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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

VII *. *N,N'*-DIARYLSULFURDIIMINE COMPLEXES OF NICKEL(0) AND PLATINUM(0) OF THE TYPE $[(\text{PPh}_3)_x\text{M}(\text{RNSNR})]_y$ AND FORMATION OF A NOVEL COMPLEX $[\overline{\text{Pt}^{\text{II}}[\text{SN}(1\text{-N}}\text{HR}')(\text{R})](\text{PPh}_3)_2]$ FROM $[\text{Pt}^0(\text{RNSNR})(\text{PPh}_3)_2]$, VIA AN IRREVERSIBLE INTRAMOLECULAR REARRANGEMENT INVOLVING N—C(aryl) BOND FORMATION AND N=S BOND BREAKING

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Summary

The complexes $[\text{Ni}(\text{PPh}_3)(\text{4-tolylN=S=N-4-tolyl})]_2$ and $[\text{Pt}(\text{PPh}_3)_2(\text{RN=S=NR})]$ (R = 4-tolyl, 4-Cl-phenyl and 3,5-xylyl) are reported. It is suggested that the Ni-complex is dimeric, and spectroscopic data indicate that the N=S=N units are bridging via a σ(N—Ni) and a π((N=S)—Ni) bond. The platinum complexes are monomeric and occur in two isomeric forms: in CHCl_3 (at −30°C) the complex is probably three coordinated, with the RN=S=NR unit in the *trans,trans* configuration and linked to Pt via one of the N atoms. In CD_3NO_2 the complex is four-coordinated with the sulfurdiimine acting as a bidentate ligand coordinated to Pt via both N atoms.

The three coordinated platinum complex is fluxional between −30 to +30°C, probably because of migration of the Pt atom from one N atom to the other. At +30°C a slow irreversible process occurs which leads to the formation of $[\overline{\text{Pt}[\text{SN}(1\text{-N}}\text{HR}')(\text{R})](\text{PPh}_3)_2]$. This compound has been characterized by X-ray crystallography and spectroscopic methods. A possible mechanism for the formation of this novel platinum(II) complex involves an initial intramolecular redox process, resulting in oxidation of platinum(0) to platinum(II), followed by concerted N=S bond rupture, H-migration, and N—C(aryl) bond formation.

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* For part I—VI see ref. 1—6.

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Introduction

Previous work on the coordination properties of *N,N'*-substituted sulfurdiimine compounds [1—4] showed that these compounds can act as monodentate and as bidentate ligands; in both type of complexes this involved coordination of the N-atoms to metal atoms like palladium(II), platinum(II), rhodium(I) and iridium(I). In order to investigate other modes of coordination by these ligands (e.g. via S, or the N=S double bond; this latter type of bonding is expected on the basis of MO-calculations on these ligands [5], provided the metal atom is sufficiently electron-rich) a study of their coordinating properties towards zerovalent metals is being carried out. It has been found that chromium(0), molybdenum(0) and tungsten(0) [6,7] prefer to coordinate with the alkylsulfurdiimine via one or both of the N-atoms, although in the case of $[M(CO)_5(CH_3N{=}S{=}NCH_3)]$ a second isomer occurs in which the dimethylsulfurdiimine is probably bonded to the metal via the S-atom.

In this paper, reactions of NSN ligands with the zerovalent metals of the nickel triad are reported, since in the case of these metals side-on coordination by one of the double bonds of cumulenes and pseudo-cumulenes can also be expected. Examples of this type of coordination have been reported in the case of nickel(0) complexes of CO_2 [8,9], $RN{=}C{=}CR_2$ [10], CS_2 [11] and the platinum(0) complexes of $R_2C{=}C{=}CR_2$ [12,13] and CS_2 [11,14], while SO_2 coordinates via the S-atom, as an electron acceptor to platinum(0) [15—17]. Furthermore, in the case of $[(PPh_3)_2Rh(NO)(SO_2)]$ the SO_2 is side-on coordinated [18].

In a future paper an extensive investigation of the coordination of RNSNR with other low valent, electron-rich, metal complexes will be described.

Experimental

All reactions were carried out under dry, oxygen free nitrogen, while solvents were dried and distilled under nitrogen before use. Sulfurdiimines [1,2], $[Ni(COD)_2]$ [19,20], $[Ni(PPh_3)_2(C_2H_4)]$ [21], $[Pt(PPh_3)_4]$ [22], $[Pt(PPh_3)_2(C_2H_4)]$ [22] were prepared by published methods.

Preparation of $[Ni(PPh_3)(4\text{-}MeC_6H_4NSN4\text{-}MeC_6H_4)]_2$ *(I)*

Method A. Di-4-tolylsulfurdiimine (DTSD) (0.38 mmol) was added to a stirred suspension of $[Ni(PPh_3)_2(C_2H_4)]$ in ether (0.38 mmol in 50 ml). The mixture immediately turned dark brown. After one hour of refluxing (or a few hours at ambient temperature) the solution was filtered and concentrated. After standing at —30°C black crystals were obtained (yield about 16%) very slowly. Traces of oxidized product were removed by washing with hexane.

Method B. DTSD (1 mmol) was added to a stirred suspension of $[Ni(COD)_2]$ (1 mmol in 50 ml ether) followed by PPh_3 (1 mmol). The reaction was stopped after 3 h, and subsequently the same procedure was followed as for method A.

The complex $[Ni(PPh_3)(DTSD)]_2$ is insoluble in n-hexane and soluble in ether, benzene and toluene, while it reacts immediately with $CHCl_3$. The crystals slowly turn green when exposed to air. No molecular weight measurements were possible owing to the very low solubility of the complex.

Reactions with other diarylsulfurdiimines did proceed, as indicated by NMR spectra of solutions, but did not give satisfactory crystalline products. No reaction occurred when CO was bubbled through a solution of the nickel complex in C_6D_6.

Both $[Ni(COD)_2]$ and $[Ni(PPh_3)_2(C_2H_4)]$ gave dark red solutions upon treatment with di-t-butylsulfurdiimine (DBSD), but the products appeared to be unstable and could not be isolated.

Preparation of $[Pt(PPh_3)_2(ArylN{=}S{=}NAryl)]$ *(Aryl = 4-tolyl (IIa), 4-Cl-phenyl (IIb) and 3,5-xylyl (IIc))*

ArylN=S=NAryl (1 mmol) was added to a stirred suspension of $[Pt(PPh_3)_2(C_2H_4)]$ (1 mmol) in 20 ml ether. After one hour the yellow precipitate was filtered off and washed with n-hexane until the washings were colourless. After drying under vacuum the yield was about 76%. The complexes are insoluble in ether, benzene, and n-hexane, and soluble in chloroform and nitromethane, although they are not stable in chloroform at ambient temperature, and so molecular weight measurements were not possible. Contrary to CO addition, an addition of PPh_3 to the complexes in $CDCl_3$ at —35°C caused no reaction.

Preparation of $[\overline{Pt\{SN(1\text{-}NHR}')(R)\}(PPh_3)_2]$ *(R = 4-tolyl (IIIa), 4-Cl-phenyl (IIIb) and 3,5-xylyl (IIIc))*

Method A. ArylN=S=NAryl (1 mmol) was added to a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (1 mmol) in benzene or toluene (50 ml). After 24 h the yellow crystalline precipitate was washed with n-hexane and dried under vacuum. A second and third fraction were obtained from the dark liquor after two and six days respectively. The total yield was about 60%. Solvent molecules were removed by recrystallization from a hexane/dichloromethane mixture.

The compounds IIIa, IIIb and IIIc are insoluble in ether, benzene, n-hexane, nitromethane, and acetonitrile, and soluble in chloroform.

Method B. ArylN=S=NAryl (0.5 mmol) was added to a solution of $[Pt(PPh_3)_4]$ (0.5 mmol) in benzene or ether (50 ml). After 24 h the yellow precipitate was filtered off, washed with n-hexane, and dried under vacuum. Yield 60%.

Method C. Compound IIc (0.25 mmol) was dissolved in $CHCl_3$ (5 ml) to give a dark-red solution. After a few days at ambient temperature n-hexane (25 ml) was added. The precipitate, consisting of [*cis*-$Pt(PPh_3)_2Cl_2$] and $[Pt(PPh_3)Cl_2(DXSD)]$ (DXSD = dixylylsulfurdiimine), was filtered off and the $CHCl_3$/n-hexane solution was left at —20°C to give yellow crystals in 14% yield. When the same procedure was used for IIa in CH_2Cl_2 the complex IIIa was the only product isolated (63% yield). Similar results were observed for a suspension of IIc in acetonitrile, methanol and ethanol. After a few days standing at ambient temperatures crystals of IIIc were formed. Complex III did not react with PPh_3, CO, or H_2 in $CDCl_3$ at ambient temperature.

Spectroscopic measurements and analytical data

The ^1H NMR spectra were recorded on Varian A60, T60A and HA 100 spectrometers. The ^{13}C NMR spectra were taken with a Varian CFT 20, while the ^{31}P NMR spectra were recorded with a Varian XL 100 spectrometer.

The ^1H NMR spectra of IIa, IIb and IIc were recorded at —35°C with samples

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES[a]

Compound[b]	Analysis (found (calcd) (%))				
	C	H	N	S	P
I $[Ni(PPh_3)(DTSD)]_2$	67.90 (68.23)	5.34 (5.19)	4.97 (4.97)		5.57 (5.50)
IIa $Pt(PPh_3)_2(DTSD)$[c]	61.98 (62.43)	4.97 (4.61)	2.83 (2.91)	3.15 (3.33)	6.10 (6.44)
IIb $Pt(PPh_3)_2(DClPhSD)$	57.07 (57.49)	4.52 (3.82)	2.58 (2.79)	3.01 (3.20)	5.61 (6.18)
IIc $Pt(PPh_3)_2(DXSD)$	61.71 (63.08)	5.06 (4.89)	2.69 (2.83)	3.09 (3.24)	6.12 (6.26)
$\overrightarrow{Pt[SN(1-N}HR')(R)](PPh_3)_2$					
IIIa R = 4-tolyl[d]	59.51 (62.43)	4.58 (4.61)	2.72 (2.91)	2.96 (3.33)	5.92 (6.44)
IIIc R = 3,5-xylyl	62.89 (63.08)	5.15 (4.89)	2.68 (2.83)	2.71 (3.24)	5.66 (6.26)

[a] All complexes are yellow, except the nickel compound, which is black. [b] DTSD = di-4-tolylsulfurdiimine; DClPhSD = di-4-chlorophenylsulfurdiimine; DXSD = di-3,5-xylylsulfurdiimine. [c] The compounds IIa, IIb and IIc could not be further purified, owing to the instability in solution. [d] Difficult to purify, but spectroscopic data clearly show that IIIa is similar to the analogous compound IIIc.

which were dissolved at —50°C under pure nitrogen.

IR spectra were recorded with Beckman IR 4250 and IR 11 spectrophotometers. The electronic absorption spectra were recorded on a Cary 14 spectrophotometer.

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

Results

Nickel compounds $[Ni(PPh_3)(ArylNSNAryl)]_2$

Reactions 1 and 2 produced the complexes $[Ni(PPh_3)(ArylNSNAryl)]_2$. The

$$2\,Ni(PPh_3)_2(C_2H_4) + 2\,DTSD \rightarrow \underset{(I)}{[Ni(PPh_3)(DTSD)]_2} + 2\,PPh_3 + 2\,C_2H_4 \qquad (1)$$

$$2\,Ni(COD)_2 + 2\,DTSD + 2\,PPh_3 \rightarrow \underset{(I)}{[Ni(PPh_3)(DTSD)]_2} + 4(COD) \qquad (2)$$

composition of the complex was confirmed by ^1H NMR and elemental analysis. ^{31}P NMR spectra (Table 2) showed only one signal even at —60°C, and no exchange with additional PPh_3 was observed in the NMR time scale. ^1H NMR spectra (Table 3) showed the presence of two inequivalent aryl groups. Evidence for the possible structure of this compound was obtained from several sources.

The ^1H NMR signals of the aryl groups may be compared with the signals of the *cis,trans* and the *trans,trans* configuration of ditolylsulfurdiimine, which at low temperature (—72°C) both exist (Fig. 1) [2]. Comparison of the chemical shifts of the aryl groups with the chemical shifts of the *trans,trans* configuration

TABLE 2

^{31}P NMR DATA FOR THE COMPLEXES[a]

Compound	Temperature (°C)	Solvent	δ_1	$^1J(Pt—P)$ (Hz)	δ_2	$^1J(Pt—P)$	$^2J(P—Pt—P)$
I $[Ni(PPh_3)(DTSD)]_2$	+37	C_6D_6	24.8				
IIa $Pt(PPh_3)_2(DTSD)$	—30	$CDCl_3$	17.1	3378	17.7	4314	*b*
	+37	CD_3NO_2	20.5	2405			
IIb $Pt(PPh_3)_2(DClPhSD)$	—30	$CDCl_3$	17.0	3375	17.2	4283	*b*
	+37	CD_3NO_2	19.1	2403			
IIc $Pt(PPh_3)_2(DXSD)$	—30	$CDCl_3$	17.7	4305	21.2	3304	5
	+37	CD_3NO_2	16.0	2440			
$Pt(PPh_3)Cl_2(DXSD)$	+37	$CDCl_3$	5.8	4020			
$Pt(PPh_3)Cl_2(DnePSD)$[c]	+37	$CDCl_3$	4.1	3819			
cis-$Pt(PPh_3)_2(DTT)_2$[d]	+37	$CDCl_3$	18.3	2870			
cis-$Pt(PPh_3)_2Cl(DTT)$[d]	+37	$CDCl_3$	6.3	3037	16.3	4007	18
cis-$Pt(PPh_3)_2Cl_2$	+37	$CDCl_3$	14.3	3674			
$Pt(PPh_3)_2(CS_2)$	+37	$CDCl_3$	21.4	2818	32.9	4853	20
$\overline{Pt[SN(1\text{-}NHR')(R)]}(PPh_3)_2$							
IIIa R = 4-tolyl	+37	$CDCl_3$	17.3	3205	22.7	2517	19
IIIb R = 4-Cl-phenyl	+37	$CDCl_3$	16.5	2557	22.2	3230	20
IIIc R = 3,5-xylyl	+37	$CDCl_3$	17.7	3274	23.6	2477	18

[a] Relative to external 85% H_3PO_4, downfield with positive sign. [b] Not observed. [c] DnePSD = dineopentylsulfurdiimine. [d] From ref. 39, DTT = di-4-tolyltriazenido.

of the free ligand shows downfield shifts of all signals, which would not be expected, since nickel(0) is a strong electron donor [23,24].

However, comparison with the chemical shifts of the *cis,trans* isomer of the free ligand reveals upfield shifts. The upfield shifts for the *cis*-tolyl group is 1.09 ppm for the *ortho* protons and 0.33 ppm for the *meta* protons, while the signals of the *trans*-tolyl group hardly change with respect to the free ligand.

It is noteworthy that such upfield shifts have also been observed for the aromatic rings of aromatic nitroso complexes $[Ni(PhNO)(t\text{-}BuNC)_2]$ [25], in which the ligand is bonded to the Ni atom via the double bond of the NO group. It is therefore suggested that a similar type of bonding occurs in the case of $[Ni(PPh_3)(DTSD)]_2$. From the composition of the complex, one would not expect a monomeric structure, as this would imply a complex with two-coordinated zerovalent nickel atoms, which is very unlikely. Therefore a dimeric structure is tentatively proposed analogous to $[(PPh_3)Ni(CS_2)]_2$ [11], with the NSN units bridging via a σ(N—Ni) and a π((N=S)—Ni) bond (See Fig. 2). Molecular weight experiments could not be made.

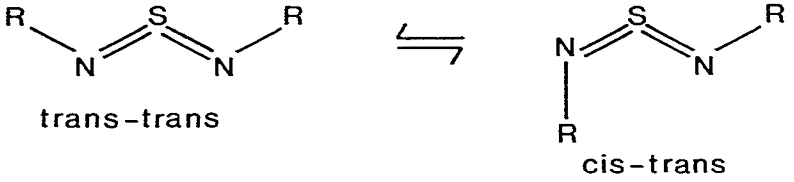

Fig. 1. The two conformations of the sulfurdiimine ligand in solution.

TABLE 3

^{1}H NMR DATA FOR THE COMPLEXES (δ, relative to TMS)

Compound	Temperature (°C)	Solvent	*ortho* [a]		*meta* [a]		*para* [a]		CH_3 [a]		N—H
I [Ni(PPh_3)DTSD)]$_2$	+35	C_6D_6	7.31	6.58	6.52	6.74			1.95	1.93	
IIa Pt(PPh_3)$_2$(DTSD) [b]	−30	$CDCl_3$	6.55	6.81	6.58	6.81			2.05	2.31	
	+35	$CDCl_3$	6.68		6.68				2.15		
	+35	CD_3NO_2	6.98		6.98				2.20		
IIb Pt(PPh_3)$_2$(DClPhSD)	−30	$CDCl_3$	6.61	6.88	6.61	7.00					
	+35	$CDCl_3$	6.72		6.72						
	+35	CD_3NO_2	7.00		6.57						
IIc Pt(PPh_3)$_2$(DXSD)	−30	$CDCl_3$	c	c			c	c	1.73	1.95	
	+35	$CDCl_3$	6.70				6.25		1.86		
	+35	CD_3NO_2	6.72				6.47		2.20		
Pt[SN(1-NHR′)(R)](PPh_3)$_2$											
IIIa R = 4-tolyl	+35	$CDCl_3$	d	f	d	f			2.08	2.35	5.73
IIIb R = 4-Cl-phenyl	+35	$CDCl_3$	e	f	e	f					5.70
IIIc R = 3,5-xylyl [c]	+35	$CDCl_3$	6.11	6.97			6.43	6.82	2.00 1.99	2.20	5.62

[a] The first value is due to the aryl group bonded to the nitrogen coordinated to platinum. [b] See also fig. 5. [c] Could not be assigned, a multiplet at about 6.42 ppm. [d] Could not be assigned, 6.63, 6.43 and 5.83 ppm. [e] Could not be assigned, 6.60, 6.43 and 5.82 ppm. [f] Covered by the absorptions of the PPh_3 groups.

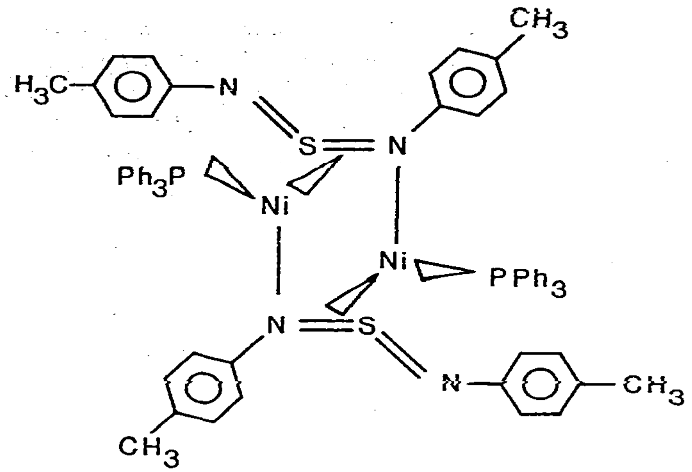

Fig. 2. The proposed structure of $[Ni(PPh_3)(DTSD)]_2$.

The IR spectra show a decrease of the ν_s(NSN) from 962 [26] to 906 cm^{-1}, which appears to be fairly small for π-bonding. However, a lowering of frequency caused by π-bonding may be partly compensated by a concomitant frequency increase of ν(NSN) as a result of the coordination to Ni by N, just as has been found for $[Pt(PPh_3)_2(RNSNR)]$ (vide infra) and for$[M(CO)_4(RNSNR)]$ (increase of 4—39 cm^{-1}) [6]. It should be noted that a very similar coordination was observed for $[Fe_2(CO)_6(3\text{-}Cl\text{-}2\text{-}CH_3C_6H_3NO)]$ [27] and for $[Pd_3(PhNO)_3\{P(t\text{-}Bu)_3\}_3]$ [28], i.e. one metal bonded to the N lone pair and the other to the N=O double bond.

In the far infrared region a strong absorption at 169 cm^{-1} is tentatively assigned to the ν(Ni—P) stretch, in accordance with literature data [29].

No evidence for the proposed structure of the nickel complex could be obtained from the electronic absorption spectra (Table 4). However, a new broad band in the visible region is tentatively assigned to a metal to NSN ligand charge transfer band.

TABLE 4

ELECTRONIC ABSORPTION[a] AND INFRARED[b] DATA FOR THE COMPLEXES (values in cm^{-1})

Compound	Solvent	$\pi(L) \rightarrow \pi^*(L)$	$M \rightarrow \pi^*(L)$	ν_s(NSN)	ν(NH)	ν(MP)
I $[Ni(PPh_3)(DTSD)]_2$[c]	C_6H_6		15200	906 s[d]		169 s
IIa $Pt(PPh_3)_2(DTSD)$	CH_2Cl_2	23400 27500 (9000);(7000)		974 s		
IIb $Pt(PPh_3)_2(DClPhSD)$	CH_2Cl_2	24400 (8400)		966 s		
IIc $Pt(PPh_3)_2(DXSD)$	CH_2Cl_2	24000 (5600)		971 s		
$Pt[\overline{SN(1\text{-}N}HR')(R)](PPh_3)_2$						
IIIa R = 4-tolyl					3368 w	
IIIb R = 4-Cl-phenyl					3364 w	
IIIc R = 3,5-xylyl					3368 w	

[a] Molar extinctions in parentheses. [b] In nujol mull or KBr disc. [c] Other absorptions; 20.400 and 23000 cm^{-1}. [d] s, strong; w, weak.

The ^{1}H NMR spectrum of the reaction mixture from $[Ni(COD)_2]$ and DBSD gave a singlet at 1.10 ppm, which indicates a bidentate mode of bonding with the sulfurdiimine in the *trans,trans* configuration, as in $[W(CO)_4(DBSD)]$ [6,30]. A possible formulation is $[Ni(DBSD)_2]$, analogous to the tetrahedral bis(diazabutadienenickel) prepared by tom Dieck et al. [31]. The complex could not be isolated, however.

Complexes $[Pt(PPh_3)_2(ArylNSNAryl)]$ (IIa, IIb, IIc).

Reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with ArylNSNAryl (Aryl = 4-tolyl (IIa), 4-Cl-phenyl (IIb) and 3,5-xylyl (IIc)) in ether quickly gave a yellow precipitate according to reaction 3. This complex reacted with CO, but not with PPh_3.

$$Pt(PPh_3)_2(C_2H_4) + ArylNSNAryl \xrightarrow[\text{ether}]{\text{R.T.}} Pt(PPh_3)_2(ArylNSNAryl) \qquad (3)$$

The IR spectra of $[Pt(PPh_3)_2(ArylNSNAryl)]$ showed that $\nu_s(NSN)$ increased by 12, 6 and 19 cm^{-1} for IIa, IIb and IIc, respectively, with respect to the free ligand (Table 4).

The electronic absorption spectra (Fig. 3 and Table 4) hardly change upon coordination. The IR and UV spectra therefore indicate that the π-electron system of the RNSNR is scarcely affected by coordination to platinum(0), which implies that the sulfurdiimine is bonded via N or S to the Pt atom*

The ^{1}H NMR spectra show at —30°C in $CDCl_3$ that the aryl groups are inequivalent (Table 3), which taken along with the IR and UV spectra, indicates that the platinum(0) is three coordinated with the sulfurdiimine acting as a monodentate ligand, (Fig. 4). The coordinated sulfurdiimine may be in the *cis,trans* or in the *trans,trans* configuration (Fig. 1) [2].

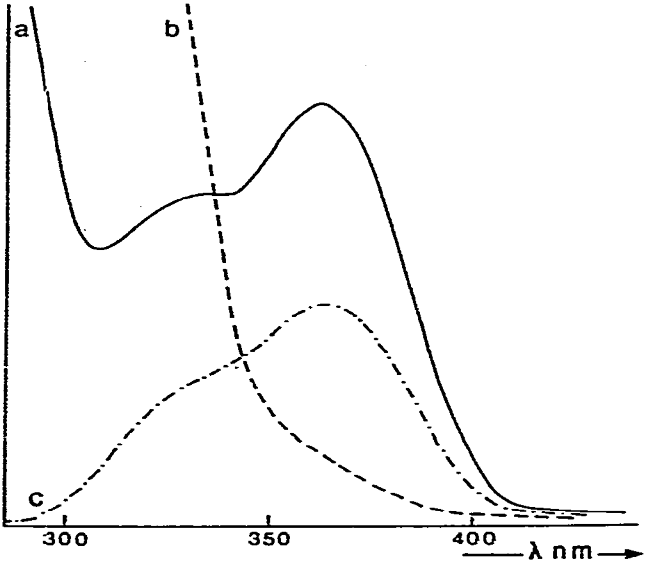

Fig. 3. The electronic absorption spectra of (a) (———) $Pt(PPh_3)_2(DTSD)$. (b) (- - - - -) $\overline{Pt[SN(1\text{-}N}H\text{-}4\text{-}MeC_6H_3)(4\text{-}MeC_6H_4)](PPh_3)_2$ and (c) (-·-·-·) DTSD in CH_2Cl_2.

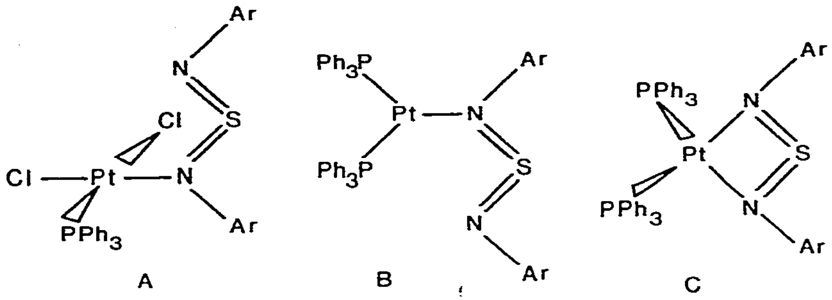

Fig. 4. The proposed structure of $PtCl_2(PPh_3)(ArNSNAr)$(A), $Pt(PPh_3)_2(ArNSNAr)$ in $CDCl_3$ (B) and $Pt(PPh_3)_2(ArNSNAr)$ in CD_3NO_2 (C).

Comparison of the aryl proton chemical shifts with those of the two isomers of the free ligand show that a *cis,trans* configuration is rather unlikely, since for this very large upfield shifts would occur. If the ligand is in the *trans,trans* configuration, as is also the case for [$PtCl_2$(ArylNSNAryl)(PPh_3)] [2] (Fig. 4a) the shifts of one of the aryl groups moves about 0.2—0.3 ppm upfield, while the proton signals of the other aryl group hardly change. It therefore seems more likely that the ligand is in the *trans,trans* configuration, although the *cis,trans* configuration is not rigorously excluded. If the ligand is in the *trans,trans* configuration the higher field signals belong to the aryl group of the coordinated N-aryl group, while the lower field signals belong to the non-coordinated N-aryl group. The upfield shifts of the protons of one aryl group, in contrast to the downfield shifts in the platinum(II) complexes [2] (Fig. 4a), are caused by back bonding from platinum(0) to the sulfurdiimine.

The ^{13}C NMR spectra at —35°C are rather complicated owing to the PPh_3 signals, and the spectrum could not be fully assigned (Table 5). Of interest are the large downfield shifts of about 8 ppm for the coordinated N—^{13}C side of the ligand and about 5 ppm for the non-coordinated N—^{13}C end of the ligand. The ^{13}C NMR resonances shift, with respect to the free ligand, in the opposite direction to that found for the platinum(II) complexes [2], just as do the ^1H NMR resonances.

The ^{31}P NMR spectra (Table 2) of IIa, IIb and IIc at —30°C show that the two PPh_3 groups are inequivalent, with ^1J(Pt—P) couplings of about 3300 and 4300 Hz, respectively and a ^2J(P—Pt—P) of 0—5 Hz. Therefore sulfur-bonded complexation is excluded, because in this case the two phosphorus atoms should be equivalent. Furthermore, since the sulfurdiimine is probably in the *trans,trans* configuration, one would expect for metal—sulfur bonding that the aryl groups would be equivalent, which is not the case. If we assume that the sulfurdiimine is coordinated as shown in Fig. 4b, the sulfurdiimine ligand must lie approximately in the plane of the PtP_2 unit, which gives more opportunity for backbonding than the perpendicular case [32]. The coupling constants are rather high, but may be rationalized by a large *s*-character of the Pt—P bonds in this three-coordinated complex. At higher temperatures (—10°C) a reversible intramolecular process occurs, in which the aryl groups become magnetically equivalent.

In Fig. 6 is shown the most likely process, involving a four-coordinated intermediate. Concentration dependence studies indicated that it is probably intra-

TABLE 5

^{13}C NMR DATA (solvent $CDCl_3$, values in ppm relative to TMS)

Compound	Temperature (°C)	C—N[a]		*ortho*[a]		*meta*[a]		*para*[a]		CH_3	
IIa $Pt(PPh_3)_2(DTSD)$	−35	150.08[c]	147.58[c]	119.42[c]	123.97	*b*	*b*	*b*	*b*	20.85	20.41
IIb $Pt(PPh_3)_2(DClPhSD)$	−35	151.99[c]	148.48[c]	120,10[c]	*b*	127,01	125.09	129,00	131.39		
IIc $Pt(PPh_3)_2(DXSD)$	−35	153.20[c]	150.76[c]	119,20[c]	*b*	137.50	136.48	*b*	*b*	21,00	20.74
$Pt[SN(1\text{-}NHR')(R)](PPh_3)_2$											
IIIa R = 4-tolyl	+35	141.08[c]	152.85[c]	117.22[d]	121.88	*e*	*b*	*b*	*b*	20.25	20.50
IIIc R = 3,5-xylyl	+35	*e*	*e*	114.23[d]	119.39	115.84[d]	136.79	*b*	*b*	21.21 17.54	21.86

[a] The first value is due to the aryl group bonded to the nitrogen coordinated to platinum. [b] Covered by the absorptions of the PPh_3 groups. [c] Broad. [d] The other one is not observed. [e] Not observed.

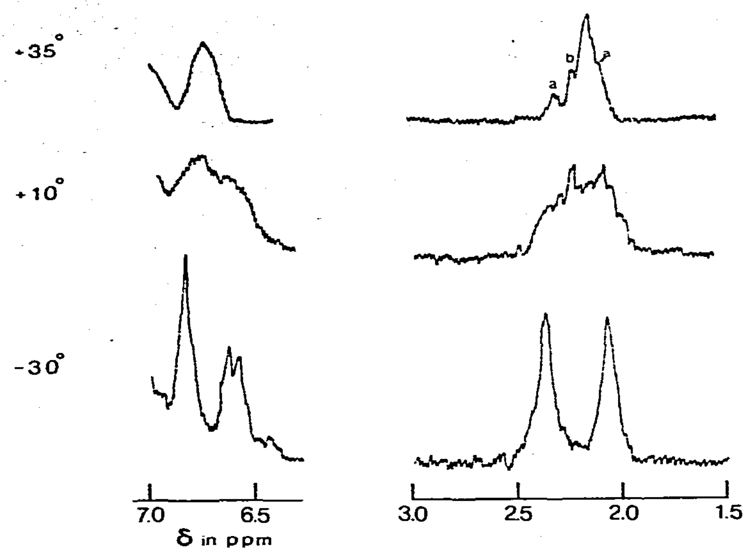

Fig. 5. The ΔT ^1H NMR of $Pt(PPh_3)_2(DTSD)$ in $CDCl_3$. Peaks marked with a and b arise, respectively, from a small amount of IIIa and from an impurity.

molecular, although this was difficult to study owing to a second, irreversible, process (vide infra).

It is of interest to note that, if IIa, IIb and IIc are dissolved in CD_3NO_2, a symmetrical structure is observed, as indicated by the ^{31}P NMR spectra (equivalent PPh_3 groups with $^1J(Pt-P)$ of about 2400 Hz) and ^1H NMR spectra (equivalent aryl groups). The $^1J(Pt-P)$ are smaller than in the three-coordinated com-

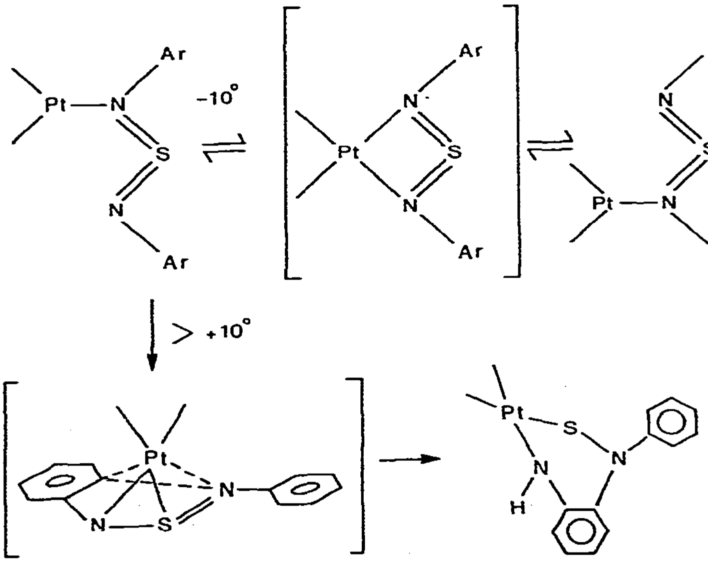

Fig. 6. The proposed mechanism for the intramolecular reversible interconversion of the aryl groups of $Pt^0(PPh_3)_2(ArNSNAr)$ and the intramolecular irreversible rearrangement to $Pt^{II}[SN(1\text{-}NHR')(R)](PPh_3)_2$.

plex; a lower s-character in the Pt—P bonds would be expected, since the sulfurdiimine is probably bonded as a bidentate, with four-coordinated platinum(0) (Fig. 4c).

Solvent effects thus play an important role in the stabilization of the four-coordinated intermediate in the exchange process involving the three-coordinated platinum(0) compounds $[\mathrm{Pt(PPh_3)_2(RNSNR)}]$. Reactions of $[\mathrm{Pt(PPh_3)_2(C_2H_4)}]$ with 2,4,6-mesityl-NSN-2,4,6-mesityl and t-Bu-NSN-t-Bu did not give complexes of the type II. Instead, platinum cluster type complexes, similar to those reported by Taylor et al. [33], were formed. These were not further studied.

Complexes $[\overline{\mathrm{Pt}\{\mathrm{SN}(1\text{-}\mathrm{NHR'})(\mathrm{R})}\}(\mathrm{PPh_3})_2]$ *(IIIa, IIIb and IIIc)*

Complexes IIa, IIb and IIc are converted slowly in $\mathrm{CDCl_3}$ at about 30°C into complexes $[\overline{\mathrm{Pt}\{\mathrm{SN}(1\text{-}\mathrm{NHR'})(\mathrm{R})}\}(\mathrm{PPh_3})_2]$ (IIIa, IIIb and IIIc, respectively) with *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ and $[\mathrm{PtCl_2(PPh_3)(RNSNR)}]$ as by-products.

Complexes III were also formed directly at ambient temperature within a few hours by reaction of $[\mathrm{Pt(PPh_3)_2(C_2H_4)}]$ with RNSNR in tetrahydrofuran or in benzene, or by reaction of $[\mathrm{Pt(PPh_3)_4}]$ with RNSNR in ether, tetrahydrofuran or benzene.

Complexes III are monomeric, and do not react with $\mathrm{PPh_3}$, $\mathrm{H_2}$ and CO. Single crystal X-ray crystallography showed that the complex $[\overline{\mathrm{Pt}\{\mathrm{SN}(1\text{-}\mathrm{NH}\text{-}3{,}5\text{-}\mathrm{Me_2C_6H_2})}(3{,}5\text{-}\mathrm{Me_2C_6H_3})\}(\mathrm{PPh_3})_2]$ has the structure shown in Fig. 7 and 8.

Some relevant bond distances and bond angles are listed in Table 6. The full details will be published elsewhere [34]. The coordination around platinum is square planar, indicating an intramolecular oxidation to platinum(II). Unusual are the S=N bond breaking and the formation of a N—C(aryl) bond. The hydrogen has moved to N(1). The other NS bond is lengthened from 1.53 Å in the free ligand [35] to 1.72 Å, and has lost its double bond character.

This structure is in agreement with the ^{1}H NMR data (See Fig. 7 for the assignment) and the ^{31}P NMR spectrum (Table 2). The two phosphorus atoms are inequivalent, with ^1J(Pt—P) couplings of about 2500 and 3200 Hz respectively

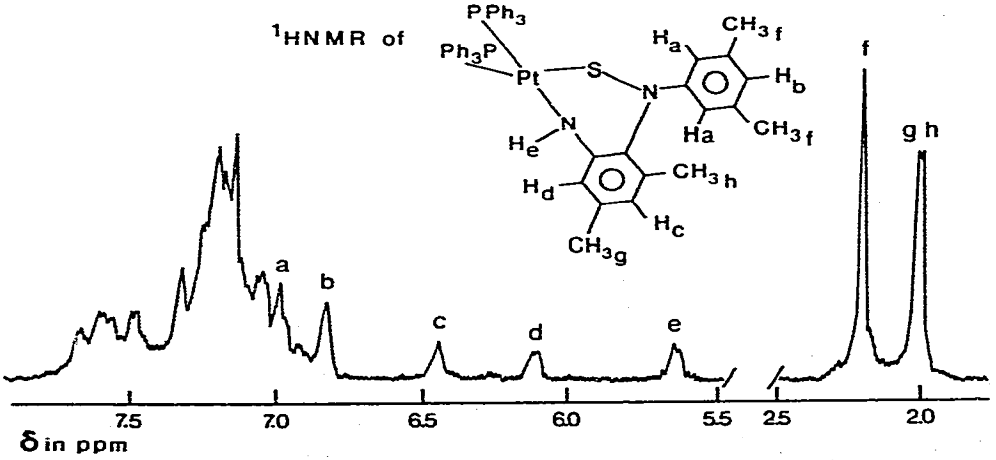

Fig. 7. The ^{1}H NMR of $\overline{\mathrm{Pt[SN(1\text{-}NH\text{-}3.5\text{-}Me_2C_6H_2)}}\mathrm{(3.5\text{-}Me_2C_6H_3)](PPh_3)_2}$.

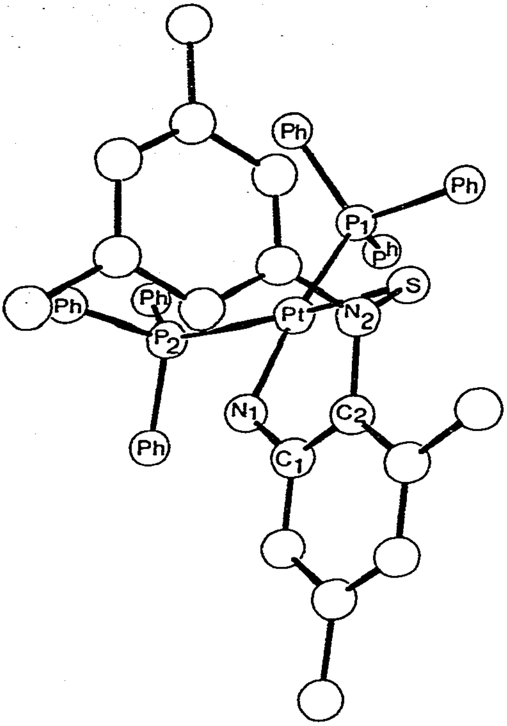

Fig. 8. The crystal structure of $\overline{\text{Pt[SN(1-N}}\text{H-3,5-Me}_2\text{C}_6\text{H}_2\text{)(3,5-Me}_2\text{C}_6\text{H}_3\text{)](PPh}_3\text{)}_2$. From the phenyl groups in PPh_3 only the first C-atoms are drawn.

and a *cis* ^1J(P—Pt—P) of about 19 Hz. The signal with the lower ^{195}Pt—^{31}P coupling probably has to be assigned to the PPh_3 group *trans* to N, while the signal with the larger coupling to the PPh_3 *trans* to S, as can be seen in the ^{31}P NMR of $[Pt(PPh_3)_2(CS_2)]$ (Table 2). Both ^{1}H and ^{31}P NMR spectra did not show any temperature dependence.

The IR spectra show that the ν_s(NSN) is completely missing, while a new weak absorption at 3368 cm^{-1} is assigned to the N—H stretch. The $\pi \rightarrow \pi^*$ transitions

TABLE 6

BOND DISTANCES (in Å) AND BOND ANGLES (in degrees) OF $\overline{\text{Pt[SN(1-N}}\text{H-3,5-Me}_2\text{C}_6\text{H}_2\text{)(3,5-Me}_2\text{C}_6\text{H}_3\text{)](PPh}_3\text{)}_2$ [a]

(Standard deviations brackets)

		S—Pt—N(1)	89.10 (88)
Pt—P(2)	2.31(1)	P(2)—Pt—P(1)	100.08 (25)
Pt—P(1)	2.25(1)	P(2)—Pt—N(1)	83.63 (85)
Pt—N(1)	2.07(2)	S—Pt—P(1)	87.78 (27)
Pt—S	2.32(1)	Pt—N(1)—C(1)	127.07(218)
N(1)—C(1)	1.38(4)	N(1)—C(1)—C(2)	121.22(249)
N(2)—C(2)	1.43(4)	C(1)—C(2)—N(2)	117.03(246)
N(2)—S	1.72(2)	C(2)—N(2)—S	112.14(180)
C(1)—C(2)	1.45(1)	N(2)—S—Pt	101.82(101)

[a] See fig. 8.

of the concerned ligand in the electronic absorption spectra of the complexes II are missing in the complexes III (Fig. 3), which is consistent with the disappearance of the cumulene π-bond of the sulfurdiimine ligand.

Discussion

A point of interest is that reactions of $[(PPh_3)_2Ni(C_2H_4)]$ and $[(PPh_3)_2Pt(C_2H_4)]$ with diarylsulfurdiimines lead to different products, viz. $[(PPh_3)Ni(RNSNR)]_2$ and $[(PPh_3)_2Pt(RNSNR)]$, respectively. Similar behaviour (products with one PPh_3 for nickel(0) and two for platinum(0)) is found in reactions with allene or CS_2, which afforded the compounds $[Ni(C_9H_{12})(PPh_3)]$ [13], $[Pt(C_3H_4)(PPh_3)_2]$ [12] $[Ni(CS_2)(PPh_3)]_2$ [11] and $[Pt(CS_2)(PPh_3)_2]$ [14].

Another feature is that the nickel compound reacts with both diaryl- and dialkyl-sulfurdiimines, while the platinum compound only reacts with diarylsulfurdiimines. This is probably due to the fact [23] that nickel(0) is a stronger electron donor than platinum(0). Nickel(0) is better able to give backbonding with the relevant lowest empty orbitals (π^*) of the sulfurdiimines. Because of conjugation the π^* orbital of an arylsulfurdiimine lies lower than the π^* orbital of an alkylsulfurdiimine. Strict comparison of Ni and Pt cannot be made, however, since the products are different.

The behaviour of $[Pt(PPh_3)_2(RNSNR)]$ in various solvents is interesting, since a symmetric four-coordinated compound is observed in CD_3NO_2 and an asymmetric probably three-coordinated configuration, in $CDCl_3$. It is assumed that in $CDCl_3$ the four-coordinated symmetric structure may be present, through which the aryl groups interchange their position to the three-coordinated complex (Fig. 6). The process is similar to the one observed in $[PtCl_2(PPh_3)(ArylNSNAryl)]$ [2].

The most interesting observation is the irreversible process by which $[Pt(PPh_3)_2(RNSNR)]$ is converted into $[Pt\{SN(1\text{-}NHR')(R)\}(PPh_3)_2]$ (Fig. 6). The proposed mechanism probably involves an isomerization of the sulfurdiimine from the *trans,trans* configuration to the *cis,trans* configuration, and movement of the $(PPh_3)_2Pt$ unit from the N atom to a N=S double bond. In this intermediate configuration the $(PPh_3)_2Pt$ unit acts as a template, and is close to the aryl C—H bond and the N-atom of the other sulfurdiimine. The closeness of the N atom to the C—H bond is also clear from the crystal structure of di-*p*-tolylsulfurdiimine [35]. Nucleophilic attack of the N atom on the activated C—H bond produces the N—C bond. Concomitant H migration and N=S bond rupture affords complex III.

This type of reaction is rather similar to that of azobenzene with iron carbonyls [36] which leads to the formation of *μ-N,N'*-dehydrosemidinatobis(tricarbonyliron). In that case also N=N-bond rupture takes place with migration of an *ortho* proton of one of the phenyl rings to the nitrogen atom bonded to that ring. The metal carbonyl fragment promotes the migration of the second N atom to the *ortho* position [36].

Few conversions of sulfurdiimines have previously been observed [37,38], and so this new reaction provides a possible novel route into the preparation of new types of compounds containing N and S atoms.

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References

1 J. Kuyper and K. Vrieze, J. Organometal. Chem., 74 (1974) 289.
2 J. Kuyper and K. Vrieze, J. Organometal. Chem., 86 (1975) 127.
3 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 108 (1976) 257.
4 J. Kuyper, Mrs. L.G. Hubert-Pfalzgraf, P.C. Keijzer and K. Vrieze, J. Organometal. Chem., 108 (1976) 271.
5 A. Schouten and A. Oskam, Inorg. Chim. Acta, 22 (1977) 149.
6 R. Meij, J. Kuyper, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 110 (1976) 219.
7 R. Meij, T.A.M. Kaandorp, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 128 (1977) 203.
8 M. Aresta and C.F. Nobile, J. Chem. Soc. Chem. Commun., (1975) 636.
9 M. Aresta and C.F. Nobile, J. Chem. Soc. Dalton, (1977) 708.
10 D.J. Yarrow, J.A. Ibers, Y. Tatsuno and S. Otsuka, J. Amer. Chem. Soc., 95 (1973) 8590.
11 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.
12 J.A. Osborn, J. Chem. Soc. Chem. Commun., (1968) 1231.
13 S. Otsuka, K. Tani and T. Yamagata, J. Chem. Soc. Dalton, (1973) 2491.
14 R. Mason and A.J.M. Rae, J. Chem. Soc. A, (1970) 1767.
15 J.J. Levinson and S.D. Robinson, J. Chem. Soc. Dalton, (1972) 2013.
16 D.C. Moody and R.R. Ryan, Inorg. Chem., 15 (1976) 1823.
17 P.G. Eller, R.R. Ryan and D.C. Moody, Inorg. Chem., 15 (1976) 2442.
18 D.C. Moody and R.R. Ryan, J. Chem. Soc. Chem. Commun., (1976) 503.
19 B. Bogdanović, M. Kröner and G. Wilke, Liebigs Ann. Chemie, 699 (1966) 1.
20 R.A. Schunn, Inorganic Synthesis, 15 (1974) 5.
21 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1969) 3019.
22 F.R. Hartley, Organometal. Chem. Rev. A, 6 (1970) 119.
23 R.L. de Kock, Inorg. Chim. Acta, 19 (1976) L27.
24 J.W. Bassi, C. Benedicenti, M. Calcaterra and G. Rucci, J. Organometal. Chem., 117 (1976) 285.
25 S. Otsuka, J. Aotani, Y. Tatsuno and T. Yoshida, Inorg. Chem., 15 (1976) 656.
26 R. Meij, to be published.
27 M.J. Barrow and O.S. Mills, J. Chem. Soc. A, (1971) 864.
28 M. Calligaris, T. Yoshida and S. Otsuka, Inorg. Chim. Acta, 11 (1974) L15.
29 K. Nakamoto, Infrared spectroscopy of inorganic and coordinated compounds, Wiley, New York, 1970, p. 206.
30 R. Meij and K. Olie, Cryst. Struct. Commun., 4 (1975) 515.
31 H. tom Dieck, private communication.
32 K.S. Wheelock, J.H. Nelson, L.C. Cusachs and H.B. Jonassen, J. Amer. Chem. Soc., 92 (1970) 5110.
33 N.J. Taylor, P.C. Chieh and A.J. Carty, J. Chem. Soc. Chem. Commun., (1975) 448.
34 J. Bode, D. Heijdenrijk, J.D. Schagen and H. Schenk, Cryst. Struct. Commun., to be published
35 G. Leandri, V. Busetti, G. Vall and M. Mammi. J. Chem. Soc. Chem. Commun., (1970) 413.
36 P.E. Baikie and O.S. Mills, Inorg. Chim. Acta, 1 (1967) 55.
37 J. Kuyper, P.C. Keijzer and K. Vrieze, J. Organometal. Chem., 116 (1976) 1.
38 O.J. Scherer and R. Schmidt, J. Organometal. Chem., 16 (1969) P11.
39 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1974) 1205.