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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

VIII *. *N*-SULFINYLANILINE AND SULFURDIIMINE COMPLEXES OF PLATINUM(0) OF THE TYPE $[Pt(PPh_3)_2L]$ IN WHICH L IS π-BONDED TO Pt; CRYSTAL AND MOLECULAR STRUCTURE OF $[Pt(PPh_3)_2$-2,4,6-$Me_3C_6H_2—N=S=O)]$; DETERMINATION OF $^2J(^{31}P—^{15}N)$ AND $^1J(^{195}Pt—^{15}N)$ BY ^{31}P AND ^{195}Pt NMR

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Summary

A crystal and molecular structure determination of $[Pt(PPh_3)_2$(2,4,6-mesitylN=S=O)] shows a side-on coordination via the N=S unit to Pt^0, while the mesityl group is in the *cis* configuration with respect to S=O. The same structure persists in solution, as shown by IR, UV, ^1H-, ^{31}P- and ^{195}Pt-NMR studies on $[Pt(PPh_3)_2(RNSO)]$ (R = Ph, 4-tol, 2-tol, 3,5-xylyl and 2,4,6-mesityl). In the case of $[Pt(PPh_3)_2(Ph^{15}NSO)]$, ^{31}P- and ^{195}Pt-NMR gave the *cis*- and *trans*-couplings $^2J(^{31}P—Pt—^{15}N)$, $^1J(^{31}P—^{195}Pt)$ and $^1J(^{195}Pt—^{15}N)$. The PPh_3 groups interchange their positions intramolecularly, probably via a rotation about the Pt—(N=S) axis. From the isotopic shifts (^{15}N) in the vibrational spectra of both the free and coordinated PhNSO it is concluded that there is hardly any coupling between ν(SO) and ν(NS).

In the light of these conclusions, the unstable $[Pt(PPh_3)_2(RNSNR)]$ complexes, for which N-coordination has been tentatively proposed on the basis of the IR and UV spectra, were reinvestigated. It may now be concluded from ^{31}P- and ^{195}Pt-NMR that for $[Pt(PPh_3)_2(Ph^{15}NS^{15}NPh)]$ the sulfurdiimine is also side-on coordinated via one N=S bond. At elevated temperatures the complex is fluxional, and it is proposed that, in addition to a probable rotation about the Pt—(N=S) bond, there is also an intramolecular migration of the $(PPh_3)_2Pt$

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* For parts I—VII see refs. 1—6 and 9.

unit from one N=S π-bond to the other. IR studies on ^{15}N enriched samples show that coordination of the NSN-ligand in $[Pt(PPh_3)_2(Ph^{15}NS^{15}NPh)]$ causes a decoupling of both N=S stretching modes.

Introduction

It has been shown that sulfurdiimines, RNSNR, coordinate via one or both N-atoms to metal atoms such as Pt^{II} [1,2], Pd^{II} [3], Rh^{I}, Ir^{I} [4] and Cr^{0}, Mo^{0}, W^{0} [5,6,7] although S-coordination to W^{0} was also inferred [5,6]. In view of the novel results concerning reactions of ArN=S=NAr [8,9,10] and 5,6-dimethyl-2,1,3-benzothiadiazole, which produced $[\overline{PtS\{N(1-N}\underline{H-Ar')Ar}\}(PPh_3)_2]$ via an unstable intermediate $[Pt(PPh_3)_2(ArNSNAr)]$ and $[Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}3,4\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2(Ph)]$ [11], it was considered necessary to investigate in detail the complexes $[Pt(PPh_3)_2(RN{=}S{=}O)]$ which have been reported for R = C_6H_5, p-$ON_2C_6H_4$, p-$CH_3C_6H_4$, p-$CH_3C_6H_4SO_2$ [12] but for which only IR data viz. the ν(S=O), were given.

In this paper we report crystallographic and spectroscopic studies (IR, UV, ^{1}H, ^{31}P and ^{195}Pt NMR) on $[Pt(PPh_3)_2RN{=}S{=})]$ and on 100% ^{15}N enriched samples. Furthermore we reinvestigated the unstable intermediate complex $[Pt(PPh_3)_2(PhNSNPh)]$ with particular emphasis on IR and ^{31}P and ^{195}Pt NMR studies with ^{15}N enriched samples.

Experimental

All reactions were carried out under dry oxygen-free nitrogen, while the solvents were dried over sodium wire and distilled under pure N_2 before use.

The preparation of *N*-sulfinylanilines [13] and of sulfurdiimines [14] have been reported before, while enriched $Ph^{15}NSO$ and $Ph^{15}NS^{15}NPh$ were prepared from $Ph^{15}NH_2$ obtained from Merck and Co. $[Pt(PPh_3)_2(C_2H_4)]$ [15], $[Pt(PPh_3)_2(ArNSO)]$ [12], and $[Pt(PPh_3)_2(RNSNR)]$ [9] were prepared as described in the literature. As an example, the preparation of $[Pt(PPh_3)_2(PhNSO)]$ is described.

Preparation of $[Pt(PPh_3)_2(PhNSO)]$

To a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (0.5 mmol) in toluene (20 ml), PhN=S=O (0.5 mmol) was added. The solution immediately turned yellow. n-Hexane (60 ml) was added and a yellow precipitate was formed. After filtration, washing with n-C_7H_{14}, and drying in vacuum, the yield was about 80%. The complexes were only soluble in $CHCl_3$, CH_2Cl_2 and C_6H_5Cl.

Preparation of $[Pt(PPh_3)_2(SO_4)](C_6H_5Cl)$

$[Pt(PPh_3)_2(4\text{-tolNSO})]$ (0.27 mmol) was dissolved in chlorobenzene (10 ml), which was not dried and deoxygenated. After filtration through silica gel, off-white needles (0.05 mmol) separated from the red solution.

Spectroscopic measurements and analytical data

The ^{1}H NMR spectra were recorded on Varian A60 and T60A spectrometers and the ^{31}PNMR spectra on a Varian XL-100 spectrometer. The ^{195}Pt NMR spectra were measured by Dr. W.E. Hull in Karlsruhe on a Bruker WP 200 spectrometer using a concentration of 0.05 *M* (^{14}N) and 0.03 *M* (^{15}N enriched). The pulse width was 5 μsec and the pulse delay was zero. The complex [Pt(PPh$_3$)$_2$-(PhNSNPh)] was measured on a Bruker WP 90 in Utrecht by Drs. J.W. Marsman with a concentration of 0.03 *M* and a pulse width of 10 μsec with a pulse delay of 5 sec.

The IR spectra were recorded on a Beckman IR 4250 spectrophotometer, which was calibrated in the usual way. The electronic absorption spectra were recorded on a Cary 14 spectrophotometer.

Elemental analyses (Table 1) were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht.

Crystallographic data

From single crystal diffractometry (Cu-K_α, λ = 1.5418 Å): a = 9.830(2), b = 10.761(3), c = 20.184(5) Å, α = 87.93(4)°, β = 88.98(4)°, γ = 68.47(3)°, Z = 2. The space group is triclinic, $P\bar{1}$.

Intensity data, structure determination and refinement

4071 independent reflections of which 3422 proved to have an intensity significantly different from zero were measured on a Nonius CAD 4 diffractometer. The structure has been solved by means of the heavy atom technique and refined by a block diagonal least squares methods. The final *R*-value was 0.066. The positions of the carbon atoms in the aromatic rings have been refined in groups. Therefore the standard deviations of the positions, the distances, and the angles of the rings have not been presented.

Results and discussion

The *N*-sulfinylanilines have been reported [13,16] to occur in solution in one

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Compound $[Pt(PPh_3)_2(L)]$[a]		Analysis Found (calcd.) (%)				
No.	L	C	H	N	P	S
I	PhNSO	57.57	4.83	1.33	6.05	
		(58.74)	(4.11)	(1.63)	(7.21)	
II	4-TNSO	59.85	4.52	1.42	6.56	
		(59.17)	(4.27)	(1.60)	(7.10)	
III	2-TNSO	57.74	4.81	1.37	5.67	
		(59.17)	(4.27)	(1.60)	(7.10)	
IV	3,5-XNSO	58.41	4.76	1.41	6.80	3.35
		(59.59)	(4.32)	(1.58)	(6.98)	(3.62)
V	2,4,6-MNSO	59.76	4.68	1.49	6.63	
		(59.99)	(4.59)	(1.55)	(6.88)	
VI	$SO_4 \cdot ClC_6H_5$[b]	54.40	3.93		6.86	3.68
		(54.34)	(3.80)		(6.68)	(3.45)

[a] Ph = phenyl; 4-T = 4-tolyl; 2-T = 2-tolyl; 3,5-X = 3,5-xylyl; 2,4,6-M = 2,4,6-mesityl. [b] Cl: 3.83 (3.82).

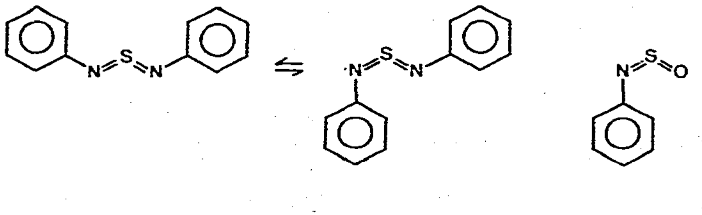
isomeric form, which is the *cis*-configuration. In contrast, in almost all cases the sulfurdiimines occur in solution as two isomers, i.e. a *cis, trans* and a *trans, trans* configuration [1,2,17,18], which rapidly interconvert above —45°C on the NMR time scale, probably via inversion at the N-atoms (Fig. 1). Blake and Reynolds [12] reported the formation of yellow $[Pt(PPh_3)_2(ArN{=}S{=}O)]$ by reaction of $[Pt(PPh_3)_2(C_2H_4)]$, and they proposed on the basis of the IR data for ν(S=O) only, that the ligand was bonded side-on via the N=S π-bond.

We prepared $[Pt(PPh_3)_2(RN{=}S{=}O)]$ (R = Ph, 4-tol, 2-tol, 3,5-xylyl and 2,4,6-mesityl). As neither ^1H, ^{31}P NMR nor IR affords sufficient evidence for the type of coordination, a crystal structure determination was undertaken for $[Pt(PPh_3)_2(2,4,6\text{-mesityl}N{=}S{=}O)]$. A side-on coordination was found, with the aryl group in the *cis*-position (Figure 2) to S=O.

The ^1H NMR spectra, which are not particularly revealing, show upfield shifts in going from the free ligand to the complexed ligand (Table 2). No temperature dependence was observed in the range —50° to +50°C.

More interesting are the ^{31}P NMR spectra (Table 3 and Fig. 3) which show that the P-atoms are inequivalent at —30°C, with ^{195}Pt—^{31}P couplings of about 3500 and 4500 Hz, respectively. At elevated temperatures (+35°C) the ^{31}P-signals broadened to finally coalesce at temperatures above 60°C with a $^1J(^{195}Pt—^{31}P)$ of about 4000 Hz. As the coupling is retained an intramolecular interchange must occur, which is probably a rotation about the Pt—(N=S) axis. When extra PPh_3 was added at ambient temperatures only a broad line was found, with a chemical shift depending on the concentration of added free phosphine, which indicates that in addition to the intramolecular process there is also an intermolecular exchange of PPh_3. Also, ^{31}P NMR spectra were taken on a 100% enriched ^{15}N complex $[Pt(PPh_3)_2(Ph^{15}NSO)]$ (Fig. 4, Table 3). It appears that the ^{31}P resonance with the largest $^1J(^{195}Pt—^{31}P)$ is due to PPh_3 *trans* to N ($^2J(^{31}P—^{15}N)$ = 25 Hz), while the resonance with the smaller $^1J(^{195}Pt—^{31}P)$ has to be assigned to the PPh_3 *cis* to N, as *cis*-$^2J(^{31}P—^{15}N)$ = 2 Hz.

Thus the *trans* effect in these complexes is larger for S than for N. These $^{31}P—^{15}N$ couplings are significantly lower than those found in *cis*-$[Pt(^{15}NCS)(SC^{15}N)\{P(OPh)_3\}_2]$ and *cis*-$[Pt(^{15}NCS)_2\{P(OPh)_3\}_2]$ [19]; for which compounds the *cis* and *trans* couplings are 6—7 Hz and 91—95 Hz, respectively. To our knowledge, the $^{31}P—^{15}N$ couplings which reported for $[M(SC^{15}N)(^{15}NCS)(P—P)]$ and $[M(^{15}NCS)_2(P—P)]$ (M = Pd, Pt; P—P = $Ph_2PCH_2CCF_3CHPPh_2$) are the only other previously reported data (54—57 Hz) [20].



A.trans-trans B.cis-trans C.cis

Fig. 1. The two conformations of the sulfurdiimine ligand in solution: A *trans, trans* and B *cis, trans;* C: the structure of the sulfinylaniline ligand.

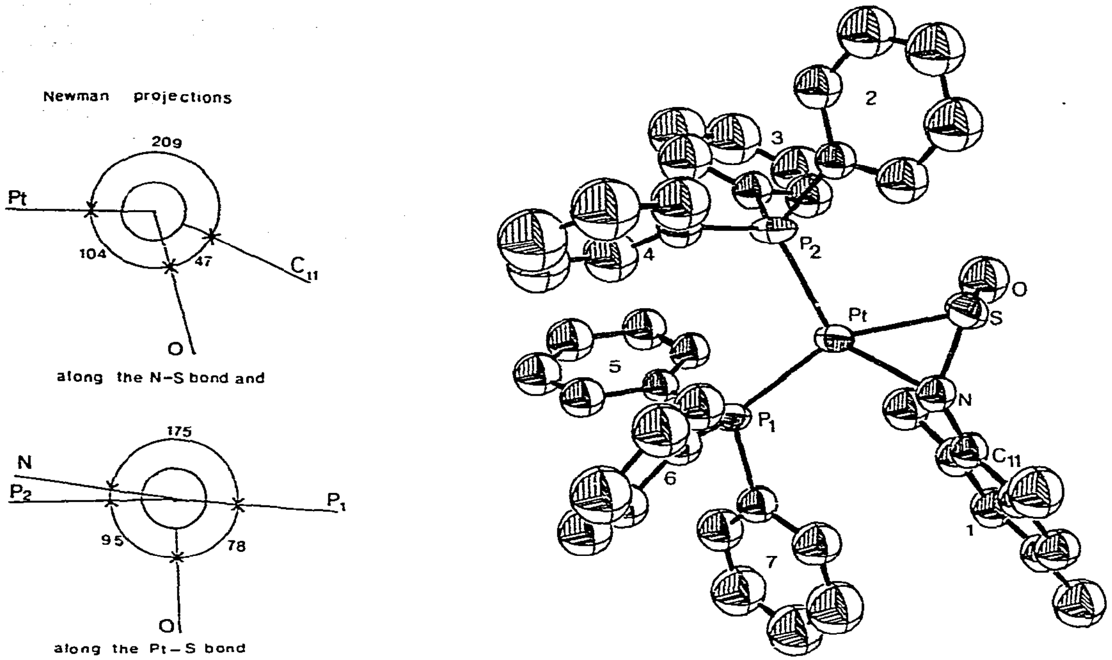


Fig. 2. The crystal structure of platinumbis(triphenylphosphine)2,4,6-mesitylsulfinylaniline and the Newman projections along the N—S and the Pt—S bond.

The ^{195}Pt NMR, spectrum of [Pt(PPh$_3$)$_2$(Ph^{15}NSO)] (Table 2, Fig. 5) at —30°C show a $^1J(^{195}\mathrm{Pt}—^{15}\mathrm{N})$ of about 139 Hz, which is low compared to the reported couplings with ligands such as amine [21,22] nitrate [21], azo group [23] and thiocyanate. For this latter ligand ^{195}Pt—^{14}N couplings have been reported [24,25]. The couplings vary, depending on the *trans* ligands, from about 205—523 Hz. The low $^1J(^{195}\mathrm{Pt}—^{15}\mathrm{N})$ reported above must be due to the

TABLE 2

^{1}H NMR AND ^{195}Pt NMR DATA FOR THE COMPLEXES IN CDCl$_3$ (δ, RELATIVE TO TMS)

Complex [Pt(PPh$_3$)$_2$(L)]		*o*	*m*	*p*	CH$_3$	Ξ^a	δPt^b	*J*(Pt—N) (Hz)
No.	L							
II	4-TNSO	6.78 (0.90)^c	6.48 (0.55)		2.05 (0.27)			
III	2-TNSO				2.28 (0.02)			
IV	3,5-XNSO	6.45 (0.93)		6.23 (1.04)	1.83 (0.45)			
V	2,4,6-MNSO		6.47 (0.31)		2.13^d; 2.22^e (0.04); (0.05)^f			
I	Ph^{15}NSO^g					21406800	—660	136 ± 10
VIII	PhNSNPh^g					21402500	—860	

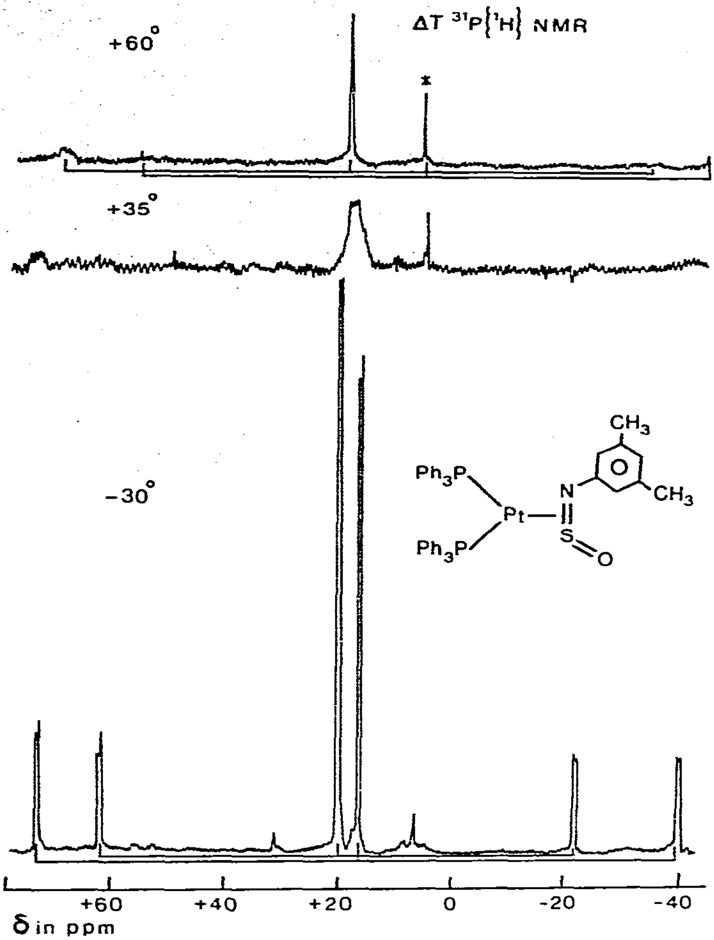
^{a} Ξ is the ^{195}Pt resonance frequency corrected to the field strength at which the protons in TMS resonate at exactly 100 MHz. ^{b} Relative to *cis*-PtCl$_2$(SMe$_2$)$_2$, Ξ = 21420980 Hz [44]. ^{c} The values between parentheses are the upfield shifts caused upon coordination. ^{d} *para*. ^{e} *ortho*. ^{f} Downfield shift. ^{g} At −30°C.

TABLE 3

^{31}P NMR DATA FOR THE COMPLEXES IN $CDCl_3$ AT −30°C

Complex P [Pt(PPh$_3$)$_2$(L)]		δ_1 [a]	^1J(Pt—P) [b]	^2J(N—Pt—P)	δ_2	^1J(Pt—P)	^2J(N—Pt—P)	^2J(P—Pt—P)
No.	L							
I	Ph^{15}NSO [c]	20.0	3407	2	16.3	4587	25	9
II	4-TNSO	20.0	3483		16.6	4580		11
III	2-TNSO	18.8	3498		15.5	4531		14
IV	3,5-XNSO [d]	19.7	3388		16.0	4560		9
V	2,4,6-MNSO	16.6	3560		15.1	4545		13
VI	SO_4 [e]	5.8	4015					
VII	O_2 [e]	14.9	4068					
VIII	Ph^{15}NS^{15}NPh	17.4	3368	8	17.4	4320	29	0

[a] Relative to external 85% H_3PO_4, downfield shifts being positive. [b] In Hz. [c] See also Fig. 4. [d] See also Fig. 3. [e] At +37°C.



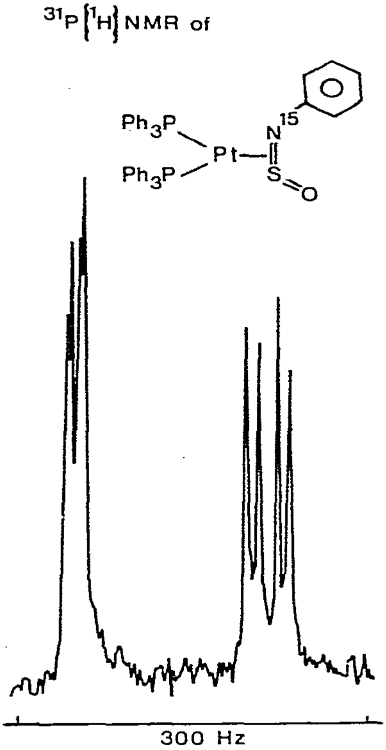


Fig. 3. The temperature dependent ^{31}P NMR spectra of $[Pt(PPh_3)_2(3,5\text{-xylylNSO})]$ in $CDCl_3$. The peaks marked with an asterisk arise from $[Pt(PPh_3)_2(SO_4)]$.

Fig. 4. The ^{31}P NMR spectrum of $[Pt(PPh_3)_2(Ph^{15}NSO)]$ in $CDCl_3$ at —30°C. The platinum phosphor couplings are omitted.

low s-character of the Pt—N bond of the side-on bonded N=S group.

The electronic absorption spectra afforded little information beyond the fact that the π-π^* transitions of the ligand could be observed (Table 4). They appeared as a shoulder on the charge transfer transitions from the Pt-atom to the PPh_3 groups. The absorption maxima was difficult to obtain, but it appears that, within the margin of error, there is probably no shift of the transitions upon coordination. This is remarkable in view of the strong π-coordination of the ligand to platinum. It may therefore be that this band does not belong to the coordinated ligand but to free ligand formed by partial dissociation of the complex at very low concentrations.

The IR spectra of the free and the coordinated ligands in particular of the ^{15}N-labeled compound, offered some interesting features. Substitution of ^{15}N shows that in the free ligand the ν(N=S) and the ν(S=O) hardly couple. The

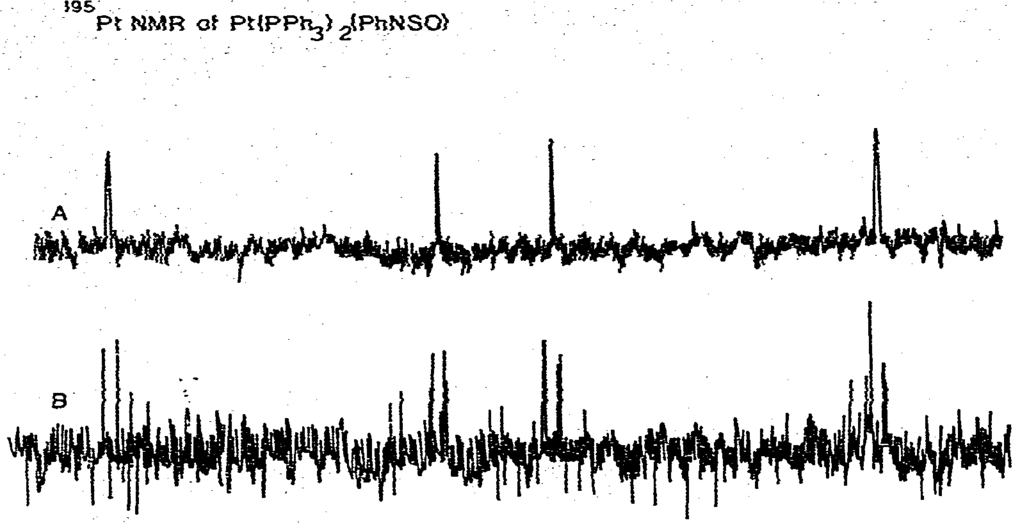


Fig. 5. The ^{195}Pt NMR spectra of [Pt(PPh$_3$)$_2$(Ph^{14}NSO)] (A) and [Pt(PPh$_3$)$_2$(Ph^{15}NSO)] (B) in CDCl$_3$ at —30°C.

TABLE 4

ELECTRONIC ABSORPTION [a] AND IR [b] DATA FOR THE COMPLEXES (VALUES IN cm^{-1})

Complex [Pt(PPh$_3$)$_2$L] No.	L	$\lambda(\pi \rightarrow \pi^*)$ (ϵ)	ν(SO)/δ(NSN)	Δ [c]	ν(NS)	Δ	ν(PhN)	Δ
I	Ph^{15}NSO		1050s (1154s)	104	916m [d] (1272s)	356	1248m (1292m)	44
	Ph^{14}NSO		1051s (1155s)	104	926m [d] (1284s)	358	1256m (1299s)	43
II	4-TNSO	30000 (9000)	1056s (1156s)	100	922m (1284s)	362	1250m (1300m)	50
III	2-TNSO		1058s (1164s)	106	912w (1284s)	372	1228m (1294s)	66
IV	3,5-XNSO	31250	1040s (1144s)	104	968m (1302s)	334	1314s (1320m)	7
V	2,4,6-MNSO	26500 (2350)	1050s (1152s)	102	906w (1276s)	370	1220m (1314m)	94
VIII	Ph^{15}NS^{15}NPh		757m (792m)	35	1232s [e] (1257s) [h]	279 [g]	1278m [h] (1296m) [h]	18
					953m [d,f] (942m) [i]		1260s [i] (1213s) [i]	—47
	Ph^{14}NS^{14}NPh		766m (802m)	36	1248s [e] (1268s) [h]	278 [g]	1280 (sh) [h] (1300s) [h]	20
					970m [d,f] (960m) [i]		1274s [i] (1222s) [i]	—52

[a] In CH$_2$Cl$_2$, molar extinctions in parenthesis. [b] In nujol mull or KBr disk, the corresponding frequencies of the free ligand being given in parentheses. m = medium, w = weak, s = strong and sh = shoulder. [c] $\Delta = \nu$(ligand) — ν(complex). [d] Also measured in solution (CH$_2$Cl$_2$) at —80°C. [e] ν(uncoordinated). [f] ν(coordinated). [g] $\Delta = \nu$(uncoord.) — ν(coord.). [h] (*asym.*). [i] (*sym*).

assignment of the IR and Raman spectra of the *N*-sulfinylanilines will be published in detail elsewhere [26].

In the case of $[Pt(PPh_3)_2(PhNSO)]$ only two vibrations are sensitive to ^{15}N-substitution (Table 4). The band at 1256 cm^{-1} decreased 8 cm^{-1} on substitution of ^{15}N and is assigned to $\nu(Ph—N)$, while the band at 926 cm^{-1}, which decreased 10 cm^{-1} is assigned to $\nu(N{=}S)$. This latter vibration is 358 cm^{-1} lower than the corresponding vibration of the free ligand. The $\nu(S{=}O)$ at 1051 cm^{-1} in the complex, already assigned by Blake and Reynolds [12] hardly changed upon ^{15}N-substitution just as in the free ligand and was 104 cm^{-1} lower than the corresponding vibration in the free ligand. These frequencies are comparable with those which are found in $[Fe(C_5H_5)(CO)_2\{C{=}C(R)S(O)N(C_6H_5)CH_2\}]$: $\nu(S{=}O) = 1052—1070$ cm^{-1} and $\nu(N{=}S) = 925—933$ cm^{-1} [27].

It should be noted that when $[Pt(PPh_3)_2(ArNSO)]$ is dissolved in incompletely dried and deoxygenated solvent, $[Pt(PPh_3)_2(SO_4)]$ (see Fig. 6) is formed containing one mole of C_6H_5Cl of crystallization. This complex was identified by analysis, IR [28] and ^{31}P-NMR. ^{31}P-NMR of solutions of $[Pt(PPh_3)_2(ArNSO)]$ in $CDCl_3$, aged a few days, showed a decomposition in only two platinum complexes: *cis*-$[Pt(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_2(SO_4)]$. The sulfato complex was also prepared from PhenylNSO and $[Pt(PPh_3)_2O_2]$ by Blake and Reynolds [12], Cenini et al. [29] and by Kolomnikov et al. [30]. These authors [30] erroneously formulated the complex as $[Pt(PPh_3)_2O_2(PhNSO)]$.

The crystal and molecular structure of $[Pt(PPh_3)_2(2,4,6\text{-}Me_3C_6H_2NSO)]$

The atomic coordinates are given in Table 5. The bond distances and bond angles are listed in Tables 6 and 7, respectively.

The coordination around platinum is approximately square planar. The dihedral angle between plane 1 (Pt, P_1, P_2) and plane 2 (Pt, N, S) is 7.1° (Table 8). Comparison of the relevant distances and angles of the coordinated ligand affords the following conclusions. In the first place it appears reasonable that the N=S distance will not be appreciably influenced by the substituent as may be deduced by comparing the N=S distance in e.g. $H_3—N{=}S{=}N—CH_3$ (1.532(10) Å) [31] and in *p*-tolyl—N=S=N—*p*-tolyl (1.53 and 1.56 Å) [32]. The N=S distance of 1.525(4) Å in $H_3C—N{=}S{=}O$ [33], as derived from an electron diffraction study, lies in the same region, so also inclusion of an oxygen atom has little influence. The N=S bond distance is 1.63(1) Å which reflects a bond order of about 1.5, since a single N—S bond lies around 1.71 Å c.f. the crystal structure of $[PtS\{N(1\text{-}NH\text{-}3,5\text{-}Me_2C_6H_2)(3,5\text{-}Me_2C_6H_3)\}(PPh_3)_2]$ [9,10]. Similar NS distances (1.633(2) Å) have also been reported by others [34]. In these compounds there were π-delocalisation effects. The N=S=O bond angle has hardly changed i.e. from 117(2)° in $H_3C—N{=}S{=}O$ to 116.4(7)° in the complex. The S=O distance also hardly changed i.e. 1.466(4) Å in $H_3C—N{=}S{=}O$ to 1.455(12) Å. It has about the same bond length (1.480(8) Å) as the terminal SO in $[Fe(C_5H_5)(CO)_2(C_3H_5SO_2)]$ [35].

The P_2Pt plane is almost perpendicular to the N=S=O plane (104°). (See the Newman projection in Fig. 2), which clearly shows that the N=S bond is π-bonded to the Pt atom. A second distinctive behaviour of such bonding is the change of the coordination around N from sp^2 to sp^3 hybridisation; thus the $N—C_{11}$ bond is bent away from the NSO plane, upon coordination. This is there-

TABLE 5

ATOMIC COORDINATES (WITH STANDARD DEVIATIONS)[a]

Atom	X	Y	Z	Atom	X	Y	X
Pt	0.17720(6)	0.25299(5)	0.27076(2)	C_{36}	—0.0659	0.1178	0.1953
P_1	0.1020(4)	0.1758(4)	0.3648(2)	C_{41}	0.3924	—0.0636	0.2200
P_2	0.2254(4)	0.0788(3)	0.2004(2)	C_{42}	0.4642	—0.0648	0.2789
S	0.1521(5)	0.4724(4)	0.2907(2)	C_{43}	0.5956	—0.1685	0.2936
N	0.2262(13)	0.4016(12)	0.2222(6)	C_{44}	0.6551	—0.2710	0.2495
O	0.0027(14)	0.5684(13)	0.2860)6)	C_{45}	0.5833	—0.2697	0.1906
C_{11}	0.2233	0.4676	0.1587	C_{46}	0.4519	—0.1660	0.1758
C_{12}	0.1035	0.5089	0.1166	C_{51}	0.1861	—0.0020	0.3875
C_{13}	0.1068	0.5794	0.0579	C_{52}	0.2945	—0.0437	0.4355
C_{14}	0.2300	0.6085	0.0413	C_{53}	0.3712	—0.1793	0.4478
C_{15}	0.3498	0.5672	0.0835	C_{54}	0.3394	—0.2732	0.4121
C_{16}	0.3464	0.4967	0.1422	C_{55}	0.2309	—0.2316	0.3641
C_{17}	0.4764	0.4519	0.1880	C_{56}	0.1543	—0.0960	0.3517
C_{18}	—0.0301	0.4773	0.1346	C_{61}	—0.0963	0.2177	0.3622
C_{19}	0.2337	0.6851	—0.0225	C_{62}	—0.1789	0.3452	0.3379
C_{21}	0.2572	0.1161	0.1138	C_{63}	—0.3301	0.3858	0.3343
C_{22}	1827	0.0872	0.0624	C_{64}	—0.3988	0.2988	0.3550
C_{23}	2139	0.1132	—0.0030	C_{65}	—0.3161	0.1711	0.3793
C_{24}	0.3195	0.1681	—0.0168	C_{66}	—0.1649	0.1306	0.3828
C_{25}	3940	0.1970	0.0348	C_{71}	0.1253	0.2535	0.4401
C_{26}	0 0.3629	0.1710	0.1001	C_{72}	0.2296	0.3124	0.4417
C_{31}	0.0734	0.0193	0.1940	C_{73}	0.2493	0.2710	0.4993
C_{32}	0.0902	—0.1136	0.1872	C_{74}	0.1649	0.3705	0.5552
C_{33}	—0.0231	—0.1481	0.1816	C_{75}	0.0606	0.3117	0.5535
C_{34}	—0.1714	—0.0497	0.1829	C_{76}	0.409	0.2531	0.4960
C_{35}	—0.1882	0.0832	0.1898				

[a] All carbon atoms of the rigid groups have been refined in groups; no standard deviations can be given.

fore the first evidence for such a type of bond. For phenylsulfinylaniline it is assumed that the configuration is in the *cis* conformation and has an planar geometry [13,16]. Substitution of methyl groups in the *ortho*-positions causes a strong steric hindrance between these methyl groups and the oxygen atom. To alleviate the steric strain the mesityl group may bend away from the *cis*- to the *trans*-situation, as found for the free ligand dimesitylsulfurdiimine [2], or it may turn around the C—N axis out of the N=S=O plane. It is clear that the latter possibility applies here (see Fig. 2 and Table 8).

TABLE 6

BOND DISTANCES IN Å (WITH STANDARD DEVIATIONS IN PARENTHESES)[a]

Pt—P_1	2.263(4)	P_1—C_{51}	1.83
Pt—P_2	2.296(4)	P_1—C_{61}	1.83
Pt—N	2.056(13)	P_1—C_{71}	1.82
Pt—S	2.332(4)	P_2—C_{21}	1.83
O—S	1.455(12)	P_2—C_{31}	1.84
N—S	1.629(12)	P_2—C_{41}	1.83
N—C_{11}	1.44		

[a] The standard deviations of the N—C and P—C distances vary between 0.01 and 0.02 Å.

TABLE 7

BOND ANGLES IN DEGREES (WITH STANDARD DEVIATIONS IN PARENTHESES) [a]

P$_2$—Pt—P$_1$	103.1(1)	Pt—P$_2$—C$_{41}$	114.1
P$_2$—Pt—N	108.2(3)	Pt—P$_2$—C$_{31}$	113.3
P$_1$—Pt—S	105.9(1)	Pt—P$_2$—C$_{21}$	115.5
N—Pt—S	43.1(3)	P$_1$—C$_{51}$—C$_{52}$	119
Pt—N—S	77.8(5)	P$_1$—C$_{51}$—C$_{56}$	120
Pt—S—N	59.1(5)	P$_1$—C$_{61}$—C$_{62}$	116
Pt—S—O	114.3(7)	P$_1$—C$_{61}$—C$_{66}$	124
Pt—N—C$_{11}$	143.9	P$_1$—C$_{71}$—C$_{72}$	120
N—C$_{11}$—C$_{12}$	124	P$_1$—C$_{71}$—C$_{76}$	121
N—C$_{11}$—C$_{16}$	116	P$_2$—C$_{41}$—C$_{42}$	119
O—S—N	116.4(7)	P$_2$—C$_{41}$—C$_{46}$	121
S—N—C$_{11}$	126.4	P$_2$—C$_{31}$—C$_{32}$	124
Pt—P$_1$—C$_{71}$	114.8	P$_2$—C$_{31}$—C$_{36}$	116
Pt—P$_1$—C$_{61}$	109.8	P$_2$—C$_{21}$—C$_{22}$	122
Pt—P$_1$—C$_{51}$	118.8	P$_2$—C$_{21}$—C$_{26}$	118

[a] The standard deviation of angles involving one and two carbon atoms respectively are approximately 0.5 and 1.0°.

Reinvestigation of [Pt(PPh$_3$)$_2$(RNSNR)

In previous articles [8,9] we proposed that [Pt(PPh$_3$)$_2$(RNSNR)], which could only be studied in solution at temperatures below —30°C because of its instability, contains a N-coordinated monodentate sulfurdiimine. This tentative conclusion was based mainly on IR and UV results, although a side-on coordination was not rigorously excluded. The present ^{31}P results for [Pt(PPh$_3$)$_2$(ArNSO)], which are very similar to those for [Pt(PPh$_3$)$_2$(ArNSNAr)], prompted us to reinvestigate the complex in detail by using ^{15}N substitution, which was comparatively difficult as the complex is only stable at low temperatures. Except for the fact that the ^{31}P resonances accidentally coincide, it can be seen that both the δ^{31}P and δ^{195}Pt are much alike those in the PhNSO complex. Also the $^1J(^{195}$Pt—^{31}P), and the $^2J(^{31}$P—^{15}N) have similar values for both complexes. So it seems now more reasonable, in the absence of a crystal structure determination, to propose a side-on coordination (Fig. 6c). The slight differences in ^2J(P—P) (see Table 3 and Table 2 in ref. 9) are probably due to slightly different P—Pt—P bond angles. The UV results [9] can now be explained in the same way as for the ArNSO-complexes, viz. a partial dissocation of the complex at low concentrations.

The IR data are still remarkable because the ν(N=S) change very differently upon coordination in both types of complexes: a decrease of 358—371 cm^{-1}for

TABLE 8

ANGLES BETWEEN DIFFERENT PLANES (°)

plane 1 (Pt, P$_1$, P$_2$)	and plane 2 (Pt, N, S)	172.9
plane 3 (N, S, O)	and plane 2	103.7
plane 4 (N, S, C$_{11}$)	and plane 2	150.3
plane 4	and plane 3	46.5
plane 5 (N, C$_{11}$—C$_{19}$)	and plane 2	76.6
plane 5	and plane 3	120.5
plane 5	and plane 4	99.3

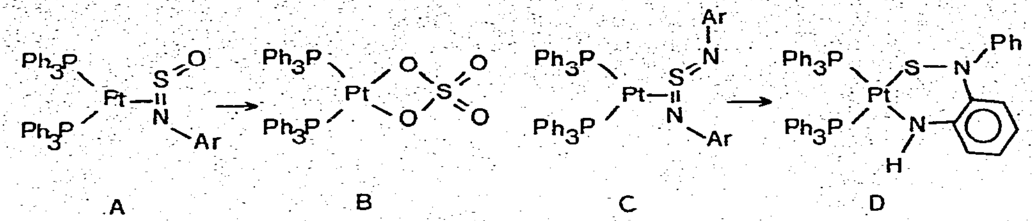


Fig. 6. The structures of [Pt(PPh$_3$)$_2$(L)] with L = ArNSO (A), SO$_4$ (B), ArNSNAr (C) and SN(1-NH-Ar′)(Ar) (D).

the ArNSO complexes and an increase of 6—19 cm^{-1} (see Table 4 in ref. 9) for the ArNSNAr complexes.

It should be mentioned that for both ligands and their complexes the NS stretching modes have been unambiguous assigned by ^{15}N substitution [26]. The remarkable difference between these two ligands can be explained by the fact that the NS stretching modes in the complexes of PhNSNPh and PhNSO are comparable, viz. 970 and 926 cm^{-1}, respectively, but that it is not realistic to compare the ν(NS) in the free ligand situation of both ligands. As mentioned before, no coupling exists in PhNSO between ν(NS) and ν(SO), whereas in PhNSNPh two NS stretching modes couple to a ν(NS) asymmetric and a ν(NS) symmetric [26]. When the sulfurdiimine ligand is coordinated via one NS bond, the two NS bond are no longer identical, and give rise to a ν(NS) coordinated, belonging to the π-coordinated NS bond, and a ν(NS) uncoordinated, belonging to the uncoordinated NS bond in the complex, in such a way that the coupling between these two vibrations is much diminished. The ν(NS) uncoordinated is 1248 cm^{-1} which value is comparable with the ν(NS) of the free ligand PhNSO (1272 cm^{-1}). Furthermore the ν(NS) coordinated has about the same frequency (970 cm^{-1}) as the corresponding ν(NS) of the coordinated PhNSO (926 cm^{-1}). Therefore it seems more likely that the lowering of the ν(NS) upon coordination is now approximately the difference between the ν(uncoordinated) and the ν(coordinated) in the complex i.e. 1248—970 = 278 cm^{-1}, which is comparable with the lowering of 358 cm^{-1} found for the PhNSO complex, 202 cm^{-1} in the complex [Rh(PPh$_3$)$_2$(NO)(SO$_2$)] [36] and 250 cm^{-1} in [Pt(PPh$_3$)$_2$(H$_2$C=C=CH$_2$)] [37,38]. The origin of the large reduction of the coupling between the ν(NS) coordinated and the ν(NS) uncoordinated in the complex can be caused by two effects: (i) the difference in energy between these two stretching frequencies has become too large, and (ii) the NSN angle has changed upon coordination. Van Gaal et al. [39] have calculated that when a cumulene, linear ligand shows side-on coordination, the couplings between these double bonds will change as a result of the bending of the ligand upon coordination. In any case it should be clear that IR results for these type of ligands (cumulated double bonds) should be treated with extreme caution.

Other IR frequencies which have been assigned are ν(Ph—N) *sym*. at 1274 cm^{-1} (increase of 52 cm^{-1}), ν(Ph—N) *asym*. at 1280 cm^{-1} (decrease of 20 cm^{-1}) and the δNSN) at 766 cm^{-1} (decrease of 36 cm^{-1} upon coordination). A *cis, trans* configuration for the coordinated sulfurdiimine is proposed (see Fig. 6c) on the basis of the following arguments. Upon reaction with the dimesitylsulfurdiimine, a ligand which exists only in the *trans, trans* configuration [2] with platinum(0), no sulfurdiimine complex could be isolated.

Moreover, with this type of side-on coordination an upfield shift is expected for the protons in the aryl rings which are attached to the NS fragment coordinated to Pt^0 [9,40]. Such shifts are found for the *cis* group upon coordination when a *cis, trans* conformation is adopted with the *cis* group bonded to the coordinated NS fragment, i.e. the *ortho* protons in the *cis-p*-tolyl group in di-*p*-tolylsulfurdiimine shift upfield upon coordination from 8.10 to 6.55 ppm (Table 3 in ref. 9). This upfield shift is larger than is found in $[Ni(0)(PPh_3)(4\text{-}MeC_6H_4NSN4\text{-}MeC_6H_4)]_2$ (1.09 ppm) [9] and for *p*-tolyl-N=S=O (0.90 ppm). The chemical shifts of the protons in the *trans* aryl ring hardly change upon coordination.

The fluxional behaviour of the sulfurdiimine, previously described [8,9], is not a N—N jump, but it is proposed that, in addition to a probable rotation about the Pt—(N=S) bond as found for the ArNSO complexes, there is also an intramolecular movement of the $(PPh_3)_2Pt$ unit from one N=S π-bond to the other. At the same time both aryl groups must change their positions from a *cis* to a *trans* configuration and vice versa. The most likely process is an inversion round nitrogen. It is noteworthy that the analogous Pt complex of allene [36, 37] is rigid. This effect may be rationalized by the different spatial arrangement of the π-orbitals in the NSN-ligands and the allene. In the sulfurdiimines both π-orbitals are perpendicular to the NSN plane, and in the allene molecule these π-orbitals are perpendicular to each other.

The complexes $[Pt(PPh_3)_2(ArNSNAr)]$ discussed above are intermediates for the forming of $[PtS\{N(1\text{-}NH\text{-}Ar')(Ar)\}(PPh_3)_2]$ (see Fig. 6c and 6d). So it is now proved that this rearrangement proceeds via a π-bonded complex which we al already have proposed [8,9]. It seems therefore reasonable that the same reaction path can be assumed for similar rearrangements of azobenzene with $[Fe_2(CO)_9]$ [41,42] and $[Mo(C_5H_5)(CO)_3]_2$ [43].

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