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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

X *. *N*-SULFINYLANILINE COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) OF THE TYPE $[MCl(PR_3)_2L]$ IN WHICH L IS COORDINATED VIA THE π-N=S AND VIA THE SULFUR ATOM RESPECTIVELY; CRYSTAL AND MOLECULAR STRUCTURE OF $[RhCl(P\text{-}i\text{-}Pr_3)_2\text{-}(4\text{-}MeC_6H_4N{=}S{=}O)]$; DETERMINATION OF THE $^1J(^{103}Rh—^{15}N)$ BY ^{15}N NMR SPECTROSCOPY

R. MEIJ, D.J. STUFKENS, K. VRIEZE *,

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

W. VAN GERRESHEIM and C.H. STAM

Laboratorium voor Kristallografie, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

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Summary

Each of the compounds $[MCl(Pr_3)_2(ArylNSO)]$ (M = Rh^I, Ir^I; R = i-Pr, Cy: Aryl = C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$) appears to exist as two isomers both in the solid state and in solution. The molecular and single crystal structure of one of the isomers of $[RhCl(P\text{-}i\text{-}Pr)_3)_2(4\text{-}Me_6H_4NSO)]$ shows that the *N*-sulfinylaniline ligand is in the *cis*-configuration and coordinated to the rhodium atom via the sulfur-atom. The ligand lies in a plane which includes the rhodium atom and is in agreement with the Rh—S distance of 2.10 Å. IR results of the compounds (solid and solutions), ^{31}P NMR data and ^{15}N NMR of a ^{15}N labelled compound, which yielded a $^{103}Rh—^{15}N$ coupling constant of 15.5 Hz, show that in the second isomer the *N*-sulfinylaniline ligand is probably bonded to the metal atom via the π-N=S bond.

The ratio of the metal—π-N=S bonded isomer and the metal—S bonded isomer decreases in the order Aryl = 4-ClC_6H_4 > C_6H_5 > 4-MeC_6H_4; R = i-Pr > Cy and M = Rh > Ir. The interconversion of the two isomers is intramolecular and becomes observable on the ^{31}P NMR time scale at about 40°C for M = Rh.

In the case of $[IrCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)]$, cyclometallation of the sulfinylaniline is observed via the *ortho*-carbon atom, whereas cyclometallation via

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* For part IX see ref. 1.

P-i-Pr_3 is observed when the *ortho*-positions are blocked by methyl groups, e.g. when L = 2,4,6-$Me_3C_6H_2NSO$.

Introduction

The coordination properties of the isoelectronic cumulated double bond systems R—N=S=N—R, R—N=S=O and O=S=O are of special interest because of the possibility of changing the type of metal and the type of ligand bonded to the metal atom influencing the mode of bonding to the metal.

Previous work on the coordination properties of the *N,N'*-substituted sulfurdiimines RN=S=NR has shown that they can bind as a monodentate ligand via N, for which three configurations are possible (Fig. 1A, 1B and 1C) [2—7], as a bidentate ligand via two N-atoms (Fig. 1D) [5—7], very rarely as a monodentate one via the S-atom (Fig. 1E) [6,7], and formally as monodentate one via the π-N=S bond (Fig. 1F) [8]. Furthermore the RNSNR ligand may probably also bridge two metal atoms through a metal—σ-N bond and a metal—π-N=S bond (Fig. 1G) [9]. The type of coordination depends strongly on the basicity of the metal atom e.g. in the case of Pt^{II} only metal—N linkages are observed [2,3,5], while for the strongly basic Pt^0 the ligand is bonded via the π-N=S bond [8].

In the case of the SO_2 ligand, metal—S bonding predominates [10], while exclusive metal—π-S=O bonding has been observed in $[Rh(PPh_3)_2(NO)(SO_2)]$ [11]. Furthermore SO_2 can act as a bridging ligand via the S-atom [10].

Collins and Glass [12] predicted that $C_6H_5N{=}S{=}O$ should not function as a ligand, the electronic donating and accepting properties being estimated to be of the same order as benzene. Nevertheless Blake and Reynolds [13] isolated $[Pt(PPh_3)_2(ArNSO)]$, for which they proposed a metal—π-N=S linkage (Fig.

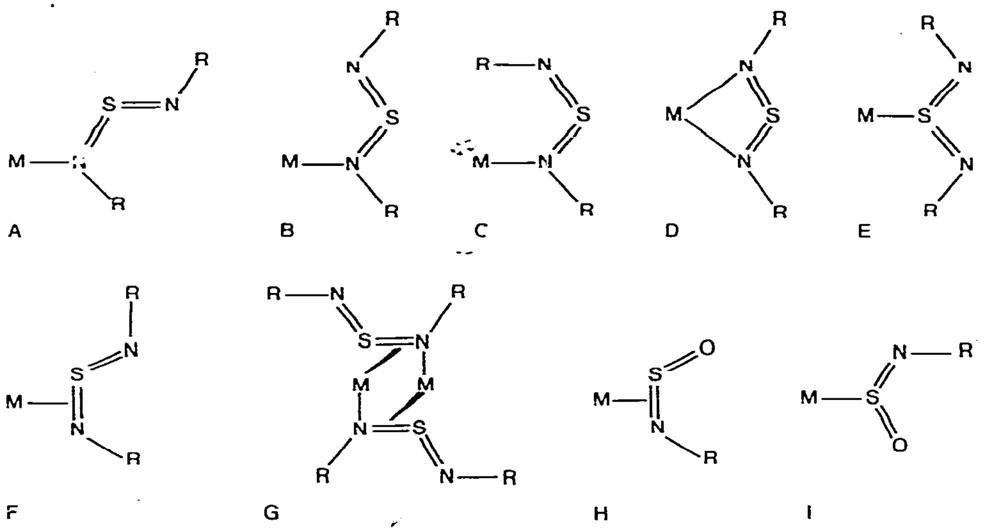

Fig. 1. Known bonding modes of the sulfurdiimines and *N*-sulfinylanilines.

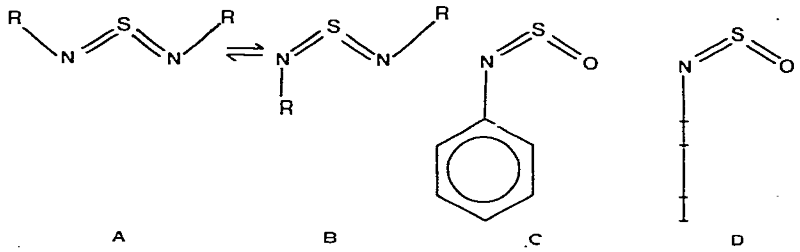

Fig. 2. The two conformations of RN=S=NR in solution (A: *trans,trans* and B: *cis,trans*) and the conformation of ArN=S=O (C: general and D: when both ortho-positions are occupied by CH_3 groups.

1H), which was confirmed by spectroscopic studies and a crystal structure determination [8]. A similar suggestion was made recently for the analogous Ni^0 complexes $[Ni(PPh_3)_2(ArylNSO)]$ [14]. A metal—sulfur bonded complex (Fig. 1I) has been proposed for the product of the reaction of $[Ir(PPh_3)_2(CO)Cl]$ with *p*-nitro-*N*-sulfinylaniline [13].

Since there is clearly little known about the coordination properties of ArylN=S=O, which is expected to be intermediate in behaviour between RN=S=NR and O=S=O, it appeared worthwhile to extend our investigations to the coordination properties of ArN=S=O. Of special interest was a study of the reactions with Rh^I and Ir^I, since it has been shown that RN=S=NR coordinates via the N-atom [5] while O=S=O strongly favours S-coordination [15].

In this article we report crystallographic, spectroscopic (IR, ^1H, ^{31}P and ^{15}N NMR) and thermochemical studies of complexes of Rh^I and Ir^I with ArNSO.

Experimental

All reactions were carried out under dry oxygen-free nitrogen, and solvents were dried over sodium wire and distilled under N_2 before use. The preparation of *N*-sulfinylanilines [16], $[M(COT)_2Cl]_2$ (COT = cyclooctene) [17] and $[IrCl(PPh_3)_2N_2]$ [18] have been reported before. The complexes $[MCl(PR_3)_2(L)]$ (M = Rh, Ir; R = i-Pr (isopropyl), Cy (cyclohexyl) and L = C_6H_5NSO, $4\text{-}MeC_6H_4NSO$, $2,4,6\text{-}Me_3C_6H_2NSO$, $4\text{-}ClC_6H_4NSO$, SO_2) were prepared by the same method. An example is given for one of them.

Preparation of $[RhCl\{P(i\text{-}Pr)_3\}_2(4\text{-}MeC_6H_5NSO)]$. To a solution of 0.5 mmol $[RhCl(COT)_2]_2$ in 15 ml toluene was added 2 mmol $P\text{-}i\text{-}Pr_3$. After 15 min 1 1 mmol $4\text{-}MeC_6H_4NSO$ was added. After removal of the solvent the complex was recrystallized from n-hexane to give dark coloured crystals. Yield 0.57 mmol (57%).

When PPh_3 was used instead of $P\text{-}i\text{-}Pr_3$, only $[RhCl(PPh_3)_2]_2$ was isolated. The reaction of $[IrCl(PPh_3)_2N_2]$ with $4\text{-}MeC_6H_4NSO$ in toluene yielded a dark-coloured solution, which indicated the formation of $[IrCl(PPh_3)_2(4\text{-}MeC_6H_4NSO)]$ but the complex was too unstable to be isolated.

Spectroscopic measurements and analytical data

The ^1H NMR spectra were recorded on Varian A60 and T60A spectrometers, the ^{31}P NMR spectra on a Varian XL-100, and the ^{15}N NMR spectrum on a Bruker WH-270 spectrometer. The ^{15}N NMR spectrum was measured with a

TABLE 1

ANALYTICAL DATA FOR $[\mathrm{MCl(PR_3)_2L}]$

Compound		Analysis (found (calcd.) (%))				
		C	H	N	P/S	Cl
I	$[\mathrm{RhCl(P\text{-}i\text{-}Pr_3)_2(C_6H_5NSO)}]$	47.88	8.11	2.22		
		(48.20)	(7.92)	(2.34)		
II	$[\mathrm{RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)}]$	49.00	8.08	2.34	9.81	5.69
		(49.06)	(8.07)	(2.34)	(9.81) [a]	(5.69)
III	$[\mathrm{RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}ClC_6H_4NSO)}]$	45.57	7.50	2.11		
		(45.58)	(7.33)	(2.21)		
IV	$[\mathrm{RhCl(P\text{-}i\text{-}Pr_3)_2(2,4,6\text{-}Me_3C_6H_2NSO)}]$	50.61	8.29	2.14		
		(50.60)	(8.35)	(2.14)		
VI	$[\mathrm{RhCl(P\text{-}i\text{-}Pr_3)_2(CO)}]$	46.73	8.24			
		(46.68)	(8.70)			
VII	$[\mathrm{RhCl(PCy_3)_2(4\text{-}MeC_6H_4NSO)}]$	59.25	8.69	1.82		
		(60.58)	(8.63)	(1.64)		
VIII	$[\mathrm{RhCl(PCy_3)_2(SO_2)}]$	55.71	8.10			
		(56.65)	(8.72)			
IX	$[\mathrm{IrCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)}]$	42.66	7.11	1.90	8.73	4.87
		(42.81)	(7.04)	(2.00)	(8.83) [a]	(4.87)
IXd	$[\mathrm{IrCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_3NSO)H}]$	41.64	7.03	1.77	5.18	
		(42.81)	(7.04)	(2.00)	(4.57) [b]	
X	$[\mathrm{IrCl(P\text{-}i\text{-}Pr_3)_2(2,4,6\text{-}Me_3C_6H_2NSO)}]$	44.52	7.21	2.00		
		(44.46)	(7.32)	(1.92)		
Xe	$[\mathrm{IrCl(PCH(CH_3)CH_2\text{-}i\text{-}Pr_2)(P\text{-}i\text{-}Pr_3)_2H\text{-}(2,4,6\text{-}Me_3C_6H_2NSO)}]$	43.19	7.60	1.55		
		(44.46)	(7.32)	(1.92)		
XI	$[\mathrm{IrCl(P\text{-}i\text{-}Pr_3)_2(SO_2)}]$	34.55	6.95		4.88	
		(35.32)	(6.92)		(5.24) [b]	
XII	$[\mathrm{IrCl(P\text{-}i\text{-}Pr_3)_2(CO)}]$	38.89	7.06			
		(39.61)	(7.35)			

[a] P analysis. [b] S analysis.

100% enriched ^{15}N sample using a concentration of 0.1 *M*. The pulse width was 50 μsec. and the pulse delay was 10 sec. The IR spectra were recorded on a Beckman IR 4250 spectrophotometer, which was calibrated in the usual way. The samples were usually examined as KBr discs, but Nujol mulls were used for the low frequency region. Thermogravimetry (TG) and DTA measurements were carried out simultaneously with a Mettler Thermoanalyser type 1. Elemental analyses (Table 1) were carried out by the elemental analytical section of the Institute for Organic Chemistry TNO, Utrecht.

Crystal data

From single crystal diffractometry: a 9.779(1), b 9.875(1), c 16.101(1) Å, α 96.49(1), β 97.18(1), γ 99.29(1)°, Z 2, triclinic, space group $P\bar{1}$.

Intensity data, structure determination and refinement

1098 independent reflections were measured on a Nonius CAD 4 automatic four circle diffractometer (Cu-K_α, θ—2 θ scan), 600 of which were below the 2.5 σ level and were treated as unobserved. The structure was solved by locating the Rh, S, Cl and P atoms from an E^2-Patterson synthesis. A subsequent Fourier synthesis revealed the positions of the other atoms. Refinement proceeded by anisotropic block-diagonal least square methods to a final R value of 4.7% for the 2498 reflections. Towards the end of the refinement a difference Fourier synthesis revealed the H atoms, which were included in the refinement with fixed parameters.

Results

The complexes were prepared by the following route, which has already been described for other heteromolecules by Van Gaal et al. [19]:

$$[\mathrm{MCL(COT)_2}]_2 + 4\mathrm{PR_3} + 2\ \mathrm{ArNSO} \rightarrow 2[\mathrm{MCl(PR_3)_2(ArNSO)}] + 4(\mathrm{COT})$$

The molecular structure of $[RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)]$

The atomic coordinates, bond distances, bond angles and dihedral angles are listed in Table 2, 3, 4 and 5 respectively. The *p*-methyl-*N*-sulfinylaniline ligand is in the *cis*-configuration and is coordinated to rhodium via the sulfur atom. For the electronically and structurally related SO_2 group two coordination modes for bonding via the S-atom have been reported: a planar and a bent $M—SO_2$ moiety [10]. From the Ortep drawing and the Newman projection in Fig. 3, it can clearly be seen that the Rh—NSO group is planar. Also the Rh—S distance of 2.100(3) Å is in agreement with the planar situation (a Rh—S distance of 2.450(2) is found for a bent situation in $[RhCl(CO)(PPh_3)_2(SO_2)]$ [15] and a Rh—S distance of 2.096(2) Å is found for a planar situation in $[Rh(C_2H_4)(C_5H_5)(SO_2)]$ [20]). The coordination around rhodium is approximately square planar.

Comparison of the relevant distances and angles of the coordinated ligand with the free ligands H_3CNSO [21], HNSO [22] and ClNSO [23] and with the

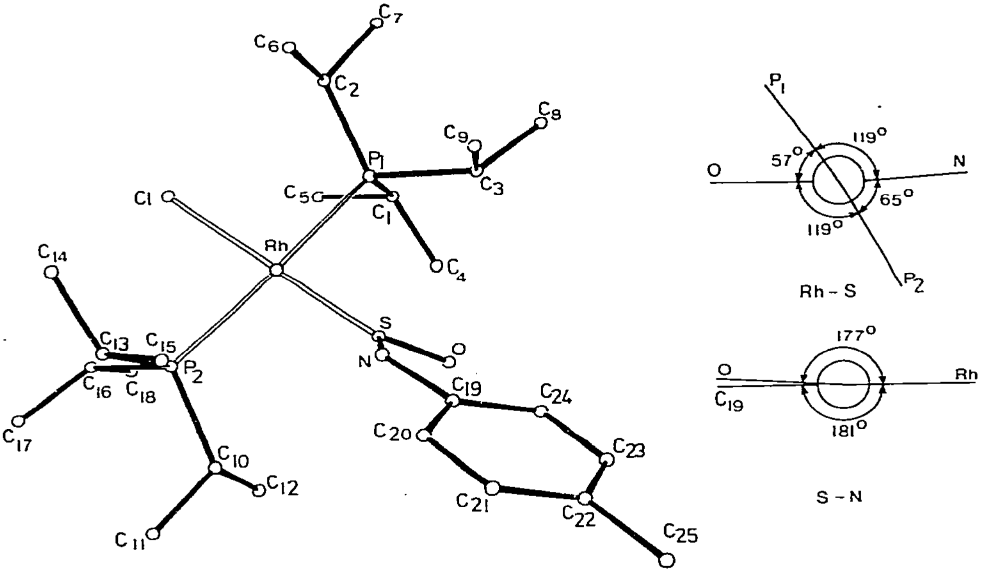

Fig. 3. The molecular structure of chlorobis(triisopropylphosphine)-4-methyl-*N*-sulfinylanilinerhodium ($[RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)]$) and the Newman projections along the Rh—S and S—N bonds.

TABLE 2

ATOMIC COORDINATES OF [RhCl(P-i-Pr_3)$_2$(4-MeC_6H_4NSO)] (standard deviations in parentheses)

Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
Rh	0.32609(8)	0.49758(8)	0.19832(5)	H(61)	0.392	0.363	—0.057
Cl	0.2025(4)	0.6308(3)	0.1162(2)	H(62)	0.277	0.478	—0.104
N	0.6051(9)	0.4229(8)	0.2816(6)	H(63)	0.367	0.524	0.007
S	0.4467(3)	0.3798(2)	0.2679(2)	H(71)	0.077	0.273	—0.143
O	0.3900(8)	0.2561(8)	0.3004(6)	H(72)	0.192	0.158	—0.097
P(1)	0.2266(3)	0.3036(3)	0.0944(2)	H(73)	0.018	0.167	—0.061
P(2)	0.3959(3)	0.6987(3)	0.3000(2)	H(81)	0.248	0.036	—0.034
C(1)	0.0543(11)	0.2172(12)	0.1174(7)	H(82)	0.327	—0.062	0.048
C(2)	0.1849(10)	0.3484(10)	—0.0136(6)	H(83)	0.150	—0.015	0.054
C(3)	0.3298(11)	0.1598(10)	0.0907(6)	H(91)	0.547	0.126	0.078
C(4)	0.0680(12)	0.1582(14)	0.2002(8)	H(92)	0.468	0.224	—0.003
C(5)	—0.0514(12)	0.3168(14)	0.1167(8)	H(93)	0.531	0.312	0.108
C(6)	0.3124(12)	0.4332(12)	—0.0434(7)	H(101)	0.541	0.595	0.392
C(7)	0.1140(12)	0.2298(12)	—0.0821(7)	H(111)	0.450	0.854	0.491
C(8)	0.2611(13)	0.0232(12)	0.0378(8)	H(112)	0.580	0.750	0.534
C(9)	0.4780(12)	0.2091(12)	0.0675(8)	H(113)	0.619	0.854	0.447
C(10)	0.4589(10)	0.6620(10)	0.4085(6)	H(121)	0.392	0.535	0.505
C(11)	0.5299(12)	0.7855(12)	0.4732(7)	H(122)	0.262	0.639	0.462
C(12)	0.3444(12)	0.5729(12)	0.4444(7)	H(123)	0.290	0.479	0.397
C(13)	0.5437(10)	0.8271(10)	0.2790(6)	H(131)	0.559	0.918	0.334
C(14)	0.5119(13)	0.8826(13)	0.1946(8)	H(141)	0.632	0.967	0.186
C(15)	0.6795(12)	0.7659(12)	0.2809(8)	H(142)	0.496	0.793	0.140
C(16)	0.2528(10)	0.8021(10)	0.3073(7)	H(143)	0.409	0.929	0.193
C(17)	0.2848(13)	0.9357(12)	0.3661(8)	H(151)	0.666	0.676	0.226
C(18)	0.1147(12)	0.7135(13)	0.3188(8)	H(152)	0.772	0.850	0.273
C(19)	0.7069(10)	0.3563(10)	0.3262(7)	H(153)	0.705	0.725	0.344
C(20)	0.8361(11)	0.4419(12)	0.3529(8)	H(161)	0.243	0.827	0.237
C(21)	0.9424(11)	0.3873(13)	0.3969(9)	H(171)	0.197	0.999	0.355
C(22)	0.9262(11)	0.2549(12)	0.4098(7)	H(172)	0.295	0.912	0.435
C(23)	0.7994(12)	0.1710(12)	0.3830(8)	H(173)	0.389	—0.997	0.357
C(24)	0.6895(11)	0.2213(11)	0.3399(8)	H(181)	0.124	0.688	0.387
C(25)	1.0482(15)	0.1975(17)	0.4589(10)	H(182)	0.025	0.775	0.307
H(11)	0.014	0.127	0.062	H(183)	0.089	0.612	0.273
H(21)	0.106	0.421	0.001	H(201)	0.872	0.556	0.338
H(31)	0.340	0.144	0.162	H(211)	1.052	0.452	0.419
H(41)	0.108	0.247	0.256	H(231)	0.776	0.060	0.396
H(42)	—0.040	0.100	0.211	H(241)	0.597	0.156	0.313
H(43)	0.146	0.082	0.201	H(251)	1.097	0.244	0.438
H(51)	—0.159	0.262	0.127	H(252)	1.034	0.200	0.521
H(52)	—0.012	0.408	0.171	H(253)	1.017	0.156	0.440
H(53)	—0.062	0.363	0.054				

TABLE 3

BOND DISTANCES (Å) OF [RhCl(P-i-Pr_3)$_2$(4-MeC_6H_4NSO)] (standard deviations in parentheses)

Rh—Cl	2.334(3)		
Rh—S	2.100(3)		
Rh—P(1)	2.384(2)		
Rh—P(2)	2.375(2)		
S—O	1.440(9)		
S—N	1.520(9)		
N—C(19)	1.44(1)		
C(19)—C(20)	1.39(1)		
C(20)—C(21)	1.40(2)	P-i-Pr_3 part:	
C(21)—C(22)	1.33(2)		
C(22)—C(25)	1.56(2)	P—C	1.85(1)—1.87(1)
C(22)—C(23)	1.37(1)	C—C	1.51(2)—1.56(2)
C(19)—C(24)	1.36(2)		

TABLE 4

BOND ANGLES (°) OF [$RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)$] (standard deviations in parentheses)

Cl—Rh—P(1)	87.4(1)	O—S—N 117.2(5)	117.2(5)
Cl—Rh—P(2)	87.1(1)	N—C(19)—C(24)	126.7(8)
Cl—Rh—S	176.7(1)	N—C(19)—C(20)	113.7(9)
P(1)—Rh—P(2)	172.6(1)		
P(1)—Rh—S	92.4(1)	$P\text{-}i\text{-}Pr_3$ part:	
P(2)—Rh—S	93.4(1)		
O—S—Rh	124.4(3)	Rh—P—C	111.3(3)—115.9(3)
N—S—Rh	118.4(4)	P—C—C	110.0(8)—117.5(8)
S—N—C(19)	127.5(7)	C—C—C	110(1)—111(1)

TABLE 5

DIHEDRAL ANGLES (°) OF [$RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)$]

Plane	Atoms defining the plane	Dihedral angles between planes
1	Rh, Cl, S, P(1), P(2)	1—2 61.2°
2	N, S, O	1—3 40.7°
3	C(19)—C(24), H(201)—H(241)	2—3 20.7°

Pt^0-π-N=S coordinated ligand $2,4,6\text{-}Me_3C_6H_2NSO$ [8] (see Table 6) leads to the conclusion that the ligand is not appreciably influenced by coordination to rhodium.

From the Newman projection in Fig. 3 can be deduced that the NSO ligand makes an angle of 60° with the Rh, S, Cl, P(1), P(2) plane. This is caused by the bulky $P\text{-}i\text{-}Pr_3$ groups. A second interaction is found in the NSO-ligand itself. The *p*-tolyl group makes an angle of 20.7° with the NSO-plane. This deviation from planarity is caused by steric hindrance between the oxygen atom and the *ortho*-proton of the aryl group. The distance is 2.4 Å, which is shorter than the sum of Van der Waals radii (2.6 Å).

IR results

A 100% enriched ^{15}N complex of compound I was prepared in order to assign the characteristic vibrations with the use of isotopic shifts. The spectra were recorded both in the solid state and in CH_2Cl_2 solution (see Table 7).

TABLE 6

THE NS AND SO DISTANCES (Å) AND THE NSO ANGLE (°) OF SOME *N*-SULFINYLAMINES

	H_3CNSO	HNSO	ClNSO	[$RhCl(P\text{-}i\text{-}Pr_3)_2$-($4\text{-}MeC_6H_4NSO$)]	[$Pt(PPh_3)_2$-($2,4,6\text{-}Me_3C_6H_2$-NSO)]
NS	1.525(4)	1.512(5)	1.559(4)	1.520(9)	1.629(12)
SO	1.466(4)	1.451(5)	1.445(4)	1.440(9)	1.455(12)
NSO	117.0(2)	120.4(5)	116.0(6)	117.2(5)	116.4(7)
Reference	21	22	23	This work	8

TABLE 7

IR DATA FOR $[MCl(PR_3)_2L]$ [a] (in cm^{-1})

Complex	M	R	L	ν(PhN)	ν(NS)	ν(SO)	ν(MCl)	ν(MS)	Others
Ia	Rh	i-Pr	$C_6H_5N^{14}SO$	1287m	1269s	1108s	338m	306m	
	Rh	i-Pr	$C_6H_5N^{15}SO$	1284w	1258s	1108s	338m	306m	
				3 [c]	11 [c]	0 [c]			
Ib	Rh	i-Pr	$C_6H_5N^{14}SO$		959s	1057s	226w		
	Rh	i-Pr	$C_6H_5N^{15}SO$		948s	1057s	226w		
					11 [c]	0 [c]			
IIa	Rh	i-Pr	4-MeC_6H_4NSO	1292s	1268s	1148s	338m	284w	
IIIa	Rh	i-Pr	4-ClC_6H_4NSO	1286s	1264s	1150s	338w	284w	
IVa	Rh	i-Pr	2,4,6-$Me_3C_6H_2NSO$	1306m	1248s	1142s	336m	283m	
V	Rh	i-Pr	SO_2			1268s 1120s	338m	278w	$\delta(SO)_2$ 570s
VI	Rh	i-Pr	CO				325w		ν(CO) 1943vs
VIIa	Rh	Cy	4-MeC_6H_4NSO	1292(sh)	1266s	1124s	304m	270w	
VIII	Rh	Cy	SO_2			1268s 1120s 1106(sh)			$\delta(SO_2)$ 572m
IXa	Ir	i-Pr	4-MeC_6H_4NSO	1290s	1264s	1148s	328w	312w	
IXd	Ir	i-Pr	4-MeC_6H_4NSO [b]		1226s	999s	258m	274m	ν(IrH) 2210m
Xa	Ir	i-Pr	2,4,6-$Me_3C_6H_2NSO$	1304m	1242s	1142s	328w	308w	
Xc, f	Ir	i-Pr [b]	2,4,6-$Me_3C_6H_2NSO$	1306m	1248s	1144s	251m	307w	ν(IrH) 2236m
XI	Ir	i-Pr	SO_2			1263s 1124s	348m	310m	$\delta(SO_2)$ 582m
XII	Ir	i-Pr	CO				306m		ν(CO) 1939vs

[a] In Nujol mull and KBr disk. [b] Metallated. [c] $\Delta(^{14}N-^{15}N)$.

Two isomers were observed. In the case of isomer Ia the band at 1269 cm^{-1} decreases 3 cm^{-1} on substitution by ^{15}N, and shows the same decrease in intensity as ν(PhN) in the free ligand [24]. Therefore this band is assigned to ν(PhN). ν(SO) is assigned to a strong absorption band at 1108 cm^{-1}, which is insensitive to ^{15}N substitution just as for the free ligand [24] and for [$Pt(PPh_3)_2(C_6H_5NSO)$] [8]. Thus here too ν(NS) and ν(SO) hardly couple. The largest shift upon ^{15}N substitution, 11 cm^{-1}, was found for a strong band at 1269 cm^{-1}. About the same isotopic shift was found in the free ligand for the ν(NS) and therefore this band is assigned to this mode. It should be noted that ν(PhN) and ν(NS) are likely to be coupled.

In compound Ia ν(PhN) is lowered upon coordination by 12 cm^{-1}, ν(NS) by 15 cm^{-1} and finally ν(SO) by 47 cm^{-1}. These small shifts to lower energy are in agreement with bonding via the sulfur atom and with data for [$RhCl(PCy_3)_2(SO_2)$] [19].

The IR spectra revealed the presence of a second isomer (Ib) and this can also be deduced from the ^{31}P NMR spectra (vide infra). A band at 959 cm^{-1}, which decreased 11 cm^{-1} on ^{15}N substitution, was assigned to ν(NS) because the same isotopic shift was found for ν(NS) of the free ligand and of isomer Ia. A strong band at 1057 cm^{-1}, which is insensitive to ^{15}N substitution, was assigned to ν(SO). ν(NS) and ν(SO) in this second isomer (Ib) are lowered 325 and 98 cm^{-1} upon coordination, respectively. These values are similar to those of *N*-sulfinylaniline in [$Pt(PPh_3)_2(C_6H_5NSO)$] [8]. It is therefore very likely, by analogy to the platinum complex, that the mode of bonding of the NSO ligand involves also a metal—π-N=S bond (see Fig. 4).

The IR spectra of compound I were also measured for a saturated solution of CH_2Cl_2 in the region of 900—1200 cm^{-1} at different temperatures. When the temperature was lowered for +50 to —80° C, the ν(SO) of isomer Ia decreased in intensity, whereas ν(SO) and ν(NS) of isomer Ib increased in intensity. This process was reversible. From this temperature behaviour it can be concluded that at low temperature isomer Ib is the most abundant isomer, whereas at higher temperatures isomer Ia is the most abundant.

For the other complexes, only for isomer Ia could the characteristic vibrations be assigned with complete certainty (see Table 7). In all the complexes ν(PhN) is lowered upon coordination by 8—12 cm^{-1}, ν(NS) by 15—20 cm^{-1} (except for IVa: 54 cm^{-1} and Xa: 34 cm^{-1}) and finally ν(SO) by 8—10 cm^{-1} (except for Ia: 47 cm^{-1} and VIIa: 32 cm^{-1}).

The NS and SO stretching vibrations are comparable in energy to the antisymmetric stretching modes of the analogous SO_2 complexes V, VIII and XI. It

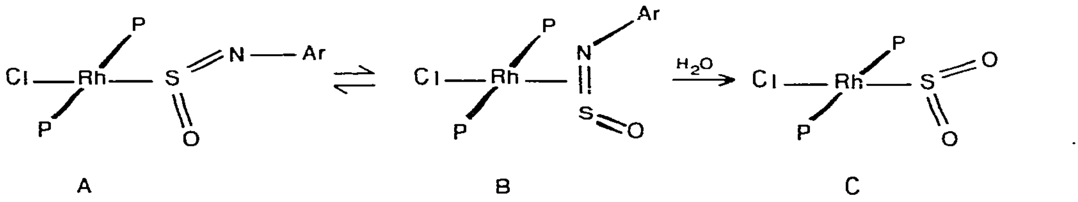

Fig. 4. The two isomers of [$RhCl(PR_3)_2(ArNSO)$] and the structure of [$RhCl(PR_3)_2(SO_2)$].

should be noted that complex VIII has already been prepared and identified by Van Gaal et al. [19]. The larger lowering of the ν(SO) upon coordination in compounds IVa and Xa may be caused by the fact that in these two complexes L is 2,4,6-$Me_3C_6H_2NSO$. This ligand differs from the other NSO ligands in the position of the aromatic ring with respect to the NSO group, i.e. perpendicular instead of in the same plane [27] (see Fig. 2). The differences between ν(NS) in Ia and VIIa and in the other compounds are not well understood.

In the low frequency region there are two vibrations of weak to medium intensity, which have been tentatively assigned to ν(MCl) and ν(MS) by analogy with published values for similar complexes [19]. These two vibrations can be expected to couple. ν(RhCl) has a frequency of 338 cm^{-1} for the P-i-Pr_3 complexes and 304 cm^{-1} for the PCy_3 complex, whereas ν(IrCl) is found at 328 cm^{-1}. ν(RhS) has a value of 260—284 cm^{-1}, except for Ia: 306 cm^{-1}, whereas the ν(IrS) value is 308—312 cm^{-1}. When the rhodium complexes are compared with the iridium complexes, the metal—chlorine stretching vibrations are higher whereas the metal—sulfur stretching vibrations are lower. The ν(RhCl) of isomer Ib is tentatively assigned to a band at 226 cm^{-1}.

^{31}P *NMR results*

The ^{31}P NMR data at —56° C for the rhodium complexes (Table 8) show two doublets in different ratios, which points to the presence of two isomers. Each doublet belongs to a square planar complex with two *trans*-phosphines and arises from coupling of the two equivalent phosphorus atoms with rhodium ($I = \frac{1}{2}$). The complexes are extremely sensitive to moisture and decompose into $[MCl(PR_3)_2(SO_2)]$ and H_2NAr (see Fig. 4). Therefore a trace of the SO_2 complex was always present, giving rise to a third doublet in the ^{31}P NMR spectrum. This was confirmed by measuring the spectra of the pure SO_2 complexes. The results of the IR spectra of complex I in solution at low temperature indicate that the most abundant isomer is Ib, and the most upfield doublet is therefore assigned to this isomer (see Fig. 5). Isomer Ia then belongs to the other doublet. The chemical shift of isomer Ia only differs 3.1 ppm from the analogous SO_2 complex V, whereas the difference between Ib and V is 10.6 ppm. This provides further evidence that complex Ia is the S-bonded isomer. This agrees with the fact that when L is 2,4,6-$Me_3C_6H_2NSO$ only one isomer is found. This compound, IVa, must according to the IR results, be an S-bonded complex. Also the ^{31}P NMR spectrum of IVa is comparable to those of isomer Ia and of the SO_2 complex V.

When the temperature was raised from —56 to 0° C the ratio of the two isomers changed and at ambient temperature the lines broadened (see Fig. 5). Finally at temperatures >60° C the signals coalesced. The chemical shift is not the weighted average of the signals of the original two complexes but is very close to that of isomer Ia, the S-bonded compound. So at low temperatures there is more of the π-N=S bonded isomer Ib, while at relatively high temperatures the S-bonded isomer Ia dominates. These results are in agreement with those obtained from the temperature dependent IR spectra. This reversible process, which is independent of the concentration and of added free ligand, is thus intramolecular.

By analogy to complex I the isomers of complexes II, III and VII have been

TABLE 8

^{31}P NMR [a] DATA FOR [MCl(PR$_3$)$_2$L]

Complex	M	R	L	Temperature (°C)	δ(^{31}P) [b] (ppm)	^{1}J(Rh—P) (Hz)	% [c]	% [d]
Ia	Rh	i-Pr	C_6H_5NSO	−3	40.2	110	33	20
Ib	Rh	i-Pr	C_6H_5NSO	−3	32.7	109	67	80
IIa	Rh	i-Pr	4-MeC_6H_4NSO	−3	40.1	112	51	31
IIb	Rh	i-Pr	4-MeC_6H_4NSO	−3	32.6	109	49	69
IIIa	Rh	i-Pr	4-ClC_6H_4NSO	−3	40.3	110	21	16
IIIb	Rh	i-Pr	4-ClC_6H_4NSO	−3	32.8	108	79	84
IVa	Rh	i-Pr	2,4,6-$Me_3C_6H_2NSO$	+37	41.7	113	100	100
V	Rh	i-Pr	SO_2	+37	43.3	108		
VI	Rh	i-Pr	CO	+37	53.0	120		
VIIa	Rh	Cy	4-MeC_6H_4NSO	−3	31.0	111	71	
VIIb	Rh	Cy	4-MeC_6H_4NSO	−3	22.8	110	29	
VIII	Rh	Cy	SO_2	+37	33.4	108		
IXa	Ir	i-Pr	4-MeC_6H_4NSO	+37	29.9		74	68
IXb	Ir	i-Pr	4-MeC_6H_4NSO	+37	15.9		12	17
IXc	Ir	i-Pr	4-MeC_6H_4NSO	+37	14.8		14	15
IXd	Ir	i-Pr	4-MeC_6H_4NSO [g]	+37	17.7			
Xa	Ir	i-Pr	2,4,6-$Me_3C_6H_2NSO$	+37	30.3		100	
Xe	Ir	i-Pr [g]	2,4,6-$Me_3C_6H_2NSO$	+37	11.8	318 [e]		
					−34.5 [f]		77	
Xf	Ir	i-Pr [g]	2,4,6-$Me_3C_6H_2NSO$	+37	9.5	324 [e]		
					−31.6 [f]		23	
XI	Ir	i-Pr	SO_2	+37	31.5			
XII	Ir	i-Pr	CO	+37	42.3			
XIIIa	Ir	Cy	4-MeC_6H_4NSO	+37	19.6		84	
XIIIb	Ir	Cy	4-MeC_6H_4NSO	+37	7.0		11	
XIIIc	Ir	Cy	4-MeC_6H_4NSO	+37	1.6		5	
XIV	Ir	Cy	SO_2	+37	20.9			

[a] In C_7D_8 as solvent. [b] Relative to external 85% H_3PO_4, downfield shifts being positive. [c] Relative abundance of the different isomers at the mentioned temperature. [d] Relative abundance of the different isomers at −56°C. [e] ^{2}J(P—Ir—P). [f] Belong to the metallated phosphines. [g] Metallated.

assigned. The proportion of the isomers a and b of these rhodium complexes at 0° C is dependent on the aryl group in the *N*-sulfinylanilines and on the phosphine. For P-i-Pr$_3$ isomer b decreases relative to a in the order Ar = 4-ClC_6H_4 > C_6H_5 > 4-MeC_6H_4 >> 2,4,6-$Me_3C_6H_2$ (100%) and for 4-MeC_6H_4NSO in the order P-i-Pr$_3$ > PCy$_3$. For compound VIIb the lines broadened at about −30° C, but they did not sharpen at lower temperature. This could be due to the presence of different conformations of the cyclohexyl groups in the PCy$_3$ ligand.

It is noteworthy that in the ^{31}P NMR spectrum of the ^{15}N labelled complex I, coupling between the ^{31}P and ^{15}N could not be observed for either isomer.

For iridium complexes too, only one isomer was observed when L is 2,4,6-$Me_3C_6H_2NSO$ (Xa), whereas for L is 4-MeC_6H_4NSO, P-i-Pr$_3$ or PCy$_3$, in addition to the peales arising from isomer a, two other peaks (b and c) close to each other and of low intensity were found at higher field. By analogy to the rhodium complexes one of these, b, is assigned to a π-N=S bonded isomer, but the origin of the other is unknown. The ^{31}P NMR spectra of the iridium complex did not show any temperature dependence, although the ratio of the isomers appeared to change slightly. So the exchange for the rhodium complexes

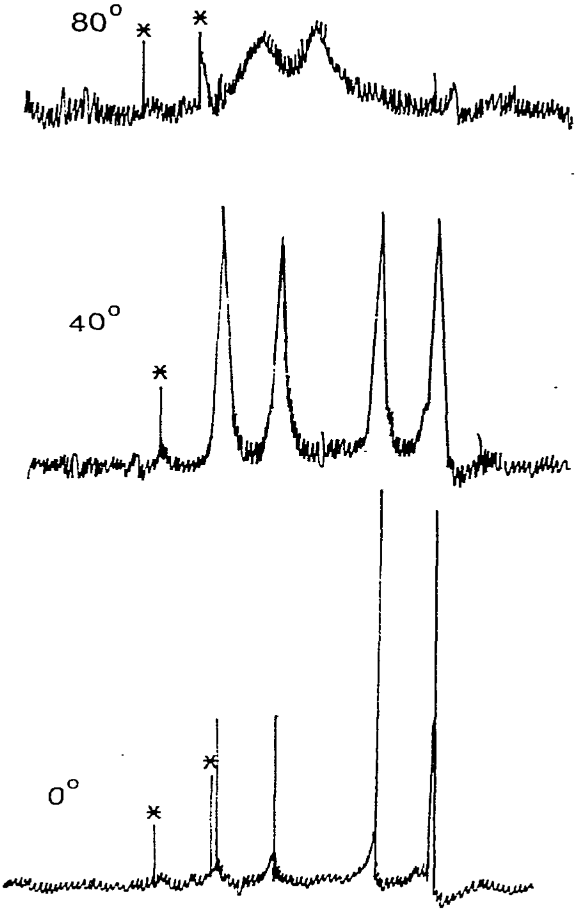

Fig. 5. The temperature dependence of the ^{31}P NMR spectrum of $[RhCl\{P\text{-}i\text{-}Pr_3\}_2(C_6H_5{}^{15}NSO)]$. The peaks which are marked with an asterisk arise from an impurity: $[RhCl(P\text{-}i\text{-}Pr_3)_2(SO_2)]$.

is faster than for the iridium complexes. Of interest is that in the case of the iridium compounds the S-bonded isomer a is the most abundant, while the opposite is true for the rhodium complexes at —56° C.

^{1}H and ^{15}N NMR results

The ^{1}H NMR spectra of the complexes are similar to those of the free ligand, except for some very small downfield shifts (see Table 9). Only one type of aryl group was found, which, in combination with the ^{31}P NMR results, shows that the two isomers must be exchanging rapidly in the ^{1}H NMR, owing probably to a very small chemical shift difference.

The ^{15}N NMR spectrum of compound I was measured for a 100% enriched ^{15}N complex. At ambient temperatures no signal was obtained, whereas at 0° C a doublet was observed with a coupling of 15.5 Hz (Table 9). This doublet probably belongs to the most abundant, M—π-N=S bonded isomer Ib. The splitting is due to rhodium coupling. The reason that the second isomer was not

TABLE 9

^1H NMR [a] AND ^{15}N NMR [b] DATA FOR $[MCl(PR_3)_2(ArNSO)]$ [c]

Complex	M	R	Ar	*o*	*m*	$CH_3(p)$	$CH_3(o)$	others
I [d]	Rh	i-Pr	$C_6H_5(^{15}N)$	7.64(d)				$J(H—^{15}N)$ 7 Hz
II [d]	Rh	i-Pr	$4-MeC_6H_4$	7.65(d)	6.83(d)	1.98(s)		
III [d]	Rh	i-Pr	$4-ClC_6H_4$	7.20(d)	6.60(d)			
IVa	Rh	i-Pr	$2,4,6-Me_3C_6H_2$		6.67(s)	2.07(s)	2.32(s)	
VII [d]	Rh	Cy	$4-MeC_6H_4$	7.68(d)	6.85(d)	1.97(s)		
IXa	Ir	i-Pr	$4-MeC_6H_4$	7.67(d)	6.93(d)	1.95(s)		
Xa	Ir	i-Pr	$2,4,6-Me_3C_6H_2$		6.65(s)	2.07(s)	2.28(s)	
Xe,f	Ir	i-Pr [e]	$2,4,6-Me_3C_6H_2$		6.65(s)	2.07(s)	2.28(s)	δ(Ir—H) ~ —18.1(m)
XIIIa	Ir	Cy	$4-MeC_6H_4$	7.63(d)	6.78(d)	1.98(s)		

[a] In C_7D_8, δ (ppm) relative to internal TMS. [b] In $CDCl_3$ at 0°C, δ (ppm) relative to external formamidine, in DMSO, $\delta(^{15}N) — 1$(d); $^1J(^{103}Rh—^{15}N)$ 15.5 Hz. [c] δ(C—H) 2.80(m), $\delta(CH_3)$ 1.31(q), *J* 7 Hz. [d] Although two isomers are present as shown by ^{31}P NMR, only one type of aryl group is observed which shows that the two isomers are already in fast exchange in the ^1H NMR spectra. [e] Metallated.

found may be that the relaxation time of ^{15}N is too large. The relaxation time of isomer Ib could be shorter because of its direct coordination to rhodium. At ambient temperature the two isomers are in an intermediate exchange on the ^{15}N NMR time scale and no signal could be observed.

The only other known $^{103}Rh—^{15}N$ coupling constants, which vary between 14—18 Hz, have been reported by Bose et al. [25] for six coordinated rhodium (III) complexes containing a direct bond between rhodium and nitrogen. We are dealing here with a four-coordinated rhodium complex and the *s*-character in the rhodium—ligand bond is expected to be higher than in the six-coordinated complexes. However, this coupling constant probably decreases again for M—π-N=S bonded complex, as has been discussed for the $^1J(^{195}Pt—^{15}N)$ in $[Pt(PPh_3)_2(C_6H_5{}^{15}NSO)]$ [8]. So the value for $^1J(^{103}Rh—^{15}N)$ of 15.5 Hz appears reasonable in the light of previously reported data.

Some properties of the complexes.

Thermochemical studies were carried out on some of the complexes. The samples were heated in a N_2 or CO atmosphere. Simultaneously the weight as function of the temperature (TG) and the differential thermal analyses (DTA) were observed. The results are reported in Table 10. The complexes melted with decomposition. First an endothermic step B, which is probably a melting process, was observed and then an exothermic step C. After these two steps there was a loss of weight corresponding to the loss of one *N*-sulfinylaniline ligand per complex molecule. This was confirmed by IR spectroscopy (NMR spectra could not be obtained owing to the insolubility of the decomposition product). For compound IX, at temperatures lower than the melting point another exothermic process A took place. In this process the aromatic ring was metallated, and this will be discussed below.

Under a carbon monoxide atmosphere, after the above-mentioned two DTA steps, a third thermochemical process D, which was endothermic, was observed. In this step the decomposition product probably reacts with CO to give [MCl-

TABLE 10

DTA AND TG DATA FOR THE COMPLEXES [MCl(P-i-Pr$_3$)$_2$(ArNSO)]

Complex	M	Ar	Atmosphere	A [a]			B [a]			C [a]			[c]	D [a]		
				T_i	T_f [b]		T_i	T_f		T_i	T_f			T_i	T_f	
II	Rh	4-MeC$_6$H$_4$	N$_2$				100	150	—	150	200	+	144.5 (153.2)			
II	Rh	4-MeC$_6$H$_4$	CO				95	150	—	150	198	+	142.7 (153.2)	198	275	—
IV	Rh	2,4,6-Me$_3$C$_6$H$_2$	N$_2$				140	178	—	186	210	+	188.6 (181.3)			
IX	Ir	4-MeC$_6$H$_4$	N$_2$	134	152	+	166	195	—	206	220	+	164.3 (153.2)			
IX	Ir	4-MeC$_6$H$_4$	CO	130	160	+				190	228	+		228	247	—
X	Ir	2,4,6-Me$_3$C$_6$H$_2$	N$_2$				143	171	—	177	205	+	189.3 (181.3)			

[a] — is endothermic and + is exothermic. [b] T_i, initial temperature; T_f, final temperature in °C. [c] Loss in molecular weight after step A—C; between brackets the calculated molecular weight of the *N*-sulfinylaniline ligands.

(P-i-$Pr_3)_2$(CO)] (VI and XII). The complexes VI and XII were identified by analyses, and ^{31}P NMR and IR spectroscopy. The CO complexes were also obtained when CO was bubbled through solutions of the NSO and the SO_2 complexes, respectively.

When compound IV was exposed to the air for 75 days an almost complete conversion into [RhCl(P-i-$Pr_3)_2$(CO)] was observed. This complex appears to react selectivily with carbon monoxide in the atmosphere which has a concentration of about 0.1 ppm [26].

Metallation reactions

During the preparation of compound X a second crystalline product was obtained in addition to the S-bonded isomer. This compound is a six-coordinated cyclometallated phosphine compound, as can be deduced from the following spectroscopic data.

The ^{31}P NMR spectrum (Table 8) shows an AB pattern with a ^2J(P—Ir—P) coupling of about 320 Hz, which points to two inequivalent *trans*-phosphines [28]. The chemical shift of one doublet lies about 43 ppm upfield with respect to the more normal shift of the other doublet. This indicates that the phosphine with the upfield shift is situated in a four-membered ring [27]. From ^{1}H NMR and IR spectroscopy (Table 7 and 9) it can be concluded that this compound contains a hydride ligand. So it is very likely that one phosphine has been involved in a metallation reaction with iridium. The characteristic 2,4,6-trimethyl-*N*-sulfinyl-aniline vibrations hardly change with respect to those in Xa; ν(IrCl) lies at 251 cm^{-1}, which indicates that Cl is *trans* to carbon. Two isomers Xe and Xf are present as indicated by the ^{31}P NMR spectrum. The proposed structures are shown in Fig. 6A and 6B.

This type of cyclometallation of tertiary aliphatic phosphines in the case of iridium compounds has already been described by Hietkamp et al. [28]. In those complexes the metallation reactions occur only in the presence of a nitrogen donor ligand such as γ-picoline or acetonitrile. Evidently an S-donor ligand can also promote cyclometallation of the phosphine.

When compound IX was heated in the solid state under N_2 to 150°C, a brown powder was obtained, for which a six-coordinated cyclometallated *N*-sulfinylaniline structure IXd is proposed on the basis of the following arguments.

The IR spectrum reveals the presence of a hydride ligand, while in the ^{31}P NMR spectrum a singlet is observed. So, both phosphines are equivalent and

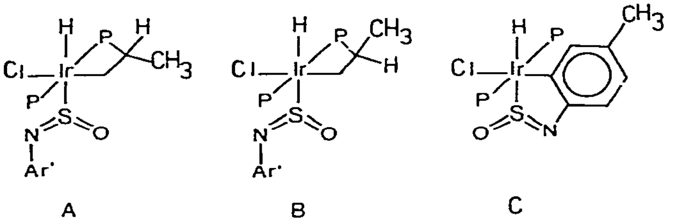

Fig. 6. The proposed structures of the two diastereoisomers of Xe and Xf (A and B) with Ar' = 2,4,6-$Me_3C_6H_2$ and the proposed structure of IXd (C).

situated *trans* to each other. The presence of the hydride ligand can thus not be accounted for, as in the case of Xe, Xf by metallation of a phosphine ligand. It is more likely that the hydrogen atom has originated from an *ortho*-metallation of the *p*-methyl-*N*-sulfinylaniline ligand, since the IR spectrum has changed drastically compared with that of IXa. A ring stretch at 1500 cm^{-1} has increased to 1582 cm^{-1}, ν(NS) decreased 40 cm^{-1}, ν(SO) decreased 149 cm^{-1} and for the δ(CH) of the aromatic ring at 818 cm^{-1} four new bands appeared at 866, 844, 808 and 776 cm^{-1}. ν(IrCl) has been lowered to 258 cm^{-1} and a band at 274 cm^{-1} is tentatively assigned to ν(IrS). These results indicate the presence of an *ortho*-metallated sulfinylaniline ligand, as shown in Fig. 6C. ν(IrH) and ν(IrCl) *trans* to S and C, respectively, are in agreement with the data for compound Xe, Xf. The lowering of ν(IrS) and ν(NS) is consistent with their presence in a ring, whereas the lowering of ν(SO) indicates a reduced double bond character. The proposed structure of compound IXd is similar to that of $[IrClH(PPh_3)_2(C_6H_4NNC_6H_5)]$ [29,30].

Discussion

For almost all the aryl groups studied, the complexes $[MCl(PR_3)_2(ArylNSO)]$ exist as two isomeric forms both in the solid state and in solution. As shown by the crystal structure determination of $[RhCl(P\text{-}i\text{-}Pr_3)_2(4\text{-}MeC_6H_4NSO)]$, one isomer contains a sulfinylaniline group S-bonded to the metal atom. The rhodium atom lies in the NSO plane, which together with the short M—S distance of 2.100(3) Å, shows clearly that there is both σ- and π-bonding in the M—S bond, analogous to that in related SO_2 complexes [10]. This isomer is also present in solution, as shown by the N=S and S=O stretching frequencies (Table 7). Further confirmation was obtained from the ^{31}P NMR data (Table 8) which are comparable with those of $[MCl(PR_3)_2(SO_2)]$. While in this isomer the sulfinylaniline behaves as a base, as does SO_2 in the comparable SO_2 compounds, this ligand is bonded to the metal in the second isomer in an olefinic way via the N=S bond. The π-backbonding in this metal-π-N=S bond must be strong because the N=S stretching frequency of the sulfinylaniline is drastically lowered both in the solid state and in solution with respect to the free ligand. Moreover, ν(SO) is lowered appreciably, and this can be associated with the delocalization of the NSO orbitals. Similar lowerings were also observed for $[Pt(PPh_3)_2(ArylNSO)]$, for which a metal—π-N=S mode of bonding was found by X-ray crystallography [8].

The two isomers undergo slow interconversion by an intramolecular process in solution, and their ratios depend on the temperature, on the aryl substituent, on the phosphine and on the metal atom, as shown by temperature dependent ^{31}P NMR and IR spectra. Both electronic and steric factors clearly influence the ratio of the isomers. In the series Aryl = $4\text{-}ClC_6H_4$, C_6H_5, $4\text{-}MeC_6H_4$ an electronic factor is apparent, since the ratio of S-bonded isomer versus π-N=S bonded isomer increases and the ligand thus behaves increasingly as an S-base as would be expected on the basis of the *para*-substituent effects. It is, however, not clear why S-coordination becomes relatively more important on going from rhodium(I) to iridium(I). It has been suggested that the metal—ligand σ-bond strength increases in going from rhodium(I) to iridium(I) [31,32]. Such an effect could favour the coordination of RNSO via S with respect to the metal-π-N=S bond. Further increase of the basicity of the metal, however, gives metal-π-N=S bonding, as observed for platinum(0) [10]. It should be noted, however, that we are dealing with small energy differences when comparing the rhodium(I) with the iridium(I) complexes, so that a more detailed discussion is unwarranted.

Steric factors are clearly of great importance, as shown by the observation that for Aryl = 2,4,6-$Me_3C_6H_2$ only the S-bonded isomer is found. In the free ligand the bulk of this group causes the mesityl group to lie perpendicular to the NSO plane (Fig. 2) [8,24]. Models show that for metal-π-N=S bonding the mesityl group would be much more sterically hindered by the phosphine ligand(s) than for metal—S bonding. Similarly, it is understandable that, although PCy_3 is more basic than P-i-Pr_3 [33], the π-N=S bonded isomer decreases with respect to the S-bonded isomer when P-i-Pr_3 is replaced by PCy_3, since the cone angle of PCy_3 (170°) is larger than that of P-i-Pr_3 (160°) [33].

Although the amount of information about the coordination behaviour of RNSO is still limited, it is of interest to make some comparisons with the behaviour of RNSNR and SO_2. In the case of rhodium(I) and iridium(I) RNSNR acts as a N-base [4], while SO_2 generally coordinates as an S-base [10] or an S-acid [10] and only in the case of $[Rh(NO)(PPh_3)_2(SO_2)]$ as a π-S=O bonded ligand [11]. Thus RNSO appears to be both a better S-base and/or weaker N-base and a better π-N=S ligand than RNSNR. Towards the more basic platinum(0), both RNSNR and RNSO behave as π-N=S ligands [8], while SO_2 acts as an S-acid [10]. It may therefore be concluded tentatively that it is easier to achieve metal-π-N=S bonding than metal-π-S=O bonding, which is supported also by the behaviour of RNSO towards rhodium(I) and iridium(I). This is also evident from the fact that RN=S=O chooses π-N=S bonding even though π-S=O bonding would give less steric hindrance.

The effect of the substitution of NR groups in RNSNR ligands by O-atoms will not be discussed further in view of the lack of sufficient theoretical studies. Spectroscopic and theoretical studies are now underway [34], and it is hoped that the results will shed more light on the observed coordination behaviour.

A final interesting point is that metallation reactions occur only in the case of the more nucleophilic iridium [35]. It appears that the ArylNSO ligand can be metallated easily in an exothermic reaction via the *ortho*-carbon atom. When the *ortho*-carbon atoms are blocked by methyl groups e.g. 2,4,6-$Me_3C_6H_2NSO$, a metallation reaction occurs in solution at ambient temperature via the P-i-Pr_3 group.

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