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S,N,N'-SUBSTITUTED SULFURDIIMINES AS LIGANDS

II *. COMPOUNDS $[(\eta^3\text{-}RC_3H_4)Pd\{R^1NS(R^2)NR^1\}]$ (R = H, CH_3; R^1 = ARYL; R^2 = CH_3, t-C_4H_9) AND SOME RELATED TRIAZENIDO AND AMIDINO COMPOUNDS OF PALLADIUM(II)

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Summary

The complexes $[(\eta^3\text{-}RC_3H_4)Pd\{R^1NS(R^2)NR^1\}]$ (R = H, CH_3; R^1 = aryl; R^2 = CH_3, t-C_4H_9) have been obtained from the reaction of $[(\eta^3\text{-}RC_3H_4)PdCl]_2$ with $[Li\{R^1NS(R^2)NR^1\}]$; two isomers are produced, differing in the orientation of the allyl group. The sulfurdiimino group has some π-allylic character. The compounds decompose in solution into azo—arenes and $[(\eta^3\text{-}RC_3H_4)Pd(SR^2)]_2$, and this is shown to be dependent upon steric and electronic factors.

The properties of the sulfurdiimino compounds are compared with those of the compounds $[(\eta^3\text{-}RC_3H_4)Pd(R^3N_3R^3)]_2$ and $[(\eta^3\text{-}RC_3H_4)Pd(R^3NC(R^4)NR^3)]_2$ (R = H, CH_3; R^3 = CH_3, aryl; R^4 = H, CH_3), which have been prepared by new methods.

Introduction

Our interest in the chemistry of pseudo-allenic [1—4] and pseudo-allylic ligands [5—10] has recently focussed on sulfurdiimino, triazenido and amidino ligands (Fig. 1).

The recently reported sulfurdiimino ligand may be formed by inserting *N,N'*-substituted sulfurdiimines R'N=S=NR' into metal—carbon bonds [5] (e.g. Li—C *, Mg—C) analogous to the insertion of allenes [11—13]. Further reaction of $[Li\{R^1NS(R^2)NR^1\}]$ with suitable metal compounds [5,15] afforded dimeric complexes $[M\{R^1NS(R^2)NR^1\}]_2$ of copper(I) and silver(I), in which the ligand is bridging, and monomeric complexes $[(CO)_2Rh\{R^1NS(R^2)NR^1\}]$, in which the ligand acts as a chelate and in its bonding characteristics bears a resemblance

* For part I see ref. 15.

* A reaction of $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ with $LiCH_3$ has been reported [14].

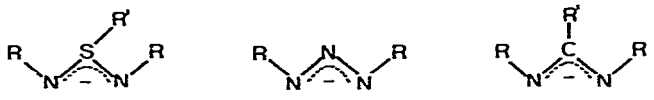


Fig. 1.

to π-allyl bonding [16]. In solution the sulfurdiiminometal compounds may decompose, one of the products being an azo—arene. The ease of this process depends on both electronic and steric factors.

In order to obtain more insight into the bonding of the sulfurdiimino ligand, complexes of palladium(II) have been prepared, along with palladium(II) complexes of the formally analogous triazenido and formamidino ligands. During the course of this work, a number of triazenido and formamidino complexes of palladium(II) were reported by others [17,18]. The complexes described here, some of them new, were prepared by different methods. The structure of one of them has been reported by us [9].

Experimental

The preparations were carried out under dry nitrogen. Solvents were dried carefully prior to use. Diaryltriazenes [19], diarylamidines [20], their silver salts [21—23], dimethyltriazenidosilver [7], *S,N,N'*-substituted sulfurdiiminolithium [5,15] and $[\eta^3$-(methyl)allylPdCl$]_2$ [24] were prepared as described in the literature.

Preparation of $[(\eta^3$-$RC_3H_4)Pd\{R^1NS(R^2)NR^1\}]$ (R = H, Me; R^1 = p-tolyl, p-ClC_6H_4, 3,5-xylyl, 2,4,6-mesityl; R^2 = Me, t-Bu)

As an example, the preparation of $[(\eta^3$-$C_4H_7)$Pd{MesNS(t-Bu)NMes}] (Mes = 2,4,6-mesityl) is given.

$[(\eta^3$-$C_4H_7)PdCl]_2$ (1 mmol) was added, with stirring, to a solution of [Li{MesNS(t-Bu)NMes}] (2 mmol) in ether (20 ml) at —30°C. After 5 min the solution was evaporated to dryness under vacuum. The residue was dissolved in cold hexane (20 ml) and LiCl was removed by filtration. At —35°C yellow crystals were obtained in 80% yield.

All methallylpalladium compounds are soluble in ether except for the *p*-Cl-C_6H_4 derivatives. In this case, and with the allylpalladium compounds, the residue was dissolved in cold benzene. LiCl was removed quickly, and cold hexane was added to induce crystallization in the cold (—20°C).

Preparation of $[(\eta^3$-$RC_3H_4)Pd(SR^2)]_2$ (R^2 = t-Bu)

t-BuSH (1.0 mmol) was added to a solution of $[(\eta^3$-$C_4H_7)PdCl]_2$ in $CHCl_3$ (20 ml). After 3 h stirring the solution was filtered and evaporated to dryness. The residue was crystallized from benzene/hexane to give orange crystals in 85% yield.

Preparation of η^3-(methyl)allyl- triazenido- and -amidino-palladium compounds *

* Analogous compounds have been prepared in a different way by Candeloro De Sanctis et al. [17, 18], and by Jack and Powell [30].

Method I

Preparation of [(η^3-RC_3H_4)Pd(DMT)]$_2$ (R = H, CH_3; DMT = dimethyltriazenido). Dimethyltriazenidosilver (2.0 mmol) was dissolved in benzene (20 ml) and [(η^3-RC_3H_4)PdCl]$_2$ (1.0 mmol) was added. After 1 h the precipitated AgCl was removed by filtration and the solution was evaporated to dryness under vacuum. The residue was recrystallized from ether. Yellow prisms were obtained in about 75% yield.

Preparation of [(η^3-RC_3H_4)Pd(ArN$_3$Ar)]$_2$ (Ar = p-tolyl, p-ClC_6H_4, 3,5-$Cl_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$). Equivalent amounts (2 mmol) of diaryltriazenidosilver and [(η^3-RC_3H_4)PdCl]$_2$ were heated under reflux in benzene (20 ml). After 1 to 2 h the AgCl was removed by filtration and the solution was evaporated to dryness under vacuum. The residue was recrystallized from benzene/hexane or chloroform/hexane and yellow crystals were obtained in about 75% yield.

Method II

Preparation of [(η^3-RC_3H_4)Pd(ArN$_3$Ar)]$_2$ (Ar = as above). Diaryltriazene (2.0 mmol) was added to a chloroform solution of [(η^3-RC_3H_4)PdCl]$_2$ (1 mmol). Subsequently KO-t-Bu (2.0 mmol) was added to the solution of [(η^3-RC_3H_4)-PdCl(diaryltriazene)] *. After 5 min the precipitated KCl was removed by filtration and the solution was worked up as above. The yields were about 85%. When KOH was used instead of KO-t-Bu a reaction time of 30 min was needed, and the yields were about 60%.

η^3-(Methyl)allylditolyl-formamidino and -acetamidino-palladium were prepared according to methods I and II.

C, H and S analyses were carried out in this laboratory (Table 1). ^{13}C and ^1H NMR spectra were recorded with a XL 100 Varian spectrometer, IR spectra with a Beckmann 4250 spectrometer. Molecular weights were measured with a Hewlett—Packard vapour pressure osmometer Model 320 B.

Results

S,N,N'-substituted sulfurdiimino(methyl)allylpalladium compounds

$$[(\eta^3\text{-}RC_3H_4)PdCl]_2 + 2Li\{R^1SN(R^2)NR^1\} \rightarrow [(\eta^3\text{-}RC_3H_4)Pd\{R^1NS(R^2)NR^1\}] + 2Li \quad (1)$$

The compounds are monomeric (Table 1) and both R' groups are equivalent (Table 2). The characteristic NSN vibrations (Table 3) are in the ranges of 850—910 and 1190 to 1250 cm^{-1}. Both NMR shifts and IR vibrations correspond well with those of [$(CO)_2Rh\{R^1NS(R^2)NR^1\}$] [5,15] which are also monomeric. Therefore, the sulfurdiimino group is bonded as a chelate and probably also has some π-allylic character [16]. Depending on the orientation of the η^3-(methyl)allyl groups two isomers can exist (Fig. 2), and these were indeed observed at low temperature.

At higher temperatures the resonances of the two isomers merge which shows that the two isomers interconvert, except for the compounds [(η^3-RC_3H_4)Pd-

* Monomeric diaryltriazenepalladium-complexes have been prepared recently and are fully discussed by Boschi et al. [25].

TABLE 1

ANALYTICAL DATA FOR $[(\eta^3\text{-}RC_3H_4)Pd\{R'NS(R^2)NR'\}]$, $[(\eta^3\text{-}RC_3H_4)Pd\{R^3N_3R^3\}]_2$ AND $[(\eta^3\text{-}RC_3H_4)Pd\{R^3N(CR^4)NR^3\}]_2$

Compound [a]	Analysis found (calcd.) (%)			Mol.wt. found (calcd.)
	C	H	S	
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-}p\text{-tolyl(NSN)}\}]$	55.48(56.50)	6.08(6.27)		410(446)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-(4-Cl-phenyl)(NSN)}\}]$	46.19(46.82)	4.38(4.51)	5.95(6.57)	488(502)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-3,5-xylyl(NSN)}\}]$	57.98(58.23)	6.83(6.75)		
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	59.55(59.76)	7.12(7.17)		
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-}p\text{-tolyl(NSN)}\}]$	56.75(57.39)	6.28(6.52)	6.24(6.95)	
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di(4-Cl-phenyl)(NSN)}\}]$	47.18(47.90)	4.20(4.71)	6.18(6.38)	460(501)
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-3,5-xylyl(NSN)}\}]$	58.00(58.95)	7.36(7.00)		484(488)
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	60.20(60.46)	7.40(7.40)	5.86(6.20)	510(516)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-Me-}N,N'\text{-di-3,5-xylyl(NSN)}\}]$	54.88(55.56)	6.10(6.02)		
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-Me-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	57.01(57.39)	6.41(6.52)		
$[(\eta^3\text{-}C_3H_5)Pd(DpTT)]_2$	54.76(54.99)	5.10(5.12)		755(742)
$[(\eta^3\text{-}C_3H_5)Pd(DpClPT)]_2$	43.52(43.69)	3.23(3.16)		
$[(\eta^3\text{-}C_3H_5)Pd(D\text{-}3,5\text{-}Cl_2PT)]_2$	37.38(37.42)	2.20(2.29)		
$[(\eta^3\text{-}C_3H_5)Pd(D\text{-}2,4,6\text{-}Cl_3PT)]_2$	32.59(32.73)	1.70(1.64)		1131(1092)
$[(\eta^3\text{-}C_4H_7)Pd(DpTT)]_2$	55.77(56.10)	5.40(5.45)		760(770)
$[(\eta^3\text{-}C_4H_7)Pd(DpClPT)]_2$	44.90(45.07)	3.60(3.52)		
$[(\eta^3\text{-}C_4H_7)Pd(D\text{-}3,5\text{-}Cl_2PT)]_2$	38.60(38.79)	2.59(2.63)		1071(990)
$[(\eta^3\text{-}C_4H_7)Pd(D\text{-}2,4,6\text{-}Cl_3PT)]_2$	33.94(34.04)	1.99(1.95)		
$[(\eta^3\text{-}C_3H_5)Pd(DMT)]_2$	27.62(27.40)	4.98(5.02)		422(438)
$[(\eta^3\text{-}C_4H_7)Pd(DMT)]_2$	31.12(30.90)	5.52(5.58)		441(466)
$[(\eta^3\text{-}C_3H_5)Pd(DpTF)]_2$	57.61(58.38)	5.35(5.41)		
$[(\eta^3\text{-}C_3H_5)Pd(DpTA)]_2$	58.91(59.38)	5.70(5.73)		
$[(\eta^3\text{-}C_4H_7)Pd(DpTF)]_2$	58.75(59.38)	5.68(5.73)		795(768)
$[(\eta^3\text{-}C_4H_7)Pd(DpTA)]_2$	59.96(60.30)	6.05(6.03)		851(796)

[a] DpTT = di-*p*-tolyltriazenido; DpClPT = di-*p*-chlorophenyltriazenido; D-3,5-Cl_2PT = di(3,5-di-chloro)phenyltriazenido; D-2,4,6-Cl_3PT = di(2,4,6-trichloro)phenyltriazenido; DMT = dimethyltriazenido; DpTF = di-*p*-tolylformamidino; DpTA = di-*p*-tolylacetamidino.

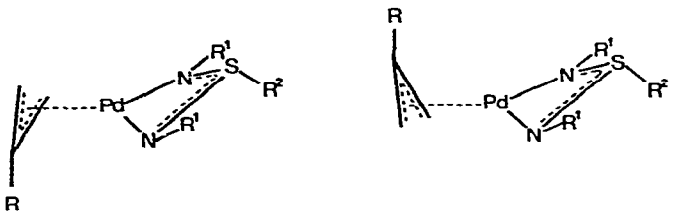


Fig. 2. Possible isomers of $[(\eta^3\text{-}RC_3H_4)Pd\{R^1NS(R^2)NR^1\}]$.

{MesNS(t-Bu)NMes}]. In this case the isomers do not interchange at 35°C.

The similarity with the rhodium compounds is also demonstrated by the decomposition which generally takes place in solution at ambient temperatures and which leads to azo—arenes. The palladium compounds offer the additional advantage that the decomposition can be more fully studied, as the SR^- group can be captured in the form of $[(\eta^3\text{-}RC_3H_4)Pd(SR^2)]_2$, which contains a bridging mercapto group. This was confirmed by comparing the NMR data of the decomposition products with those of a mixture of azo—arenes and $[(\eta^3\text{-}RC_3H_4)Pd(SR^2)]_2$. The mechanisms of the decomposition are discussed below.

Of interest is that, in contrast to the compound $[(CO)_2Rh\{MesNS(t\text{-}Bu)NMes\}]$, the mesityl groups of the corresponding (methyl)allylpalladium compound can freely rotate (Table 2) above +10°C. This agrees with the observation that the rhodium compound mentioned above, in which the mesityl groups do not rotate, is stable to decomposition into azo—arene, while the palladium compounds are not. The rate of decomposition showed the following orders: *S*-Me > *S*-t-Bu and *p*-tol > *p*-ClC_6H_4 > 3,5-xylyl > 2,4,6-mesityl. Owing to rapid decomposition the *S*-Me-*N*,*N'*-ditolyl- and the *S*-Me-*N*,*N'*-di(*p*-ClC_6H_4)-sulfurdiimino derivatives could not be isolated.

Triazenido- and amidino-(methyl)allylpalladium compounds

The complexes, some of which are already known [17,18,30] were obtained by two new methods:

$$[(\eta^3\text{-}RC_3H_4)PdCl]_2 + 2Ag(DMT) \rightarrow [(\eta^3\text{-}RC_3H_4)Pd(DMT)]_2 + 2AgCl \quad (2)$$

$$[(\eta^3\text{-}RC_3H_4)PdCl]_2 + 2DpTTH + 2KO\text{-}t\text{-}Bu \rightarrow [(\eta^3\text{-}RC_3H_4)Pd(DpTT)]_2 + 2KCl + 2HO\text{-}t\text{-}Bu \quad (3)$$

On the basis of molecular weights (Table 1), crystal structures of $[(\eta^3\text{-}C_4H_7)Pd(MeN_3Me)]_2$ [9] and of $[(\eta^3\text{-}C_3H_5)Pd\{p\text{-}MeC_6H_4N_3C_6H_4(p\text{-}Me)\}]_2$ [26] and of IR data (ν_{as}(NNN) ~ 1350—1375 cm^{-1}, characteristic for a bridging triazenido group [7]) (Table 4), it was concluded that all compounds are dimeric and have bridging triazenido or amidino groups. It has already been pointed out [17,18, 30] that three isomers are possible, in principle, in the case of the allyl compounds (Fig. 3), depending on the orientation of the allyl group. Two of these have been observed up till now [17,18,30]. The third isomer was also found, and occurs in all our compounds except for $[(\eta^3\text{-}C_3H_5)Pd\{(2,4,6\text{-}Cl_3C_6H_2)N_3(2,4,6\text{-}Cl_3C_6H_2)\}]_2$, which exists in solution in only one isomeric form. In the

TABLE 2

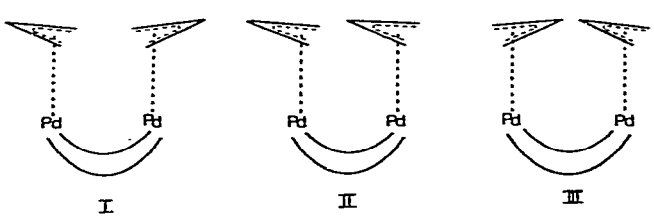
^{1}H NMR DATA FOR $[(\eta^3\text{-}RC_3H_4)Pd\{R'NS(R^2)NR'\}]$ AND $[(\eta^3\text{-}RC_3H_4)Pd(SR^2)]_2$ (chemical shifts in ppm rel. to TMS) n.o. = not observed; d = doublet, m = multiplet

Compound	Solvent	T (°C)	Isomer	Resonances of the allyl group	
				anti	*syn*
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-}p\text{-tolyl(NSN)}\}]$	C_6D_6	+30		3.33	2.13(d)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di(4-Cl-phenyl)NSN}\}]$	C_6D_6	+30		3.17(d)	2.12(d)
	C_7D_8	0		3.20(d)	n.o.
	C_7D_8	−60	I	3.19(d)	1.70(d)
	C_7D_8	−60	II	3.03(d)	2.22(d)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-3,5-xylyl(NSN)}\}]$	C_6D_6	+30		3.43(d)	2.20(d)
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-t-Bu-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	C_6D_6	+30	I	2.62(d)	2.17(d)
	C_6D_6	+30	II	2.85(d)	1.88(d)
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-}p\text{-tolyl(NSN)}\}]$	C_6D_6	+30		3.27	2.17
	C_7D_8	0		3.28	n.o.
	C_7D_8	−60	I	3.29	1.90
	C_7D_8	−60	II	3.20	2.42
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di(4-Cl-phenyl)(NSN)}\}]$	C_6D_6	+30		3.16	2.03
	C_7D_8	0		3.18	n.o.
	C_7D_8	−60	I	3.11	1.73
	C_7D_8	−60	II	3.03	2.29
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-3,5-xylyl(NSN)}\}]$	C_6D_6	+30		3.33	2.10
	C_7D_8	0		3.36	2.15
	C_7D_8	−60	I	3.36	1.88
	C_7D_8	−60	II	3.32	n.o.
$[(\eta^3\text{-}C_4H_7)Pd\{S\text{-t-Bu-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	C_6D_6	+30	I	2.48	2.13
	C_6D_6	+30	II	2.68	1.85
	C_7D_8	+10	I	2.45	2.13
	C_7D_8	+10	II	2.69	1.83
	C_7D_8	−60	I	2.37	n.o.
	C_7D_8	−60	II	2.61	1.73
$[(\eta^3\text{-}C_3H_5)Pd\{S\text{-Me-}N,N'\text{-di-2,4,6-mesityl(NSN)}\}]$	C_6D_6	+30		2.23(d)	2.03(d)
$[(\eta^3\text{-}C_3H_5)Pd(S\text{-t-Bu})]_2$	C_6D_6	+30		3.75(d)	2.57(d)
$[(\eta^3\text{-}C_4H_7)Pd(S\text{-t-Bu})]_2$	C_6D_6	+30		3.61	2.54
$[(\eta^3\text{-}C_4H_7)Pd(S\text{-Me})]_2$	C_6D_6	+30		3.37	2.33

case of the methallylpalladium compounds only one isomer (I) is possible for steric reasons (Table 5).

In contrast to the monomeric sulfurdiimino compounds the dimeric triazenido compounds are very stable in solution and they strongly resist bridge

(continued on p. 293)



I II III

Fig. 3. Possible isomers of $[(\eta^3\text{-}C_3H_5)Pd\{R^3NNNR^3\}]_2$ and $[(\eta^3\text{-}C_3H_5)Pd\{R^3NC(R^4)NR^3\}]_2$.

Resonances of the sulfurdiimino ligands			
H,Me	*S*-t-Bu,Me	Aryl	Me(aryl)
n.o.	1.20	6.93	2.18
n.o.	1.05	7.07;6.62	
n.o.	1.02	7.07;6.64	
n.o.	0.94	7.16;6.56	
n.o.	0.97		
n.o.	1.26	6.72;6.37	2.20
n.o.	0.93	6.80	
n.o.	0.87		2.77:2.18
1.63	1.21	6.97	2.20
1.74	1.20	6.97;6.85	2.19
1.69	1.12	7.03;6.84	2.26
1.90	1.18		
1.53	1.10	7.11;6.67	
1.49	1.02	7.08;6.63	
1.58	0.96	7.16;6.56	
1.73	0.99		
1.68	1.27	6.66;6.53	2.22
1.77	1.25	6.66;6.34	2.21
1.70	1.21	6.75;6.45	2.33
1.88	1.26		2.26
1.47	0.93	6.80	2.78;2.18
1.73	0.87		
1.47	0.91	6.82	2.78;2.17
1.76	0.86		
1.30	0.84	6.83;6.73	2.69;2.19
			2.16
1.61	0.77	6.78;(n.o.)	2.54;3.08
			2.16
4.73m	3.34	6.60	2.33;2.01
4.60m	1.47		
1.58	1.51		
1.63	2.50		

TABLE 3

INFRARED DATA (KBr disk) FOR $[(\eta^3\text{-}RC_3H_4)Pd\{R'NS(R^2)NR'\}]$ IN cm^{-1}

Compound	ν(NSN) [a]	
$[(\eta^3\text{-}C_3H_5)Pd\{$*S*-t-Bu-*N*,*N*′-di(4-Cl-phenyl)(NSN)$\}]$	1237	891
$[(\eta^3\text{-}C_4H_7)Pd\{$*S*-t-Bu-*N*,*N*′-di-*p*-tolyl(NSN)$\}]$	1242	897
$[(\eta^3\text{-}C_4H_7)Pd\{$*S*-t-Bu-*N*,*N*′-di(4-Cl-phenyl)(NSN)$\}]$	1245	890
$[(\eta^3\text{-}C_4H_7)Pd\{$*S*-t-Bu-*N*,*N*′-di-2,4,6-mesityl(NSN)$\}]$	1218	853

[a] Frequencies characteristic for this group.

TABLE 4

INFRARED DATA (KBr disk) FOR $[(\eta^3\text{-}RC_3H_4)Pd\{R^3N_3R^3\}]_2$ AND $[(\eta^3\text{-}RC_3H_4)Pd\{R^3NC(R^4)NR^3\}]_2$ IN cm^{-1}

Compound [a]	ν(triazenido,amidino) [b]	δ(NNN) [b]
$[(\eta^3\text{-}C_3H_5)Pd(DMT)]_2$	1357(ν_{as}); 1338; 1189(ν_s)	630
$[(\eta^3\text{-}C_3H_5)Pd(DpTT)]_2$	1366(ν_{as}); 1322; 1206(ν_s)	600
$[(\eta^3\text{-}C_3H_5)Pd(DpClPT)]_2$	1363(ν_{as}); 1323; 1201(ν_s)	593
$[(\eta^3\text{-}C_4H_7)Pd(DMT)]_2$	1357(ν_{as}); 1337; 1190(ν_s)	631
$[(\eta^3\text{-}C_4H_7)Pd(DpTT)]_2$	1366(ν_{as}); 1317; 1210(ν_s)	620
$[(\eta^3\text{-}C_4H_7)Pd(DpClPT)]_2$	1363(ν_{as}); 1317; 1205(ν_s)	609
$[(\eta^3\text{-}C_4H_7)Pd(D\text{-}2,4,6\text{-}Cl_3PT)]_2$	1360(ν_{as}); 1329; 1212(ν_s)	
$[(\eta^3\text{-}C_3H_5)Pd(DpTF)]_2$	1572(ν_{as}); 1350(ν_s)	
$[(\eta^3\text{-}C_3H_5)Pd(DpTA)]_2$	1534(ν_{as}); 1255(ν_s)	
$[(\eta^3\text{-}C_4H_7)Pd(DpTF)]_2$	1570(ν_{as}); 1349(ν_s)	
$[(\eta^3\text{-}C_4H_7)Pd(DpTA)]_2$	1534(ν_{as}); 1254(ν_s)	

[a] See note a of Table 1. [b] A tentative assignment is given of the bending vibration.

TABLE 5

^1H NMR DATA FOR $[(\eta^3\text{-}RC_3H_4)Pd(R^3N_3R^3)\}]_2$ AND $[(\eta^3\text{-}RC_3H_4)Pd\{R^3NC(R^4)NR^3\}]$ IN $CDCl_3$ (in ppm rel. to TMS) n.o. = not observed; d = doublet; t = triplet; q = quartet

Compound [a]	Isomer	Resonances of the allyl group			Resonances of the triazenido-(amidino) ligands		
		syn-H	*anti*-H	H,CH_3	Aryl [b]	CH_3-(aryl)	H,CH_3
$[(\eta^3\text{-}C_3H_5)Pd(DMT)]_2$	I	2.52(d)	3.50(d)	5.37(m)			3.35
	II	2.40(d)	3.38(d)	4.74(m)			3.30(q)
		2.79(d)	3.62(d)	5.49(m)			3.58(q)
	III	2.66(d)	3.55(d)	4.84(m)			3.50
$[(\eta^3\text{-}C_3H_5)Pd(DpTT)]_2$	I	2.76(d)	3.66(d)	5.85(m)	6.9(d);7.3(d) [c]		
	II	2.66(d)	3.60(d)	5.00(m)		2.27	
		2.96(d)	3.70(d)	5.85(m)			
	III	2.96(d)	n.o.	n.o.			
$[(\eta^3\text{-}C_3H_5)Pd(DpClPT)]_2$	I	2.80(d)	3.74(d)	5.75(m)			
	II	2.69(d)	3.65(d)	5.10(m)	7.1(d);7.3(d) [c]		
		2.95(d)	3.80(d)	5.75(m)			
	III	2.95(d)	n.o.	n.o.			
$[(\eta^3\text{-}C_3H_5)Pd(D\text{-}3,5\text{-}Cl_2PT)]_2$	I	2.90(d)	3.92(d)	5.80(m)	7.00(t);7.33(d)		
	II	2.80(d)	3.84(d)	5.10(m)	6.96(t);7.28(d)		
		3.12(d)	3.97(d)	5.80(m)	7.03(t);7.42(d)		
	III	2.95(d)	n.o.	n.o.	7.00(t);7.38(d)		
$[(\eta^3\text{-}C_3H_5)Pd(D\text{-}2,4,6\text{-}Cl_3PT)]_2$	I	3.08(d)	3.73(d)	5.30(m)	7.24		
$[(\eta^3\text{-}C_3H_5)Pd(DpTF)]_2$	I	2.79(d)	3.56(d)	5.35(m)	6.96		7.84
	II	2.71(d)	3.49(d)	4.70(m)	6.89	2.28	
		2.89(d)	3.66(d)	5.35(m)	7.03		7.77
	III	2.83(d)	n.o.	n.o.	7.00		7.69
$[(\eta^3\text{-}C_3H_5)Pd(DpTA)]_2$	I	2.69(d)	3.04(d)			2.27	
	II	2.34(d)	2.92(d)	5.15(m)	6—7 [c]	2.28	1.66
		2.60(d)	3.38(d)			2.31	
	III	2.25(d)	3.31(d)			2.25	
$[(\eta^3\text{-}C_4H_7)Pd(DMT)]_2$		3.33	2.34	2.13			3.40
$[(\eta^3\text{-}C_4H_7)Pd(DpTT)]_2$		3.49	2.75	2.27	6.96(d);7.41(d)	2.27	
$[(\eta^3\text{-}C_4H_7)Pd(DpClPT)]_2$		3.56	2.79	2.24	7.11(d);7.39(d)		
$[(\eta^3\text{-}C_4H_7)Pd(D\text{-}3,5\text{-}Cl_2PT)]_2$		3.66	2.81	2.37	7.00(t);7.40(d)		
$[(\eta^3\text{-}C_4H_7)Pd(D\text{-}2,4,6\text{-}Cl_3PT)]_2$		3.40	3.23	1.93	7.20		
$[(\eta^3\text{-}C_4H_7)Pd(DpTF)]_2$		3.33	2.63	2.28	6.93	2.26	7.78
$[(\eta^3\text{-}C_4H_7)Pd(DpTA)]_2$		2.88	2.49	1.78	6.57(d);6.85(d)	2.27	1.68

[a] See note at Table 1. [b] Not all frequencies could be assigned because of overlap. [c] 4 $AA'XX'$ patterns are observed.

breaking by most ligands. Within the NMR time scale there is no fluxional behaviour of the (methyl)allyl groups for both the triazenido * and amidino ** compounds between −50 to +115°C as indicated by ^1H and ^{13}C NMR measurments.

The triazenido and amidino groups can be replaced in chloroform by other more acidic triazenes or amidines. The order of ease of replacement is: Di-*p*-tolylacetamidine < dimethyltriazene < di-*p*-tolylformamidine < di-*p*-tolyltriazene < di-*p*-Cl-phenyltriazene.

Discussion

Comparison of the *S,N,N'*-substituted sulfurdiimino compounds of rhodium(I) and palladium(II), in which the ligand acts as a chelate, shows that there is a close structural relationship.

Because of the presence of the (methyl)allyl group in the case of palladium(II) two isomers are possible in principle (Fig. 2), and are indeed observed. Except in the case of $[(\eta^3\text{-}RC_3H_4)Pd\{MesNS(t\text{-}Bu)Mes\}]$ these isomers interconvert at room temperature in the NMR time-scale. There is also a strong chemical relationship between the palladium and rhodium compounds. In both cases the decomposition of the compounds of rhodium(I) and palladium(II) proceeds similarly. The palladium compounds decompose more rapidly than the rhodium compounds at +35°C. The order of decomposition rates is, in the case of palladium(II): *S*-Me > *S*-t-Bu and R' = *p*-tolyl > *p*-Cl-phenyl > 2,4,6-mesityl, which corresponds well with that found for rhodium.

The decomposition reaction involves the formation of azo—arenes and SR^-, but only in the case of palladium(II) could the formation of SR^- be demonstrated conclusively, by isolation of $[(\eta^3\text{-}RC_3H_4)Pd(SR^2)]_2$. On the basis of the electronic and steric influences on the decomposition rates the following mechanism is proposed (Fig. 4).

The first step is probably an attack of the metal atom on the sulfur atom via a π-allylic intermediate, which agrees with the observed steric influences. In the case of R' = 2,4,6-mesityl the formation of a π-allylic intermediate or a direct intramolecular attack of the metal atom on the sulfur atom is strongly hindered by the two *ortho*-methyl groups which point between the metal atom and the sulfur atom (see crystal structure of $[(CO)_2Rh\{MesNS(t\text{-}Bu)NMes\}]$ [15,16]). The steric hindrance can be diminished, if the mesityl groups can rotate, which is the case when *S*-t-Bu is replaced by *S*-Me. Consequently the rate of decomposition is much higher in the case of the *S*-Me substituted compound than in the case of the *S*-t-Bu compounds. We can also now understand why the *p*-tolyl- and *p*-Cl-phenyl substituted compounds decompose more rapidly than the 2,4,6-mesityl derivatives.

The rate increasing effect of electrondonating R' groups on the azo formation i.e. ringclosure of the *S,N,N'*-moiety becomes clear from a comparison

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* In accord with previous findings [17,30].

** Fluxional behaviour was proposed previously [18] on the basis of ^1H spectra only. We conclude that the reported merging of the appropriate signals is due only to temperature dependent changes of the chemical shifts without broadening.

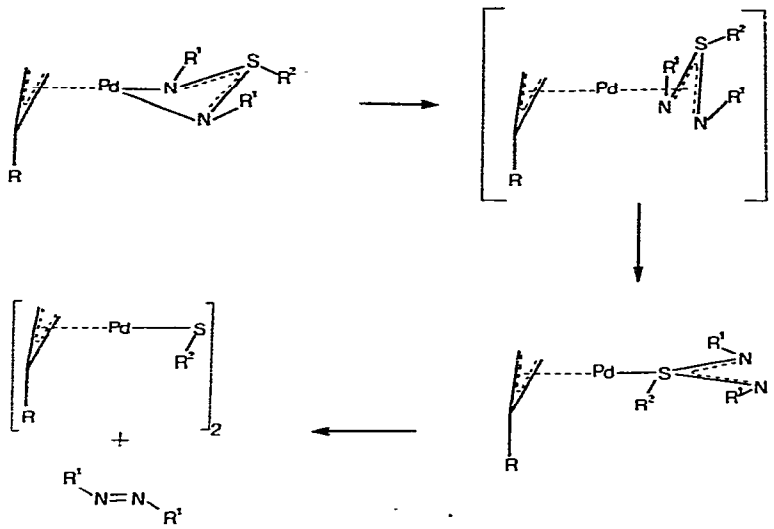

Fig. 4. Proposed mechanism for the formation of azo-arenes and $[\{\eta^3\text{-}RC_3H_4)Pd(SR^2)\}_2]$.

with O=S=O. The O—S—O angle decreases and the S—O bond length increases with increasing negative charge, since extra electronic charge will go into an orbital with S—O antibonding and O—O bonding character [27].

Comparison of the *S,N,N'*-sulfurdiimino group with the triazenido or amidino group bonded to palladium(II) shows that the first ligand prefers to be bonded as a chelate, whereas the last two ligands are bridging *. It should be noted here that the azenido group may bond as a chelate, a bridging ligand or as a monodentate [28], while the *S,N,N'*-sulfurdiimino has only been observed, up till now, to occur as a bridging ligand or as a chelate. The absence of the monodentate form is probably due to the fast decomposition into azo compounds.

The general occurrence of three isomers in the case of the η^3-allyl-triazenido- and -amidino-palladium compounds agrees well with the expected possibilities (Fig. 3). The presence of only isomer I in the case of $[(\eta^3\text{-}C_3H_5)Pd\{2,4,6\text{-}Cl_3C_6H_2)N_3(2,4,6\text{-}Cl_3C_6H_2)\}]$ is probably due to the fact that, in the isomers II and III, there is steric interaction of the allyl moieties with the *ortho*-Cl atoms. Steric interactions are also probably the reason why, in the case of the methallyl compounds, only isomer I was observed.

Finally we wish to note that the ν_{as}(NNN) in the IR spectra was found in the region of 1350—1375 cm^{-1} **, which is an additional support for our assignment in previous papers of bridging triazenido groups [6,7].

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* It should be noted that a chelate azenido group lies in a plane with the metal atom [28,29]. This is not the case for the *S,N,N'*-sulfurdiimino group which is more π-allylic in its mode of bonding [16].

** These data differ from those of others [17,18].

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