Journal of Organometallic Chemistry, 265 (1984) 311–322
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

LIGATING PROPERTIES OF THIONITROSOAMINES

II *. CRYSTAL AND MOLECULAR STRUCTURE OF *cis*-DICHLORO-(*N*-THIONITROSODIMETHYLAMINE)(TRIPHENYLARSINE)-PALLADIUM(II) COMPLEX. SYNTHESIS AND CHARACTERIZATION OF NEUTRAL BINUCLEAR COMPLEXES OF PALLADIUM(II) AND CATIONIC COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) CONTAINING *N*-THIONITROSODIMETHYLAMINE

GIUSEPPE TRESOLDI, GIUSEPPE BRUNO, PASQUALE PIRAINO, GIOVANNI FARAONE and GABRIELLA BOMBIERI

Dipartimento di Chimica Inorganica e Struttura Molecolare dell'Università, 98100 Messina (Italy)

(Received October 11th, 1983)

Summary

The crystal and molecular structure of $Pd(SNNMe_2)(AsPh_3)Cl_2$ was determined from single-crystal X-ray diffraction data. In agreement with the structure previously proposed on the basis of IR data, the complex has the *cis*-configuration with the Me_2NNS ligand *S*-bonded to the metal. It crystallizes in the space group $P\bar{1}$ with a 9.407(2), b 10.540(2), c 12.265(4) Å; α 68.1(1), β 78.3(1), γ 86.3(1)° and $Z = 2$. The structure was refined to $R = 0.029$ for 2664 diffractometer data with $I \geq 3\sigma(I)$. The palladium atom is in a nearly square planar coordination geometry with Pd–S 2.249(1), Pd–As 2.362(1), Pd–Cl(1) 2.313(1), Pd–Cl(2) 2.359(1) Å. The very short Pd–S bond length may indicate a strong $\sigma + \pi$ synergistic interaction of the Pd atom with the *N*-thionitrosodimethylamine ligand. Me_2NNS reacts with $Pd(PhCN)_2Cl_2$ to give, besides the known *cis*-$Pd(SNNMe_2)_2Cl_2$, the complex $[(\mu\text{-}Cl)_2\{Pd(SNNMe_2)Cl\}_2]$ (IIIa), and an unstable compound which is probably $[Pd(SNNMe_2)_4]Cl_2$. The stable salts $[Pd(SNNMe_2)_4](BPh_4)_2$ (IVa) and $[Pd(SNNMe_2)_4]HgCl_4$ (IVd) were obtained from this unstable compound and $NaBPh_4$ or $HgCl_2$. Alternatively the stable salts $[Pd(SNNMe_2)_4](PF_6)_2$ (IVb) and $[Pd(SNNMe_2)_4]PdCl_4$ (IVc) were obtained from Me_2NNS and $[Pd(diene)(acetone)_2](PF_6)_2$ (diene = 1,5-cyclooctadiene, norbornadiene) or Na_2PdCl_4. Me_2NNS reacts with $Pt(PhCN)_2Cl_2$ to form an unstable compound probably $[Pt(SNNMe_2)_4]Cl_2$ which was obtained in the stable form as $[Pt(SNNMe_2)_4]Y_2$ ($Y = BPh_4$ (Va), PF_6 (Vb); $Y_2 = PtCl_4$ (Vc)). The complexes $[(\mu\text{-}X)_2\{Pd(SNNMe_2)Cl\}_2]$ (X = Cl (IIIa), Br (IIIb), SCN (IIIc), SeCN (IIId)) were prepared by reaction of $Pd(PhCN)_2Cl_2$ with $Pd(SNNMe_2)_2X_2$.

---

* For part I see Ref. 1.

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

Bridge splitting and metathetical replacement reactions on IIIa were used to prepare respectively the known *cis*-Pd(SNNMe$_2$)LCl$_2$ (L = PPh$_3$, *p*-tolylPPh$_2$, P(*o*-tolyl)$_3$, AsPh$_3$, SbPh$_3$) and the compounds IIIc, IIId and [(μ-SCN)$_2${Pd(SNNMe$_2$)(SCN)}$_2$] (IIIe). The IR spectra of all the compounds are in agreement with the *S*-coordination of Me$_2$NNS.

Introduction

In the previous paper [1] we reported the synthesis and characterization of the complexes M(SNNMe$_2$)LCl$_2$ (M = Pd^{II}, L = Me$_2$NNS, PPh$_3$, *p*-tolylPPh$_2$, P(*o*-tolyl)$_3$, AsPh$_3$, SbPh$_3$; M = Pt^{II}, L = PPh$_3$, *p*-tolylPPh$_2$). All these complexes are coordinated through the sulfur atom and, in contrast to other PdL$_2$X$_2$ (L = neutral ligand, X = anionic ligand) complexes, which usually show the *trans*-configuration, have *cis*-geometry in the solid state. Moreover these complexes are stable while the free ligand is unstable [2]. It seems clear that the two resonance forms, covalent and dipolar, which contribute to the over-all electronic structure of the *N*-thionitrosodimethylamine, play an important role in determining the bonding mode of the thionitrosoamine ligand and the stability of the complexes.

With the aim of elucidating the factors which stabilize the M–S bond in the *N*-thionitrosodimethylamine-palladium(II) and -platinum(II) complexes we have carried out an X-ray structure determination of the complex *cis*-Pd(SNNMe$_2$)(AsPh$_3$)Cl$_2$, and present the results below along with an account of the synthesis and the characterization of the neutral binuclear complexes [(μ-X')$_2${Pd(SNNMe$_2$)X''}$_2$] (X' = X'' = Cl, SCN; X' = Br, SCN, SeCN, X'' = Cl) and the cationic complexes [M(SNNMe$_2$)$_4$]Y$_2$ (M = Pd^{II}, Y = BPh$_4$, PF$_6$, Y$_2$ = PdCl$_4$; M = Pt^{II}, Y = BPh$_4$, PF$_6$, Y$_2$ = PtCl$_4$).

Results and discussion

Vibrational spectrum and crystal structure of cis-Pd(SNNMe$_2$)(AsPh$_3$)Cl$_2$

The title compound, obtained as previously described [1] or from [(μ-Cl)$_2${Pd(SNNMe$_2$)Cl}$_2$] and AsPh$_3$, is stable in the solid state for some weeks and poorly soluble in the common organic solvents. The IR spectrum shows strong bands at 785 and 1135 cm^{-1} assigned respectively to the ν(N–S) and ν(N–N). The same bands in the free ligand live at 910 and 1105 cm^{-1}. The considerable shift (125 cm^{-1}) at lower wavenumbers of the ν(N–S) indicates that the *N*-thionitrosodimethylamine ligand is *S*-bonded to the metal. On the other hand the shift (30 cm^{-1}) at higher wavenumbers of the ν(N–N), indicating a greater double bond character of the N–N bond with respect to the free ligand, suggests that the coordination leads to an increase in the contribution of the dipolar form to the over-all electronic structure. Two strong band at 323 and 282 cm^{-1}, assigned to the ν(Pd–Cl)$_{\text{terminal}}$, suggest the *cis*-configuration.

The stereochemical arrangement of the complex with the atom numbering scheme is shown in Fig. 1. The structure consists of the packing of the discrete molecules of *cis*-Pd(SNNMe$_2$)(AsPh$_3$)Cl$_2$ separated by Van der Waals contacts. The palladium coordination geometry is nearly square planar. Sulfur, chlorine and arsenic deviate slightly but significantly from their weighted mean plane toward a tetrahedral

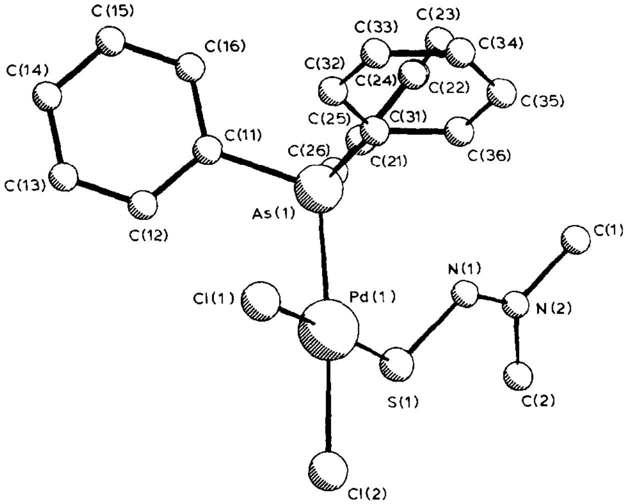
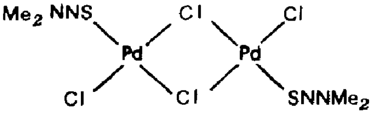


Fig. 1. Perspective view of the molecule.

geometry (the deviations are S 0.046(2), Cl(1) 0.048(2), Cl(2) −0.048(2) and As −0.004(1) Å). The S–Pd–As angle is considerably greater than the ideal value of 90° (98.9°), possibly because of the steric hindrance between arsenic and the Me_2NNS ligand, the contact distances As- -S and As- -N(1) 3.505(1) and 3.408(4) Å, respectively, being shorter than the sum of the Van der Waals radii. The Me_2NNS ligand is nearly planar, with C(1) and C(2) atoms deviating from the plane passing through S, N(1) and N(2) by −0.023(6) and 0.036(6) Å, respectively; the palladium atom is 0.224(1) Å out of this plane. The plane of the ligand is inclined at 37.8(2)° to the coordination plane. The geometrical features of the Me_2NNS ligand are quite comparable to those found in the complex $Cr(SNNMe_2)(CO)_5$ [3]. The S–N bond (1.639(4) Å) is comparable with the value found in the latter complex (1.635(2) Å) and the N–N bonds (1.272(5) against 1.279(2) Å are similarly comparable. These lengths, in agreement with the IR spectrum, indicate conjugation through the N–N and the N–S bonds. The N–C(2) bond, where the C(2) is in *cis* position with respect to the sulfur atom, is also in this case slightly shorter than the N–C(1) bond, where C(1) is *trans* related respect to the sulfur (the bond distances are respectively N(2)–C(2) 1.437(7) and N(2)–C(1) 1.462(6) Å). The N(1)–N(2)–C(2) angle of 124.5(5)° deviates significantly from the ideal value of 120° in order to reduce the steric hindrance with the adjacent sulfur atom (the C(2)- -S contact distance is 2.868(8) Å). The Pd–As bond distance (2.362(1) Å) can be compared with the values between 2.339(2) and 2.426(2) Å found in [4]. The Pd–Cl(2) bond distance (2.359(1) Å) for chlorine *trans* to arsenic is longer than the Pd–Cl(1) bond distance 2.313(1) Å), for chlorine *trans* to the sulfur, indicating that the *trans* influence of the triphenylarsine is larger than that of the Me_2NNS ligand. The Pd–S bond length (2.249(1) Å) is very short [5]. This fact, considered along with the stability and the *cis*-configuration of the $Pd(SNNMe_2)(AsPh_3)Cl_2$ complex, suggests a strong $\sigma + \pi$ synergistic interaction of Pd atom with Me_2NNS ligand, as found in the $Cr(SNNMe_2)(CO)_5$ complex, in which the $Cr–SNNMe_2$ and the Cr–CO back donations are of the same extent.

Synthesis and characterization of bridge compounds

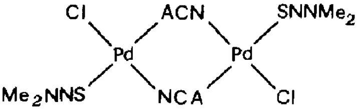
$Pd(PhCN)_2Cl_2$ reacts at room temperature in benzene solution with equimolar amount of Me_2NNS to give a yellow-brown solid, which is stable for some weeks and almost insoluble in common organic solvents. On the basis of its analysis this compound was formulated as $Pd_2(SNNMe_2)_2Cl_4$ (IIIa). Its infrared spectrum shows the bands associated with the Me_2NNS ligand at 1490s, 1375s, 1250m, 1135vs, 1030m, 860m, 770vs, 718w, 540m, 415w cm^{-1}, slightly shifted with respect to those of the ligand in the compounds [1] *cis*-$Pd(SNNMe_2)LCl_2$ ($L = Me_2NNS$, PPh_3, *p*-tolylPPh_2, P(*o*-tolyl)$_3$, $AsPh_3$, $SbPh_3$), suggesting that the coordination of the *N*-thionitrosodimethylamine ligand to the metal occurs still through the sulfur atom. The far infrared spectrum of IIIa shows a band of medium intensity at 390 cm^{-1} which is tentatively assigned to $\nu(Pd-S)$ [6], a strong band at 340 cm^{-1} characteristic of $\nu(Pd-Cl)_{terminal}$, and two bands at 295 and 275 cm^{-1} assigned to $\nu(Pd-Cl)_{bridge}$. On the basis of the spectroscopic properties [7] we attribute to IIIa the bridge *trans*-configuration.



In order to confirm the proposed configuration of IIIa and to find a general method of synthesis of analogous complexes, we treated the compounds *cis*-Pd-$(SNNMe_2)_2X_2$ (X = Cl, Br, SCN, SeCN) with $Pd(PhCN)_2Cl_2$, as in eq. 1.

$$cis\text{-}Pd(SNNMe_2)_2X_2 + Pd(PhCN)_2Cl_2 \xrightarrow[\text{acetone}]{} [(\mu\text{-}X)_2\{Pd(SNNMe_2)Cl\}_2] + 2PhCN \qquad (1)$$

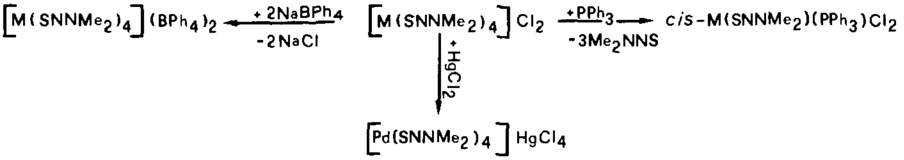
In this way were prepared the complexes $[(\mu\text{-}X)_2\{Pd(SNNMe_2)Cl\}_2]$ (X = Cl (IIIa), Br (IIIb), SCN (IIIc), SeCN (IIId)). The complexes IIIc and IIId were also prepared by metathetical exchange from IIIa and KACN (A = S, Se); in the same way IIIa and IIIc were transformed into $[(\mu\text{-}SCN)_2\{Pd(SNNMe_2)(SCN)\}_2]$ (IIIe). These compounds are stable solids, almost insoluble in the common organic solvents although the compound IIIe is slightly soluble in acetone. The infrared spectra (Table 1) show, besides the bands associated with the Me_2NNS moiety, a strong band in the range 340–300 cm^{-1} characteristic of the $\nu(Pd-Cl)_{terminal}$ and a band of medium intensity at ca. 385 cm^{-1}, tentatively assigned to the $\nu(Pd-S)$ [6]. The compounds IIIc, IIId and IIIe show a band at 2150 cm^{-1} assigned to the $\nu(C-N)$ of the bridging ACN (A = S, Se) group [8]. The compound IIIe shows also a strong band at 2105 cm^{-1} assigned to the $\nu(C-N)$ of the SCN group *S*-bonded to the metal [1]. Moreover the compounds IIIc and IIId show two weak bands in the range 370–480 cm^{-1} assigned to the $\delta(ACN)$ (A = S, Se) group [1,9]. These data are again in agreement with a bridge *trans*-configuration for the complexes IIIb, IIIc, IIId and IIIe. Moreover the slight shift of $\nu(Pd-Cl)_{terminal}$ in the compounds IIIc and the IIId, considered along with the tendency of the *N*-thionitrosodimethylamine to favour the



Pd–ACN (A = S, Se) bonding [1], suggests that the chlorine atom is *trans* to the N atom of ACN group.

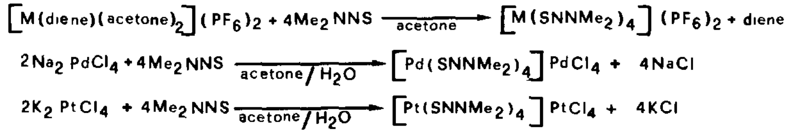
Synthesis and characterization of cationic compounds

When $Pd(PhCN)_2Cl_2$ reacts at room temperature with an excess of Me_2NNS, a yellow solid separates. This is unstable, and in acetone or dichloromethane solution decomposes slowly to give the known *cis*-$Pd(SNNMe_2)_2Cl_2$. $Pt(PhCN)_2Cl_2$ also reacts in acetone or dichloromethane at room temperature with an excess of Me_2NNS to give a yellow orange unstable product, almost insoluble in the common organic solvents. On the basis of the IR spectra, which show no bands attributable to ν(M–Cl), and the reactions depicted in Scheme 1, we think that the unstable compounds can be formulated as $[M(SNNMe_2)_4]Cl_2$ (M = Pd^{II}, Pt^{II}).



SCHEME 1

The compounds $M(SNNMe_2)(PPh_3)Cl_2$ (M = Pd^{II}, Pt^{II}) are known [1]. The salts $[M(SNNMe_2)_4]Y_2$ (Y = BPh_4, M = Pd^{II} (IVa), M = Pt^{II} (Va); Y_2 = $HgCl_4$, M = Pd^{II} (IVd)) are yellow solids stable for some days, they are slightly soluble in acetone although IVd is almost insoluble. The infrared spectra of these compounds show the bands associated with the Me_2NNS moiety slightly shifted with respect to those for the neutral complexes. Conductivity measurements for compounds IVa and Va indicate that they are bi-univalent electrolytes. The salts $[M(SNNMe_2)_4]Y_2$ (Y = PF_6, M = Pd^{II} (IVb), Pt^{II}(Vb); Y_2 = $PdCl_4$, M = Pd^{II} (IVc); Y_2 = $PtCl_4$, M = Pt^{II} (Vc)) are obtained by treating Me_2NNS with $[M(diene)(acetone)_2](PF_6)_2$ (M = Pd^{II}, Pt^{II}; diene = 1,5-cyclooctadiene, norbornadiene) or with $M'_2M''Cl_4$ (M′ = Na, M″ = Pd^{II}; M′ = K, M″ = Pt^{II}) as depicted in Scheme 2.



SCHEME 2

Complex IVb is sufficiently soluble in acetone to give a satisfactory ^1H NMR spectrum; the appearance of two singlets at 5.8 and 6τ indicates that there is restricted rotation about the N–N bond. Complex IVc is slightly soluble in acetone, in which it decomposes to form the known *cis*-$Pd(SNNMe_2)_2Cl_2$, while Vc is almost insoluble in the common organic solvents. The infrared spectra of IVc and Vc show, besides the bands associated with the Me_2NNS moiety, strong bands at 310 and 320 cm^{-1}, respectively, assigned to ν(M–Cl) for $PdCl_4^{2-}$ and $PtCl_4^{2-}$ anions [10].

The attempts to obtain mixed ligand complexes by treating the compounds IVb and Vb with tertiary phosphines failed. Treatment of the complexes $[M\{PPh_2(CH_2)_2PPh_2\}(acetone)_2](PF_6)_2$ ($M = Pd^{II}$, Pt^{II}) with Me_2NNS gave decomposition products and metal.

We conclude that the presence of strong Pd– or Pt–S bonds stabilizes the unstable Me_2NNS ligand and the $\sigma + \pi$ character of these bonds favours a *cis*-geometry for the neutral mononuclear complexes but leads to lower stability of the cationic complexes.

Experimental

The following compounds were synthesized by literature methods: $M(diene)Cl_2$ ($M = Pd^{II}$, Pt^{II}; diene = 1,5-cyclooctadiene, norbornadiene) [11], $M(PhCN)_2Cl_2$ ($M = Pd^{II}$, Pt^{II}) [12,13], $M(SNNMe_2)_2X_2$ (X = Cl, SCN, SeCN) [1], Me_2NNS [2].

The complex $Pd(1,5\text{-cyclooctadiene})Br_2$ was prepared as follows: An aqueous solution (15 cm^3) of KBr (2.2 mmol) was added dropwise to a stirred acetone solution (150 cm^3) of $Pd(1,5\text{-}C_8H_{12})Cl_2$ (1 mmol). After 2 h the solution was filtered and evaporated to ca. 15 cm^3. The precipitate was washed several times with H_2O and dried. The product was recrystallized from CH_2Cl_2/diethyl ether.

Other reagents and solvents were used as obtained from commercial sources. Elemental analyses were carried out by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and by Malissa & Reuter Analytische Laboratorien, Elbach, Germany. Infrared spectra were recorded using a Perkin–Elmer 577 spectrophotometer, as Nujol mulls in CsI pellets. Conductivity measurements were made with a WTW LBR conductivity meter. Proton NMR spectra were recorded on a Perkin–Elmer R 24B spectrometer with tetramethylsilane as internal standard. Analytical and characteristic IR data are reported in Table 1.

Preparation of cis-$Pd(SNNMe_2)_2Br_2$ (II)

The orange compound II was prepared from $Pd(1,5\text{-cyclooctadiene})Br_2$ and Me_2NNS as previously described [1] (Yield 70%).

Preparation of $[(\mu\text{-}Cl)_2\{Pd(SNNMe_2)Cl\}_2]$ (IIIa)

To a stirred solution of $Pd(PhCN)_2Cl_2$ (1 mmol) in benzene (50 cm^3) was added dropwise a solution of Me_2NNS (1 mmol) in diethyl ether (10 cm^3). The yellow-brown precipitate was filtered off, washed with acetone and diethyl ether, and dried (Yield 70%).

Preparation of $[(\mu\text{-}X)_2\{Pd(SNNMe_2)Cl\}_2]$ (IIIa, IIIb, IIIc, IIId)

To a stirred suspension of $Pd(SNNMe_2)X_2$ (X = Cl, Br, SCN, SeCN) (1 mmol) in acetone (30 cm^3) was added a solution of $Pd(PhCN)_2Cl_2$ (1 mmol) in acetone (30 cm^3). After 4 h the yellow-brown (IIIa,IIIb) or orange (IIIc, IIId) precipitate was filtered off, washed with acetone and diethyl ether, and dried (Yield ca. 90%).

Preparation of $[(\mu\text{-}ACN)_2\{Pd(SNNMe_2)Cl\}_2]$ (IIIc, IIId)

To a stirred suspension of IIIa (1 mmol) in acetone (50 cm^3) was added KACN (A = S, Se) (2 mmol). After 4 h the orange precipitate formed was filtered off, washed with H_2O, acetone, and diethyl ether, and dried (Yield 80%).

Preparation of $[(\mu\text{-}SCN)_2\{Pd(SNNMe_2)(SCN)\}_2]$ (IIIe)

The orange compound IIIe was obtained from IIIa and KSCN, molar ratio 1/4, or from IIIc and KSCN, molar ratio 1/2, as described above (Yield ca. 70%).

Preparation of $[M(SNNMe_2)_4](BPh_4)_2$ (IVa, Va)

To a solution of Me_2NNS (6 mmol) in diethyl ether (50 cm^3) was added dropwise a solution of $Pd(PhCN)_2Cl_2$ (1 mmol) in benzene (20 cm^3) or a solution of $Pt(PhCN)_2Cl_2$ (1 mmol) in acetone (20 cm^3) The yellow precipitate was filtered off, washed with diethyl ether and pentane, and dissolved in absolute ethanol. The solution was filtered into an ethanol solution of $NaBPh_4$. The yellow product was filtered off, washed several times with ethanol and diethyl ether, and dried (Yield 60%).

Preparation of $[Pd(SNNMe_2)_4]HgCl_4$ (IVd)

The yellow precipitate obtained from Me_2NNS and $Pd(PhCN)_2Cl_2$, as described above, was dissolved in acetone. The solution was filtered into an acetone solution of $HgCl_2$. The yellow product formed was collected and washed several times with acetone (Yield 70%).

Preparation of $[M(SNNMe_2)_4](PF_6)_2$ (IVb, Vb)

To a solution of $[M(diene)(acetone)_2](PF_6)_2$ ($M = Pd^{II}$, Pt^{II}), obtained from $M(diene)Cl_2$ (1 mmol) and $AgPF_6$ (2 mmol) in acetone solution (30 cm^3), was added a solution of Me_2NNS (5 mmol) in diethyl ether (30 cm^3). The yellow precipitate was washed with diethyl ether and dried (Yield ca. 60%).

Preparation of $[M(SNNMe_2)_4]MCl_4$ (IVc, Vc)

To a solution of Me_2NNS (6 mmol) in acetone (30 cm^3) was added a solution of Na_2PdCl_4 or K_2PtCl_4 (2 mmol) in H_2O (20 cm^3). The yellow product was washed with H_2O and acetone and dried (Yield ca. 60%).

X-Ray data collection and structure solution

Orange crystals of *cis*-$Pd(SNNMe_2)(AsPh_3)Cl_2$ suitable for X-ray diffraction were obtained by slowly evaporation of an acetone solution. All diffraction measurements were performed on a Siemens-Stoe four-circle diffractometer by using graphite-monochromated Mo-K_α radiation. Twenty reflections of θ10–15° were located by a random search procedure and subsequently centred. These reflections were used as a basis for the indexing. The cell constants and the orientation matrix that were obtained were refined by a least-squares fit. The crystals were found to be triclinic with unit cell dimensions a 9.407(2), b 10.540(2), c 12.265(4) Å, α 68.1(1), β 78.3(1), γ 86.3(1)°, U 1104.4 Å^3, $F(000) = 568$, $Z = 2$, and D_c 1.725 g cm^{-3}, λ(Mo-K_α) 0.7107 Å, $M_r = 573.3$, μ(Mo-K_α) 25.6 cm^{-1}, space group $P1$ or $P\bar{1}$ the last one was confirmed by structure solution and refinement.

Intensities were collected at room temperature for all independent reflections in a range $3 < 2\vartheta < 50°$. an ω/ϑ scan was used for each reflection with a scan speed of 0.03° s^{-1}, scan width 1.2° and a 10 s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of the attenuators into the beam. Three standard reflections (-2, -2, -2, -3, -4, -3 and 3,4,3) measured after approximately 100 data reflections showed only random

(Continued on p. 320)

TABLE 1

ANALYTICAL AND CHARACTERISTIC IR DATA

Complex		Found (calcd.) (%)				IR data (cm^{-1})^{a}			
		C	H	N	S	ν(N–N)	ν(N–S)	ν(M–X)	Others
(I)	Me_2NNS					1105vs	910vs		
(II)	*cis*-$Pd(SNNMe_2)_2Br_2$	10.77	2.73	12.50	14.35	1132vs	782vs	390w^{b}	
		(10.76)	(2.71)	(12.55)	(14.36)			300w^{b}	
(IIIa)	$[(\mu\text{-}Cl)_2\{Pd(SNNMe_2)Cl\}_2]$	8.95	2.32	10.45	12.02	1135vs	770vs	390m^{b}	
		(8.98)	(2.26)	(10.47)	(11.98)			340s^{c}	
								295m^{d}	
								278m^{d}	
(IIIb)	$[(\mu\text{-}Br)_2\{Pd(SNNMe_2)Cl\}_2]$	7.75	1.97	8.90		1132vs	778vs	385m^{b}	
		(7.70)	(1.93)	(8.98)				332s^{c}	
(IIIc)	$[(\mu\text{-}SCN)_2\{Pd(SNNMe_2)Cl\}_2]$	12.50	2.12	14.45		1130vs	778vs	385m^{b}	2150s^{e}
		(12.42)	(2.08)	(14.48)				310s^{c}	477w^{f}
									427w^{f}
(IIId)	$[(\mu\text{-}SeCN)_2\{Pd(SNNMe_2)Cl\}_2]$	10.72	1.85	12.42		1130vs	778vs	385m^{b}	2150s^{e}
		(10.69)	(1.79)	(12.47)				307s^{c}	412w^{f}
									370w^{f}

(IIIe)	$[(\mu\text{-SCN})_2\{Pd(SNNMe_2)(SCN)\}_2]$	15.35 (15.36)	2.00 (1.93)	17.90 (17.91)		1130vs	778vs	387m[b]	2155s[f] 2105s[g]
(IVa)	$[Pd(SNNMe_2)_4](BPh_4)_2$[h]	60.78 (60.84)	5.83 (5.83)	10.20 (10.14)		1125vs	776vs		
(IVb)	$[Pd(SNNMe_2)_4](PF_6)_2$	12.65 (12.69)	3.20 (3.19)	14.90 (14.80)		1125vs	776vs		
(IVc)	$[Pd(SNNMe_2)_4]PdCl_4$	13.40 (13.43)	3.45 (3.38)	15.60 (15.67)	17.90 (17.93)	1125vs	776vs	320s[i]	
(IVd)	$[Pd(SNNMe_2)_4]HgCl_4$	11.92 (11.87)	2.98 (2.99)	13.75 (13.67)		1125vs	776vs		
(Va)	$[Pt(SNNMe_2)_4](BPh_4)_2$[l]	56.40 (56.32)	5.42 (5.40)	9.40 (9.38)		1130vs	780vs		
(Vb)	$[Pt(SNNMe_2)_4](PF_6)_2$	11.40 (11.36)	2.92 (2.86)	13.21 (13.25)		1130vs	780vs		
(Vc)	$[Pt(SNNMe_2)_4]PtCl_4$	10.75 (10.76)	2.75 (2.71)	12.50 (12.55)		1130vs	780vs	310s[i]	

---

[a] Nujol mulls. [b] $\nu(Pd\text{–}SNNMe_2)$. [c] $\nu(Pd\text{–}Cl)_{terminal}$. [d] $\nu(Pd\text{–}Cl)_{bridge}$. [e] ν(C–N) of bridge SCN or SeCN group. [f] δ(SCN) or δ(SeCN). [g] ν(C–N) of terminal SCN group. [h] Λ_M 200 Ω^{-1} cm^2 mol^{-1} for a 5×10^{-4} *M* acetone solution. [i] ν(M–Cl) of $PdCl_4^{2-}$ or $PtCl_4^{2-}$ anions. [l] Λ_M 190 Ω^{-1} cm^2 mol^{-1} for a 5×10^{-4} *M* acetone solution.

fluctuations. Of the 4132 measured reflections, 2664 independent with $I \geqslant 3\sigma(I)$ were used for structure solution and refinement. The data were corrected for Lorentz and polarization effects but since the linear absorption coefficient is 25.6 cm^{-1}, no absorption correction was applied. The structure was refined by full matrix least-squares to convergence by using anisotropic thermal parameters for all the non-hydrogen atoms and unique isotropic thermal parameters for hydrogens (U 0.06 Å^2), which were introduced at their idealized positions (C–H 0.95 Å).

The function minimized was $\Sigma w\Delta^2$ in which $w = 1.3009/[\sigma^2(F_o) + 5.47 \times 10^{-4}(F_o)^2]$ and $\Delta = |F_o| - |F_c|$; discrepancy indices used are $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma\ w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Weighting scheme analyses showed no serious dependence of $w\Delta^2$ on either (F_o) and λ^{-1} $\sin\vartheta$.

A final difference map revealed peaks of about 0.5 e Å^{-3} near the metal positions but was otherwise featureless. Lists of observed and calculated structure factors, thermal parameters and least-square planes are available from the authors.

Atomic scattering factors were taken from Cromer and Waber's [14] tabulation for all atoms except hydrogen, for which Stewart's values [15] were used. Anomalous dispersion terms [16] for Pd were included in F_c. The final conventional R values were $R = 0.029$ and $R_w = 0.031$.

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Pd–As	2.362(1)	Cl(1)–Pd–As	84.2(1)
Pd–Cl(1)	2.313(1)	Cl(1)–Pd–S	176.6(1)
Pd–Cl(2)	2.359(1)	Cl(2)–Pd–As	175.5(1)
Pd–S	2.249(1)	Cl(1)–Pd–Cl(2)	92.0(1)
S–N(1)	1.639(4)	Cl(2)–Pd–S	84.9(1)
N(1)–N(2)	1.272(5)	S–Pd–As	98.9(1)
N(2)–C(1)	1.462(6)	Pd–S–N(1)	107.2(2)
N(2)–C(2)	1.437(7)	S–N(1)–N(2)	118.0(4)
C(11)–C(12)	1.395(7)	N(1)–N(2)–C(2)	124.5(5)
C(11)–C(16)	1.390(6)	N(1)–N(2)–C(1)	117.2(4)
C(12)–C(13)	1.385(7)	C(1)–N(2)–C(2)	118.3(5)
C(13)–C(14)	1.365(7)	C(12)–C(11)–C(16)	119.2(4)
C(14)–C(15)	1.380(8)	C(11)–C(12)–C(13)	119.7(4)
C(15)–C(16)	1.381(8)	C(12)–C(13)–C(14)	120.8(5)
C(21)–C(22)	1.386(7)	C(13)–C(14)–C(15)	119.8(5)
C(21)–C(26)	1.389(7)	C(14)–C(15)–C(16)	120.5(5)
C(22)–C(23)	1.383(10)	C(11)–C(16)–C(15)	119.9(5)
C(23)–C(24)	1.362(9)	C(22)–C(21)–C(26)	119.4(5)
C(24)–C(25)	1.383(9)	C(21)–C(22)–C(23)	119.9(5)
C(25)–C(26)	1.393(11)	C(22)–C(23)–C(24)	121.2(5)
C(31)–C(32)	1.386(7)	C(23)–C(24)–C(25)	119.4(6)
C(31)–C(36)	1.382(7)	C(24)–C(25)–C(26)	120.4(6)
C(32)–C(33)	1.372(7)	C(21)–C(26)–C(25)	119.6(5)
C(33)–C(34)	1.382(9)	C(32)–C(31)–C(36)	119.3(5)
C(34)–C(35)	1.383(9)	C(31)–C(32)–C(33)	120.5(5)
C(35)–C(36)	1.379(7)	C(32)–C(33)–C(34)	120.0(6)
		C(33)–C(34)–C(35)	119.8(5)
		C(34)–C(35)–C(36)	119.9(6)
		C(31)–C(36)–C(35)	120.4(5)

TABLE 3

FINAL FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c
Pd	2805(0)	6866(0)	67(0)
As	3321(0)	8038(0)	−2032(0)
Cl(1)	3536(2)	8891(1)	121(0)
S	2117(2)	4834(1)	124(1)
Cl(2)	2233(2)	5861(1)	2176(1)
N(1)	3205(4)	4513(4)	−965(4)
N(2)	3093(5)	3351(4)	−1037(4)
C(1)	4055(7)	3092(7)	−2027(5)
C(2)	2103(10)	2283(7)	−208(6)
C(11)	2217(5)	9700(4)	−2551(4)
C(12)	1083(5)	9972(5)	−1743(4)
C(13)	287(5)	11156(5)	−2122(5)
C(14)	605(6)	12066(5)	−3275(5)
C(15)	1721(7)	11801(6)	−4081(5)
C(16)	2508(6)	10612(5)	−3733(5)
C(21)	2979(5)	7160(4)	−3105(4)
C(22)	4031(6)	7117(5)	−4061(4)
C(23)	3726(7)	6488(6)	−4797(5)
C(24)	2399(7)	5911(6)	−4605(5)
C(25)	1339(6)	5952(6)	−3656(6)
C(26)	1614(5)	6596(6)	−2912(5)
C(31)	5346(5)	8585(5)	−2563(4)
C(32)	5797(5)	9924(5)	−2891(5)
C(33)	7248(6)	10260(6)	−3219(6)
C(34)	8271(6)	9265(7)	−3252(5)
C(35)	7832(5)	7923(6)	−2910(5)
C(36)	6373(5)	7589(5)	−2574(5)

The calculations were carried out on the IBM computer of the "Centro di calcolo" University of Messina, with the "SHELX 76" system [17] of programs. Bond distances and angles are listed in Table 2 and final fractional atomic coordinates in Table 3.

Acknowledgements

We thank the C.N.R. and the Public Education Ministry for financial support.

References

1 G. Tresoldi, G. Bruno, F. Crucitti and P. Piraino, J. Organomet. Chem., 252 (1983) 381.

2 W.J. Middleton, J. Amer. Chem. Soc., 88 (1966) 3842.

3 H.W. Roesky, R. Emmert, W. Isenberg and G.M. Sheldrick, Angew. Chem. Int. Ed. Engl., 20 (1981) 591; H.W. Roesky, R. Emmert, W. Isenberg, M. Schmidt and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1983) 183.

4 J.P. Beale and N.C. Stephenson, Acta Cryst., B26 (1970) 1655; B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1980) 1556.

5 G. Tresoldi, G. Bruno, P. Piraino, F. Faraone and G. Bombieri, Inorg. Chim. Acta, 51 (1981) 263; R. McCrindle, E.C. Alyea, G. Ferguson, S.A. Diaz, A.J. McAlees and M. Parvez, J. Chem. Soc., Dalton Trans., (1980) 137; K. Miki, N. Tanaka and N. Kasai, J. Organomet. Chem., 208 (1981) 407; R. Bardi, A. Del Pra, A.M. Piazzesi, L. Sindellari and B. Zarli, Inorg. Chim. Acta, 47 (1981) 231.
6 J.D. Woollins, R. Grinter, M.K. Johnson and A.J. Thonson, J. Chem. Soc., Dalton Trans., (1980) 1910.
7 R.J. Goodfellow, P.L. Goggin and L.M. Venanzi, J. Chem. Soc. (A), (1967) 1898.
8 J. Chatt and L.A. Duncanson, Nature, 178 (1956) 997.
9 D.M. Adams in E. Arnold (Ed.), Metal-Ligand and Related Vibrations, London, 1967, p. 327.
10 F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science, London, 1973, p. 241.
11 D. Drew and J.R. Doyle, Inorg. Synth., 13 (1972) 47.
12 M.S. Kharasch, R.C. Seyler and F.R. Mayo, J. Amer. Chem. Soc., 60 (1938) 822.
13 A.B. Goel and S. Goel, Synth. React. Inorg. Met. -Org. Chem., 11(4) (1981) 289.
14 D.T. Cromer and J.B. Mann, Acta Cryst., A24 (1968) 321.
15 R.F. Stewart, J. Chem. Phys., 42 (1965) 3175.
16 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
17 G.M. Sheldrick "SHELX 76" Computing System, University of Cambridge, Kynoch Press, Birmingham, 1976.