83.49(9) [83.6(1)]° while the O=S=C–N unit is nearly flat with a N(1)–C(108)=S(1)=O(1) torsion angle of 5.6(4) [4.9(4)]°. These structural features for the N,O-chelate bonded ligand contrast with those of the neutral, η^1-O bonded aminosulphine which is coordinated to a tin centre. Although in the latter case the NCSO part of the aminosulphine ligand is nearly flat, the coordinated tin atom is out of this plane with a Sn–O–S angle of 129.1(2)° [23]. The olefine bond of the norbornadiene ligand which is *trans* to the sulphine nitrogen atom is shorter than the olefine bond which is *trans* to the sulphine oxygen atom (1.389(6) [1.381(7)] *vs.* 1.396(6) [1.396(7)] Å). These olefinic bond lengths are in the same range as those found in, for example, acetylacetonatorhodium diene complexes (1.40 to 1.42 Å) which have similar geometries [24–28]. It is noteworthy, that the olefinic bond with the shortest C–C bond length (C(103)–C(104) 1.389(6) [1.381(7)] Å) has the longest Rh–C distances (Rh–C(103) 2.120(4) [2.126(4)] and Rh–C(104) 2.134(4) [2.124(4)] Å), while the olefinic bond which is closest to the rhodium (Rh–C(106) 2.099(3) [2.101(5)] and Rh–C(107) 2.094(3) [2.103(4)] Å) has the longest C–C bond length (C(106)–C(107) 1.396(6) [1.396(7)] Å). The observed trends in the Rh–C and C–C olefinic bond distances are related to different *trans* influences of the nitrogen and oxygen donor atoms of the anionic amidosulphine ligand, *i.e.* the metal-to-olefin backdonation seems to be larger to the olefinic moiety *trans* to the oxygen donor atom indicating this atom to be the stronger σ-donor. It is, therefore, also interesting to compare this trend of having the shorter bond lengths for the olefinic bond *trans* to a nitrogen atom than *trans* to oxygen in **1** to that recently observed in (2,6-bis(dimethylaminomethyl) phenyl)(1,5-cyclooctadiene)rhodium(I). In the latter case the C=C bond length of the olefin *trans* to the neutral nitrogen ligand amounts to 1.379(8) Å, while the olefin bond length *trans* to the negatively charged carbon atom is slightly longer being 1.391(9) Å [29]. Although the observed differences are only small the trends in the change of the C=C bond lengths in these complexes seem to be equal and in the case of the amidosulphine rhodium complex **1** point to a shift of the negative charge in the NCSO part of the monoanionic ligand to the oxygen atom (Fig. 2: canonical structure B).

(iii) Bonding and Electronic Structure of (Neutral) Aminosulphines and (Monoanionic) Amidosulphines

At this stage it is important to consider the electronic structure of the amidosulphine ligands in more detail. In an earlier paper [9] some results from semi-empirical MNDO [30] molecular orbital calculations for the neutral model aminosulphine $H_2N(H)C=S=O$ were reported. It turned out that the ligand MO which has mainly a lone pair-oxygen

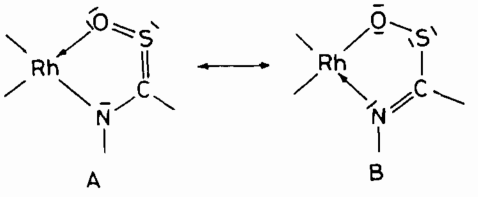

Fig. 2. Canonical structures.

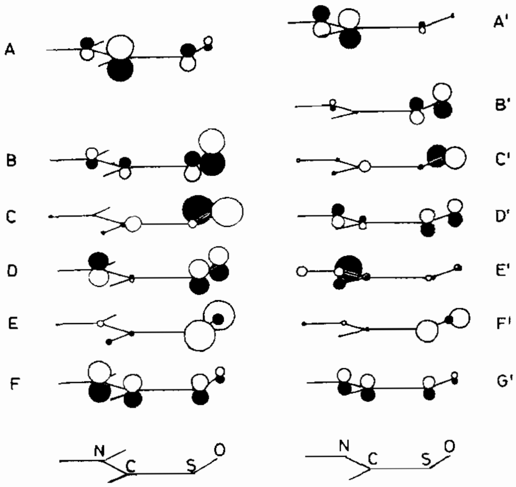

Fig. 3. PICTOR-plot of the calculated molecular orbitals. The coefficients of the molecular orbitals are reduced to approximately 30% for clarity.

TABLE VI. Charge Distribution Over the NC=S=O Part of the Ligand System

Atom	Neutral sulphine	Anionic sulphine
O	−0.65	−0.73
S	0.44	0.08
C	−0.03	−0.03
N	−0.29	−0.34

character (Fig. 3, MO, B) was readily accessible for coordination to a metal centre. This is illustrated by the η^1-O-coordination of an aminosulphine to a tin centre [9]. The final calculated charge distribution in the NC=S=O part of this general model for the neutral ligand is summarized in Table VI. When however, the MO calculations were performed on a model of the monoanionic ligand, *i.e.* on $[HN(H)C{=}S{=}O]^-$, some interesting differences with the above charge distribution were obtained. The MO plots of the six highest occupied and first lowest unoccupied molecular orbitals for the amidosulphine anion are given in Fig. 3, which have been constructed from the calculated eigenvectors by PICTOR [30]. First, the negative charge has mostly been accumulated by the S atom which therefore is less positive than in the neutral aminosulphine. Second, in the anion not only a σ orbital at the N atom (Fig. 3, MO C′) has become accessible for the formation of a σ bond to a metal, but also some extra negative charge has been shifted towards the oxygen atom. With these two effects in mind it will be clear that N,O-chelate coordination of the anionic amidosulphine ligand towards a transition metal, e.g. rhodium, is a likely possibility.

In the case of the η^1-O coordination of an aminosulphine to tin the coordination involves molecular orbital B (Fig. 3) which interacts with a suitable orbital on tin. As can been seen from the MO plot in this case the metal centre is expected to be out of the NCSO plane with a S–O–Sn angle close to 90°. It must be noted that the crystal structure determination shows that the actual S–O–Sn angle is 129.1°, indicating that this angle also is determined by other factors which are likely steric in origin.

(iv) Dynamic Behaviour in Solution

The crystal structure of **1** described above shows that in the solid state the amidosulphine ligand is N,O-chelate coordinated to rhodium. However, in solution the (thioamido S-oxide)(diene)rhodium(I) complexes show temperature dependent behaviour. NMR spectra recorded at various temperatures and various concentrations of the complex with varying amounts of added diene (the addition varied from no added diene to a molar ratio of Rh and diene of 1/1) showed that this was due to fluxional behaviour rather than to intermolecular exchange processes. We will discuss here the case of Rh[(*p*-Tol)(*p*-TolN)-CSO](NBD) as an example because the other (thioamido S-oxide)(diene)rhodium(I) complexes showed a similar behaviour (Table IV).

The room temperature ^1H NMR spectra, recorded in $CDCl_3$ of Rh[(*p*-Tol)(*p*-TolN)CSO](NBD) (**1**) show for the olefinic protons two broad lines at 3.16 and 4.20 ppm, which coalesce at 343 K at 3.72 ppm. The ^{13}C NMR spectra recorded at 223 K show two resonances for the olefinic carbon atoms at 56.4 and 49.5 ppm with a $^1J(^{103}Rh, ^{13}C)$ of 9.8 and 13.4 Hz, respectively. These facts clearly indicate that the diene is coordinated to the rhodium centre. Moreover, the observation that there are only two olefinic carbon resonances show that the molecule must possess an (apparent) molecular symmetry plane coinciding with the coordination plane. This leaves as a likely structure for the complex in solution at low temperature the one which has been established for the compound in the solid state, see Fig. 1.

The ^1H and ^{13}C NMR spectra recorded at 343 K show only one broad resonance at 3.72 and 53 ppm, respectively, for the olefinic hydrogen and carbon atoms (see Table IV). These observations indicate that the molecule is either fluxional or that intermolecular exchange processes, which are fast on the NMR time scale, are responsible for the observed coalescence of the olefinic resonances. The resonances of the substituents in the sulphine unit in, for example, **2**, are esssentially temperature independent in the temperature range 193 to 378 K. The two isopropyl–methyl groups of the prochiral

TABLE VII. Calculated Activation Parameter

Compound	T(coal.)	$\Delta G^{\ddagger}$ (kcal/mol)[a]
1	343 K	15.9
2	303 K	14.9
3	373 K	17.7
4	343 K	16.3

[a] The spectra were recorded in d_8-toluene. For the calculation of $\Delta G^{\ddagger}$ the olefinic protons of the diene were used.

isopropyl group, which is a sensitive probe for molecular dissymmetry, are equivalent in the NMR spectrum in the temperature range studied. This indicates that the molecular symmetry plane remains unaffected by the exchange process.

Finally, addition of either excess of COD, NBD or dimethyl maleate to NMR solutions in $CDCl_3$ or d_8-toluene of the (thioamido S-oxide)(diene)-rhodium(I) complexes did not affect their resonance patterns which shows that the exchange process must occur intramolecularly.

Various processes can now be envisaged to explain these observations. A first possibility involves exchange via a monodentate O-coordinated amidosulphine anion in the transition state. As a second possibility the intermediacy of a mono-coordinated diene in any part of the process can be considered. Both processes would imply the involvement of an intermediate species with a three-coordinate rhodium centre which, however, can be ruled out since in these cases excess ligand should have an effect on the exchange process. As a third, very likely possibility the process may involve the formation of a five-coordinate rhodium species by attack of a solvent molecule at the fifth coordination site. This process is supported by the observation that addition of SO_2 or PPh_3 brings the olefine fluxional process in the fast exchange limit already at probe temperature (*vide infra*). Finally, the possibility that the intramolecular exchange could proceed by a process in which the diolefine rotates around the rhodium–amidosulphine plane cannot be excluded. This process would involve a transition state with a tetrahedral geometry at rhodium. From the temperature dependence of the ^{1}H and ^{13}C NMR spectra it can be deduced that the $\Delta G^{\ddagger}$ values for this process would lie between 14.9 and 17.7 kcal/mol (see Table VII). Interestingly Knox and Woodward proposed a similar process, involving rotation of the diolefine around rhodium through a tetrahedral transition state, to explain the fluxional behaviour of $[Rh_2(CO)_2(\mu\text{-}SPh)_2(COD)]$. $\Delta G^{\ddagger}$ values of 10.5–15.0 kcal/mol [32] were found, which is in the same range as has been found for the present fluxional process of the rhodium diolefine complexes **1**–**4**.

(v) Reaction of (Thioamido S-oxide)(diene)rhodium(I) with Phosphines

The reactions of equimolar quantities of the rhodium–diene–sulphine complexes **1**–**4** with bis(diphenylphosphino)methane (DPPM) have been followed by ^{1}H NMR spectrometry. It appeared that in all cases liberation of the diene occurred with formation of a complex with a 1:1:1 ratio of rhodium, sulphine and DPPM. The ^{31}P NMR spectrum, however, showed the presence of a variety of products, which could not be separated.

The rhodium–diene–amidosulphine complexes, **1**–**4**, react with 1,2-bis(diphenylphosphino)ethane (DPPE) according to eqn. 3. This reaction, wich occurs instantaneously at room temperature, can be followed by ^{31}P NMR spectrometry at 223 K.

$$2[Rh((R)(p\text{-}TolN)C{=}S{=}O)(diene)] + DPPE \longrightarrow$$
$$\underset{\mathbf{5,\,6}}{[Rh((R)(p\text{-}TolN)C{=}S{=}O)(DPPE)]_2} + diene \qquad (3)$$

R = *p*-Tol (**5**) or i-Pr (**6**). Diene = 1,5-cyclooctadiene or norbornadiene.

Molecular weight determinations indicated that the pure compounds exist in chloroform solution as dissociating dimers (see Table I). The IR absorptions at 1025 and 996 cm^{-1} show clearly that the sulphine unit is still bonded in the Z configuration (see Table II) and this leads to the conclusion that also in these complexes the amidosulphine is N,O-chelate coordinated. The bonding of the DPPE ligands in these dimeric complexes can be deduced from the ^{1}H and the ^{31}P NMR spectra. The room temperature ^{1}H NMR spectra of the products are in accord with a DPPE to sulphine molar ratio of 1:1. The ^{1}H NMR patterns as well as the doublet found for the phosphor resonances due to $^{1}J(^{103}Rh-^{31}P)$ in the ^{31}P NMR spectra were temperature independent. The dimeric nature can be explained if either the DPPE molecule or the amidosulphine are bridging the two Rh units while the other ligands are each bonded to one Rh unit in a chelate bonding mode. A possible structure with the amidosulphine as the bridging ligand seems unlikely because of the Z configuration at the C=S bond whereas the bridge bonding would require the E configuration. Furthermore for chelate bonding of the DPPE we would expect at the slow exchange limit two signals for the two inequivalent P atoms with superimposed on them the rhodium coupling as well as a *cis*-phosphor-to-phosphor coupling. This would result in an eight line pattern whereas only two lines are observed. It is therefore the second possible structure containing chelate bonded amidosulphine and a bridging DPPE ligand that seems to be supported by the spectroscopic data. The bridging mode of the DPPE molecule can explain the equivalency of the two phosphor atoms.

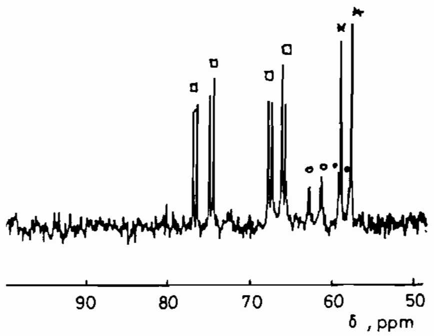

Fig. 4. ^{31}P NMR spectrum of the *in situ* generated intermediates (see text). The doublet marked with * is originating from the dimer (see Fig. 5), while the two ABX spectra marked with [ ] and o are originating from the monomers I and II as depicted in Fig. 5.

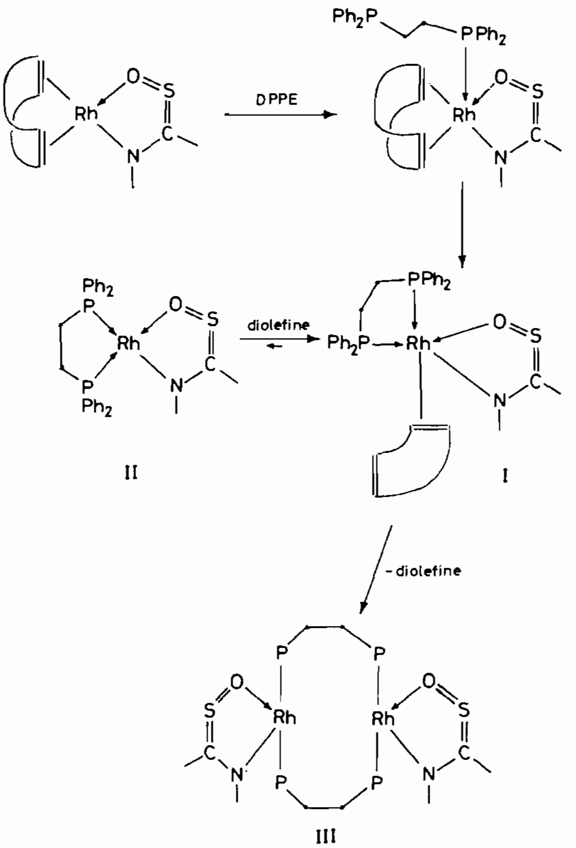

Fig. 5. Proposed reaction mechanism of the displacement of the diene by 1,2-bis(diphenylphosphino)ethane.

In order to follow the formation of the Rh(amidosulphine)(DPPE) dimer, a ^{31}P NMR spectrum was recorded immediately after addition of DPPE to a solution of Rh(*p*-Tol)(*p*-TolN)C=S=O)(NBD) in $CDCl_3$ at 223 K. The resulting spectrum shows two ABX patterns; one of major intensity at 75.8 and 66.8 ppm and one of minor intensity at 62.1 and 58.7 ppm, as well as the already described doublet (see Fig. 4).

The $^1J(^{103}Rh-^{31}P)$ for the major ABX pattern is 197 and 170 Hz, respectively, and for the minor ABX pattern 150 and 122 Hz, respectively. The $^2J(P-P)$ is 49 Hz in the former case and 20 Hz for the latter ABX pattern, which points to two *cis* positioned phosphorus atoms. From the fact that there are two sets of ABX patterns with rhodium coupling, as well as the doublet originating from the already formed dimer, we can conclude that the low temperature reaction of the rhodium(diolefine)-aminosulphine complexes with diphenyldiphosphinoethane involved the formation of two intermediates. The ^1H NMR spectrum under the same conditions showed some free NBD and chelate coordinated NBD. The ^{31}P NMR spectrum of this sample at room temperature, showed the doublet with increased intensity, while the two ABX patterns were no longer present. The ^1H NMR spectrum revealed that now the olefin was completely liberated from the rhodium centre.

The reaction proceeds probably via the following route (see Fig. 5). The first step is the incoming of one of the phosphorus atoms of the DPPE molecule, followed by dissociation of one rhodium–olefinic bond. Then the second phosphorus atom comes in. The final configuration is that of a trigonal bipyramid, with one phosphorus atom in an apical and the other phosphorus atom in an equatorial position. The diene is coordinated via only one olefinic bond in an apical position. The sulphine is still chelate bonded and resides in the equatorial plane. It is known that JRh–P_e > JRh–P_a [33]. In our case we observed JRh–P coupling constants of 197 and 170 Hz. This is in reasonable accordance with the values of 206 and 143 Hz found by Meakin and Jesson [34] for a TBP arrangement of Rh(I) in Rh[P(OCH$_3$)$_3$]$_5$B(C$_6$H$_5$)$_4$ and related complexes. We can conclude that one of the intermediates in the reaction of the Rh(diene)sulphine complexes with DPPE has a TBP arrangement with one P in axial and one P in equatorial position (see Fig. 5, I).

The other observed ABX pattern with a Rh–P coupling of 150 and 122 Hz, can be explained by assuming a square planar arrangement around rhodium. This hypothesis is supported by the results of Sanger [35] who reported for his square planar RhX(DPPE)(CO) complexes $^1J(^{103}Rh-^{31}P)$ values of *ca.* 160 and 124 Hz.

Once the trigonal bipyramidal rhodium complex consisting of the amidosulphine, DPPE and the diolefine is formed, this intermediate quickly dimerizes giving rise to a doublet in the ^{31}P NMR spectrum with $^1J(^{103}Rh-^{31}P)$ 132 Hz. Sanger described for a similar dimeric complex: [RhX(DPPP)(CO)]$_2$ a

$^1J(^{103}Rh-^{31}P)$ of 120–125 Hz depending on X [35].

The reaction of the (thioamide S-oxide)(diene)-rhodium(I) complexes with PPh_3 supports the first step of the above described mechanism (*vide infra*).

(vi) Reaction of (Thioamido S-oxide)(diene)rhodium(I) Complexes with Triphenylphosphine

A distinct interaction of PPh_3 with the (thioamido S-oxide)(diene)rhodium(I) complexes was observed. Addition of PPh_3 to a solution of the complexes **1**–**4** causes in the ^{31}P NMR spectra a shift of the signal of the phosphine which is dependent on the ratio Rh:PPh_3 as well as on the temperature (varied from 223 to 343 K). No signal of uncoordinated triphenylphosphine was recorded. The ^{31}P signal is broad, and does not decoalesce into a doublet or an ABX pattern at low temperatures as would be expected for a rhodium–phosphor complex. Addition of a small amount of PPh_3 (ratio Rh:P > 100:1) to a solution of **1**–**4** already brings the olefine fluxional process in the fast exchange limit in the 100 MHz proton NMR at probe temperature. These two observations lead to the conclusion that intermolecular exchange between the rhodium(amidosulphine)-(diene)–PPh_3 adduct, free triphenylphosphine and the (thioamido S-oxide)(diene)rhodium(I) is in the fast exchange limit even at low temperatures.

$$\text{(thioamido S-oxide)(diene)Rh(I)} + PPh_3 \rightleftharpoons \text{(thioamido S-oxide)(diene)Rh}(PPh_3) \qquad (4)$$

(vii) Reactions of (Thioamido S-oxide)(diene)-rhodium(I) with Small Molecules

(a) Addition of $HgCl_2$ or MeI to a solution of **1**–**4** showed no change in the NMR spectra indicating that no reaction occurred.

(b) Passing SO_2 gas over solutions of the complexes **1**–**4** led to a colour change of the solution from yellow to red, while this colour change reversed on removal of SO_2. Bubbling SO_2 through an NMR solution of **1**–**4** in an NMR tube for a few seconds caused coalescence of the olefinic protons in the ^1H NMR spectrum indicating that coordination of SO_2 brings the olefine fluxional process in the fast exchange limit (see above with PPh_3). Attempts to isolate the SO_2 compound formed most probably failed because of the weak bonding of SO_2.

(c) Bubbling CO through a solution of the complexes **1**–**4** for a few seconds resulted in the liberation of the olefine from the rhodium centre as confirmed by the observation of free olefine in the proton NMR spectrum of the reaction mixture. It must be noted that attempts to synthesize these complexes from $[RhCl(CO)_2]_2$ with the respective sulphine anions resulted in decomposition of the rhodium complexes. Elemental analyses of the isolated product pointed to a Rh(amidosulphine)-$(CO)_2$ stoichiometry (see Table I). The sulphine bands in the carbonyl complex formed are found at 1032 and 1015 cm^{-1} indicating that, compared to the olefin complex ($\nu CSO = 1030$, 1016 cm^{-1}) the sulphine configuration is unchanged, and thus has still the Z configuration and is chelate bonded. The infrared spectrum of $Rh[(p\text{-Tol})(p\text{-TolN})CSO](CO)_2$ shows two CO stretching bands at 2072 and 2003 cm^{-1} and in the case of $Rh[(p\text{-Tol})(i\text{-PrN})CSO](CO)_2$ at 2069 and 1994 cm^{-1}. The values of νCO are consistent with terminal CO ligands in the *cis* position [36]. To further confirm the structure of the carbonyl compound the ^{13}C NMR spectra of ^{13}C-enriched CO compounds were recorded. The ^{13}C NMR spectra show basically an ABX spectrum with a $^2J(^{13}C-^{13}C)$ of 9.8 Hz and $^1J(^{103}Rh-^{13}C)$ of 60–70 Hz (see Table IV and Fig. 6). The $^2J(^{13}C-^{13}C)$ of 9.8 Hz is in good agreement with the value of 9.15 Hz found by Varskavskii *et al.* for their $Rh(Oxq)(^{13}CO)_2$ complex (Oxq = the radical of 8-hydroxyquinoline) [37]. Superimposed on the already described ABX pattern is a pattern of two doublets, each arising from only one ^{13}C signal with ^{103}Rh coupling. The latter doublets belong to the presence of a few percent of $Rh^{13}CO^{12}CO$sulphine and $Rh^{12}CO^{13}CO$sulphine which are formed because of the use of 95% enriched ^{13}CO.

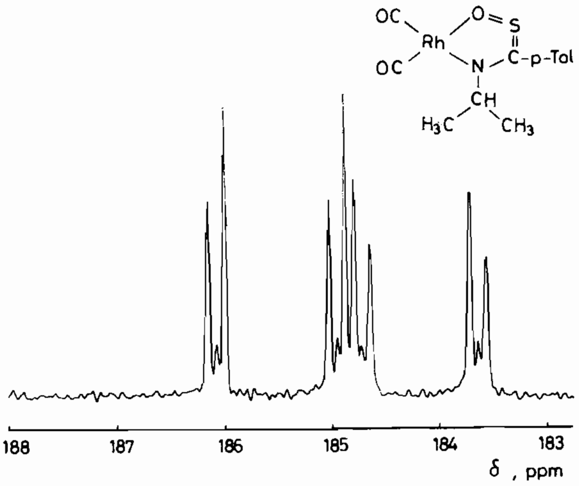

Fig. 6. 62.9 MHz ^{13}C NMR spectrum (CO region) of the ^{13}C enriched complex $Rh((p\text{-Tol})(i\text{-PrN})CSO)(CO)_2$.

From the ^{13}C NMR data of the enriched compound and the IR spectra we can conclude that in the Rh(amidosulphine)$(CO)_2$ complexes the amidosulphine is chelate coordinated and both carbon monoxide molecules are in the *cis* position. The replacement of the diolefine by CO probably proceeds via the same mechanism as the formation of the Rh(amidosulphine)(DPPE) complexes.

Conclusions

The above results show that the monoanionic amidosulphines [(*p*-Tol)(*p*-TolN)CSO]$^-$ and [(*p*-Tol)-(i-PrN)CSO]$^-$ have a preference for the N,O chelate bonding mode towards rhodium(I). The complexes **1**–**4** are remarkably stable, although long periods of storage cause decomposition. On heating the complexes to 373 K little decomposition occurred. The chelate bonding of the sulphine is very strong, even in a reaction with DPPE, a ligand that prefers chelate rather than bridged bonding, the amidosulphine anion remains chelate bonded. The stability of these complexes is in contrast with the low stability of the neutral, coordinated aminosulphines. The η^1-O coordinated aminosulphine in diorganotin dihalide complexes, decompose rapidly upon heating, to products originating from C=S and C=O bond cleavage [23].

Supplementary Material

Tables of thermal parameters, positional parameters for the hydrogen atoms, a complete list of bond distances and angles and a listing of observed and calculated structure factors are available on request from the author (A.L.S.).

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