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Ligating Properties of Coordinated Thiocarboxamido Group. Synthesis, Crystal and Molecular Structure of μ-Chloro-μ-thiocarboxamido-dichlorobis(triphenylphosphine)dipalladium·Acetone Solvate

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The reaction, in acetone, of the thiocarboxamido complexes [MCl(CSNMe$_2$)(PPh$_3$)$_2$] (M = Pd (1); M = Pt (2)) with some metal halides have been studied. The salts FeCl$_3$, AlCl$_3$ and ZnCl$_2$ react with (1) and (2) to give the dimeric dicationic complexes [M$_2$(PPh$_3$)$_4$(μ-CSNMe$_2$)]$^{2+}$ in which FeCl$_4^-$, AlCl$_4^-$ and ZnCl$_4^{2-}$ are the counter ions. The reactions of (1) with HgCl$_2$, NiCl$_2$ and PtCl$_2$ occur with PPh$_3$ transfer to metal halide and [Pd$_2$Cl$_2$(μ-CSNMe$_2$)$_2$-(PPh$_3$)$_2$ and the complexes [Hg(PPh$_3$)Cl$_2$]$_2$, [Ni(PPh$_3$)$_2$Cl$_2$], cis-*[Pt(PPh$_3$)$_2$Cl$_2$] respectively are the products. The reactions of (2) with HgCl$_2$, NiCl$_2$, PdCl$_2$ and PtCl$_2$ proceed analogously. By reacting (1) with PdCl$_2$ or Na$_2$PdCl$_4$ in acetone orange crystals of [Pd$_2$(PPh$_3$)$_2$Cl$_2$(μ-Cl)(μ-CsNMe$_2$)]·CH$_3$COCH$_3$ are obtained. Analogously [Pd$_2$(PPh$_3$)$_2$-Br$_2$(μ-Br)(μ-CSNMe$_2$)] CH$_3$COCH$_3$ was obtained from the reaction of (1) with Na$_2$PdBr$_4$.*

The crystal and molecular structure of the title compound has been determined as its acetone solvate by three-dimensional single-crystal X-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ in a cell of dimensions a = *16.788(5),* b = *12.784(4),* c = *10.796(4) Å, α = 98.94(8), β = 101.65(8) and γ = 105.08(7)° with two formula weights corresponding to [(PPh$_3$)$_2$Pd$_2$Cl$_3$(CSNMe$_2$)]·Me$_2$CO per unit cell.*

The structure was solved by standard heavy-atom methods and refined by least-squares to a final discrepancy factor R *of 0.052. In the dimer the two Pd atoms (Pd(1)–Pd(2) 3.122(1) Å) are held together through a C(S)NMe bridging ligand (Pd(1)–C(37) 1.963(8) Å and Pd(2)–S 2.294(2) Å) and an asymmetric chlorine bridge (Pd(1)–Cl(3) 2.453(2) Å and Pd(2)–Cl(3) 2.495(2) Å) and possesses essentially square-planar coordination geometries; the two coordination geometries are completed by two chlorine and two phosphorus atoms from the triphenylphosphine ligands (Pd(1)–Cl(1) 2.356(3); Pd(2)–Cl(2) 2.330(2); Pd(1)–P(1) 2.266(3); Pd–P(2) 2.244(2) Å).*

Spectral data of the products are discussed and a possible scheme for the reactions is proposed.

Introduction

The sulphur atoms of CS groups bonded through carbon to a transition metal as, for example, in thiocarbonyl, dithioester, η^2-carbon disulphide metal complexes, show a pronounced nucleophilic character as indicated by their ease of alkylation and their ability to act as sulphur donor ligands towards different metal atoms [1–13]. As regards thiocarboxamido metal complexes, coordination to metal of CSNR$_2$ group can occur through carbon (η^1-coordination), through carbon and sulphur to give a three membered ring (η^2-coordination) and bridging through carbon and sulphur to give bimetallic compounds (μ-coordination). The nucleophilic character of sulphur atom of the thiocarboxamido ligand was enhanced in the methylation reactions of [Mo(CO)$_2$(η^5-C$_5$H$_5$)(CSNMe$_2$)] and [Mn(CO)$_3$(CSNMe$_2$)(PPh$_3$)] [14]. However, attempted protonation by HBF$_4$ of [MCl(CSNMe$_2$)L$_2$] (M = Pd, Pt; L = tertiary phosphine) species was accompanied by HCl loss and formation of the ionic dinuclear complexes [M$_2$(CSNMe$_2$)$_2$L$_4$]$^{2+}$ [15]. The tendency of thiocarboxamido group to give μ-coordination to the metal prompted us to explore the reactions of [MCl(CSNMe$_2$)L$_2$] (M = Pd (**1**); M = Pt (**2**); L = PPh$_3$) with some metal halogenides with the aim to obtain heteronuclear bimetallic complexes by μ-coordination of CSNMe$_2$ group.

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The results obtained on a full X-ray structure determination undertaken on a single crystal of the title compound are here reported.

Experimental

The complexes $[MCl(CSNMe_2)(PPh_3)_2]$ (M = Pd, Pt) were prepared as described in the literature [15]. All the other chemicals were reagent grade and used without further purification. Infrared spectra were recorded using a Perkin-Elmer 457 spectrometer, as Nujol mulls in CsI pellets. Proton NMR were obtained using a Perkin-Elmer R 24B spectrometer. a WTV LBR conductivity meter was used for conductivity measurements. Elemental analyses were by Laboratorium of Organic Chemistry Institute of Milan, Italy, and by Bemhardt Mikroanalytisches Laboratorium, Elbach, Germany

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use.

Preparation of $[Pd_2(\mu\text{-}CSNMe_2)_2(PPh_3)_4][FeCl_4]_2$

$FeCl_3$ (0.032 g, 0.2 mmol) was added to a stirred solution (100 cm^3) of (1) (0.15 g, 0.2 mmol). The solution turns rapidly from yellow to pale-yellow. After 5 min, the solution volume was reduced under vacuum. On treatment with diethyl ether the product precipitated as a yellow solid. This was collected, washed several times with diethyl ether and dried. Yield 99%. *Anal.* Found:C, 49.98; H, 3.99; N, 1.48; Cl 15.40. $C_{78}H_{72}Cl_8Fe_2N_2P_4Pd_2S_2$ requires: C, 51.07; H, 3.95; N, 1.52; Cl, 15.46%. Using the appropriate metal chloride $[Pd_2(\mu\text{-}CSNMe_2)_2(PPh_3)_4][AlCl_4]_2$ (Found: C, 52.71; H, 4.11; N, 1.57; Cl, 15.88. $C_{78}H_{72}Al_2Cl_8N_2P_4Pd_2S_2$ requires: C, 52.74; H, 4.08; N, 1.57; Cl, 15.96%) and $[Pd_2(\mu\text{-}CSNMe_2)_2(PPh_3)_4][ZnCl_4]$ (Found: C, 56.96; H, 4.43; N, 1.70; Cl, 8.58. $C_{78}H_{72}Cl_4N_2P_4Pd_2S_2Zn$ requires: C, 56.91; H, 4.41; N, 1.70; Cl, 8.61%) were prepared and isolated similarly, as yellow solids. The compound $[Pt_2(\mu\text{-}CSNMe_2)_2(PPh_3)_4][FeCl_4]_2$ was similarly obtained, as yellow solid, by reacting (2) and $FeCl_3$. Yield 97%. (Found: C, 46.50; H, 3.65; N, 1.43; Cl, 14.18. $C_{78}H_{72}Cl_8Fe_2N_2P_4Pt_2S_2$ requires: C, 46.58; H, 3.61; N, 1.39; Cl, 14.10%).

Reaction of $[MCl(CSNMe_2)(PPh_3)_2]$ *(M = Pd, Pt) with* $M'Cl_2$ *(M' = Hg, Ni, Pt)*

All these reactions take place in the same manner and so only the reaction of (1) with $HgCl_2$ is described.

By adding an acetone solution (40 cm^3) of $HgCl_2$ (0.054 g, 0.2 mmol) to a stirred solution (100 cm^3) of (1) (0.151 g, 0.2 mmol) in the same solvent a mixture of solids was formed. This was separated by filtration and, after treatment with $CHCl_3$, gives an orange solution and $[Hg(PPh_3)Cl_2]_2$ as residue. By adding diethyl ether to the concentrated solution the product $[Pd_2(CSNMe_2)_2Cl_2(PPh_3)_2]$ was obtained as orange solid (yield 88%). *Anal.* Found: C, 51.26; H, 4.28; N, 2.81; Cl, 7.11. $C_{42}H_{42}Cl_2N_2P_2Pd_2S_2$ requires: C, 51.20; H, 4.30; N, 2.84; Cl, 7.19%.

$NiCl_2$ and $PtCl_2$ react similarly with (1) and the reaction products were the dimer $[Pd_2(\mu\text{-}CSNMe_2)_2Cl_2(PPh_3)_2]$ and $[NiCl_2(PPh_3)_2]$ and *cis*-$[PtCl_2(PPh_3)_2]$ respectively. Owing to the solubility of $[NiCl_2(PPh_3)_2]$ in acetone, in the reaction of (1) with $NiCl_2$ the product was obtained as $[Pd_2(\mu\text{-}CSNMe_2)_2Cl_2(PPh_3)_2]0.5CH_3COCH_3$, by mixing the reagents.

The reactions of (2) with $HgCl_2$, $NiCl_2$, $PdCl_2$ and $PtCl_2$ proceed similarly. Working up as above the orange solid $[Pt_2(\mu\text{-}CSNMe_2)_2Cl_2(PPh_3)_2]$ (found: C, 43.22; H, 3.68; N, 2.37; Cl, 6.18. $C_{42}H_{42}Cl_2N_2P_2Pt_2S_2$ requires: C, 43.41; H, 3.64; N, 2.41; Cl, 6.10%) and $[HgCl_2(PPh_3)]_2$, $[Ni(PPh_3)_2Cl_2]$, $[Pd_2(PPh_3)_2Cl_4]$, *cis*-$[Pt(PPh_3)_2Cl_2]$ respectively are obtained.

Preparation of $[Pd_2(\mu\text{-}CSNMe_2)(\mu\text{-}Cl)Cl_2(PPh_3)_2]\text{-}CH_3COCH_3$

To an acetone solution (200 cm^3) of (1) (0.075 g, 0.1 mmol), $PdCl_2$ (0.018 g, 0.1 mmol) was added and the mixture stirred until the $PdCl_2$ dissolves (about 3 h). The initial yellow colour of the solution changed to orange. On letting the filtered solution stand for about two days orange crystals of the product were formed. Additional product was obtained by adding diethyl ether to the acetone solution. (Yield 78%). *Anal.* Found: C, 51.04; H, 4.31; N, 1.44; Cl, 10.68. $C_{42}H_{42}Cl_3NOP_2Pd_2S$ requires: C, 50.92; H, 4.27; N, 1.41; Cl, 10.73%.

The same product was obtained starting from (1) and Na_2PdCl_4 (molar ratio 1:1) and working up as above.

Preparation of $[Pd_2(\mu\text{-}CSNMe_2)(\mu\text{-}Br)Br_2(PPh_3)_2]\text{-}CH_3COCH_3$

This compound was obtained in the same manner as $[Pd_2(\mu\text{-}CSNMe_2)(\mu\text{-}Cl)Cl_2(PPh_3)_2]CH_3COCH_3$, starting from (*1*) and Na_2PdBr_4. (Yield 72%). *Anal.* Found: C, 44.82; H, 3.80; N, 1.22; Br, 21.22. $C_{42}H_{42}Br_3NOP_2Pd_2S$ requires: C, 44.88; H, 3.76; N, 1.24; Br, 21.33%.

X-ray Structure Analysis

Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard errors were obtained from least-squares refinement of 2θ, ω, χ and ϕ values of 16 carefully centered high angle reflections.

Intensity data were collected from a crystal of approximate dimensions 0.17 × 0.10 × 0.22 mm on a Siemens-Stoe four-circle diffractometer by using graphite monochromatized MoKα radiation. Intensities were collected at room temperature in a range $2^\circ < \theta < 25^\circ$. An $\theta-\omega$ scan was used with a 0.5 s count at each of 120 steps of 0.01° for each reflection and a 30 s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of attenuators into the beam. 2 standard reflections measured after approximately 50 data reflections showed only random fluctuations. Of the 6837 measured independent reflections 4860 with $I > 2{,}5\sigma(I)$ were used for structure solution and refinement.

The data were corrected for Lorentz, polarization and absorption effects.

Crystal Data

$C_{42}H_{42}Cl_3NOP_2SPd_2$. M = 990.0 Triclinic, space group $P\bar{1}$, $a = 16.788(5)$, $b = 12.784(4)$, $c = 10.796(4)$ Å, $\alpha = 98.94(8)$, $\beta = 101.65(8)$, $\gamma = 105.08(7)$, $F(000) = 996$, $V = 2137.5$ Å^3, $d_c = 1.54$ g cm^{-3} for $Z = 2$, MoKα radiation, $\lambda = 0.71069$ Å, μ(MoKα) = 10.8 cm^{-1}.

Structure Solution and Refinement

The molecular structure was solved by the heavy-atom method and Fourier maps based on palladium phases revealed the complete structure. The refinement of the structural model, was by the method of full-matrix least-squares, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structures amplitude and w = 1. Weighting-scheme analyses showed no serious dependence of the mean $w\Delta^2$ on either $|F_o|$ and $\lambda^{-1} \sin\theta$. The atomic scattering factors for Pd were taken from ref. [16] for the other non-hydrogen atoms from ref. [17] and for hydrogen atoms from ref. [18]. The anomalous dispersion terms used for palladium and phosphorus were those of ref. [19]. The phenyl rings of the triphenylphosphine were refined as rigid groups (symmetry D_{6h}; C–C 1.395 Å) with individual isotropic thermal parameters. Hydrogen atoms were included in the scattering model in calculated idealized positions (C–H = 0.95 Å) with a common thermal parameter (B = 5 Å^2) but not varied.

Anisotropic temperature factors were then assigned to the non group atoms. Few cycles of least-squares refinement lowered the discrepancy factor $R = 0.075$.

The prominent feature of a difference map calculated at this point was a collection of peaks, interpreted as a disordered acetone molecule with two different orientations. A refinement was then performed introducing the two acetone molecules with occupancy factors f and 1-f and constant thermal factors. The most acceptable result was f 0.6 but with rather irrealistic values of distances and thermal parameters. With this rather approximate model for the acetone molecule the refinement converged at $R = 0.052$.

The final positional and thermal parameters are given in Tables I and II. All data processing and computations were carried out using the SHELX 76 [20] and X-Ray 72 [21] program package.

A listing of the observed and calculated structure factors for those reflections used in the refinement is available from the authors.

Results and Discussion

The metal halides considered react with $[M(CSNMe_2)Cl(PPh_3)_2]$ (M = Pd (1); M = Pt (2)) complexes in different way and three types of reactions can be distinguished.

Reactions in which the Metal Halide Acts as a Lewis Acid towards Cl^-

The existence in solution of the equilibrium

$$2[ML_2Cl(CSNMe_2)] \rightleftarrows [M_2L_4(CSNMe_2)_2]^{2+} + 2Cl^-$$

(M = Pd, Pt; L = tertiary phosphine) has been proved by NMR spectroscopy [15]; by adding HBF_4 to an acetone solution of (1) or (2), the dimeric complexes $[M_2L_4(\mu\text{-}CSNMe_2)_2][BF_4]_2$ have been isolated [15]. Such a reaction was observed by us when (1) or (2) and salts as $FeCl_3$, $AlCl_3$ or $ZnCl_2$ are left standing in acetone for a short time; in these conditions dimerization of (1) and (2) to give the dicationic complexes $[M_2L_4(CSNMe_2)_2]^{2+}$ occurs very easily and $FeCl_4^-$, $AlCl_4^-$ are the counter ions. These complexes closely resemble the reported [15] corresponding BF_4^- salts and were characterized by elemental analyses, conductivity measurements and IR spectra.

Reactions which Occur with Transfer of Triphenylphosphine Ligand from (1) or (2) to Metal Halide

The reaction of (1) with $HgCl_2$, $NiCl_2$, $PtCl_2$, in equimolar amounts, in acetone, results in the formation of the neutral dimeric complex $[Pd_2(PPh_3)_2Cl_2(\mu\text{-}CSNMe_2)_2]$ (3) and of the triphenylphosphine complexes $[Hg(PPh_3)Cl_2]_2$ [22], $[Ni(PPh_3)_2Cl_2]$ [23] and *cis*-$[Pt(PPh_3)_2Cl_2]$ [24] respectively. Compound (2) reacts with $HgCl_2$, $NiCl_2$, $PdCl_2$ and $PtCl_2$ in the same way to give $[Pt_2(PPh_3)_2Cl_2(\mu\text{-}CSNMe_2)_2]$ (4); in the reaction with $PdCl_2$, $[Pd_2(PPh_3)_2Cl_4]$ [25] is the second reaction product. Apparently these reactions occur by transfer of the PPh_3 ligand from (1) or (2) to the metal halide. Experimental data do not indicate if the formation of compounds (3) and (4) results from loss of the ligand from (1) and (2), in a dissociative step, under equilibrium conditions and dimerization

TABLE I. Fractional Coordinates ($\times 10^4$) with e.s.d.'s in Parentheses and Isotropic U ($\times 10^3$).

	x	y	z	U		x	y	z
Pd(1)	2424(0)	2164(1)	5640(1)	–				
Pd(2)	1451(0)	2952(1)	3360(1)	–				
Cl(1)	3423(2)	3809(2)	6969(3)	–				
Cl(2)	1402(2)	4776(2)	3612(3)	–				
Cl(3)	1240(1)	2961(2)	5583(2)	–				
S	1225(2)	1069(2)	2949(2)	–				
P(1)	3477(1)	1387(2)	5467(2)	–				
P(2)	1717(1)	3017(2)	1413(2)	–				
N	1215(5)	–91(6)	4748(8)	–				
C(37)	1553(5)	852(7)	4480(8)	–				
C(38)	1439(8)	–288(10)	6053(11)	–	H(1)	1001	–939	6031
					H(2)	1431	306	6695
					H(3)	1977	–419	6257
C(39)	588(7)	–1037(8)	3789(12)	–	H(4)	278	–1554	4195
					H(5)	880	–1393	3277
					H(6)	204	–764	3252
C(1)	4132(4)	2021(5)	4456(6)	41(2)				
C(2)	4242(4)	3130(5)	4396(6)	61(3)	H(2)	3966	3554	4863
C(3)	4758(4)	3617(5)	3648(6)	75(3)	H(3)	4834	4373	3607
C(4)	5163(4)	2995(5)	2962(6)	76(3)	H(4)	5515	3327	2453
C(5)	5053(4)	1886(5)	3023(6)	71(3)	H(5)	5329	1463	2555
C(6)	4537(4)	1399(5)	3770(6)	56(2)	H(6)	4462	644	3811
C(7)	3140(4)	–92(4)	4705(5)	45(2)				
C(8)	2748(4)	–419(4)	3380(5)	52(2)	H(8)	2664	122	2897
C(9)	2479(4)	–1540(4)	2764(5)	65(3)	H(9)	2212	–1763	1861
C(10)	2602(4)	–2334(4)	3473(5)	74(3)	H(10)	2419	–3097	3053
C(11)	2994(4)	–2007(4)	4798(5)	69(3)	H(11)	3078	–2547	5281
C(12)	3263(4)	–886(4)	5414(5)	60(3)	H(12)	3531	–663	6317
C(13)	4201(3)	1503(5)	7009(6)	45(3)				
C(14)	3924(3)	1630(5)	8142(6)	62(3)	H(14)	3371	1703	8109
C(15)	4457(3)	1649(5)	9322(6)	75(3)	H(15)	4269	1736	1.0094
C(16)	5268(3)	1542(5)	9370(6)	73(3)	H(16)	5632	1555	1.0174
C(17)	5545(3)	1415(5)	8237(6)	68(3)	H(17)	6098	1342	8270
C(18)	5012(3)	1396(5)	7056(6)	52(2)	H(18)	5200	1309	6285
C(19)	1777(3)	1707(4)	556(5)	44(2)				
C(20)	2534(3)	1429(4)	837(5)	56(2)	H(20)	3034	1954	1404
C(21)	2556(3)	378(4)	285(5)	66(3)	H(21)	3071	189	476
C(22)	1821(3)	–393(4)	–549(5)	66(3)	H(22)	1837	–1109	–925
C(23)	1065(3)	–115(4)	–829(5)	67(3)	H(23)	564	–640	–1397
C(24)	1042(3)	935(4)	–277(5)	54(2)	H(24)	527	1125	–468
C(25)	2730(4)	4010(5)	1464(5)	48(2)				
C(26)	3141(4)	4869(5)	2556(5)	62(3)	H(26)	2902	4921	3281
C(27)	3903(4)	5651(5)	2584(5)	69(3)	H(27)	4183	6235	3328
C(28)	4254(4)	5575(5)	1519(5)	72(3)	H(28)	4772	6107	1538
C(29)	3843(4)	4716(5)	427(5)	69(3)	H(29)	4081	4665	–299
C(30)	3081(4)	3934(5)	399(5)	63(3)	H(30)	2801	3350	–345
C(31)	875(3)	3306(6)	317(6)	47(2)				
C(32)	985(3)	3594(6)	–845(6)	66(3)	H(32)	1512	3648	–1068
C(33)	323(3)	3802(6)	–1681(6)	73(3)	H(33)	398	3997	–2473
C(34)	–450(3)	3722(6)	–1354(6)	72(3)	H(34)	–902	3864	–1923
C(35)	–560(3)	3435(6)	–192(6)	72(3)	H(35)	–1087	3381	31
C(36)	102(3)	3227(6)	644(6)	57(2)	H(36)	27	3031	1436

Acetone molecule (disordered)

	x	y	z	U	K
C(40)	2821(16)	7797(21)	8061(24)	96(7)	0.6

(continued on facing page)

TABLE I. *(continued)*

	x	y	z	U	K
C(41)	1835(20)	6691(23)	7212(28)	96(7)	0.6
C(42)	2463(28)	5960(36)	8018(51)	157(14)	0.6
O(1)	1221(15)	6486(17)	6610(21)	154(7)	0.6
C(43)	2355(24)	6917(32)	7836(35)	68(9)	0.4
C(44)	2413(40)	5923(52)	7236(63)	168(24)	0.4
C(45)	2726(42)	6236(53)	8912(68)	194(26)	0.4
O(2)	2403(26)	7745(35)	7695(38)	133(14)	0.4

TABLE II. Anisotropic Thermal Parameters ($\times 10^3$) in the Form $\exp[-2\pi^2 \Sigma U_{ij} a_i^* a_j^* h_i h_j]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd(1)	44.6(4)	41.4(4)	39.8(4)	6.7(3)	9.6(3)	13.1(3)
Pd(2)	44.7(4)	40.8(4)	43.7(4)	14.8(3)	14.5(3)	16.0(3)
Cl(1)	68(2)	61(2)	77(2)	−19(1)	1(1)	16(1)
Cl(2)	97(2)	52(2)	74(2)	21(1)	34(2)	40(1)
Cl(3)	41(1)	47(1)	43(1)	20(1)	21(1)	16(1)
S	57(2)	41(1)	46(1)	13(1)	5(1)	8(1)
P(1)	41(1)	39(1)	43(1)	10(1)	8(1)	12(1)
P(2)	47(1)	39(1)	43(1)	12(1)	12(1)	12(1)
N	52(5)	48(5)	67(5)	26(4)	25(4)	10(4)
C(37)	43(5)	39(5)	48(5)	13(4)	20(4)	9(4)
C(38)	80(8)	83(8)	88(9)	52(7)	40(7)	27(7)
C(39)	74(8)	39(6)	112(10)	24(6)	23(7)	−4(5)

or from a two step reaction involving initial interaction of the metal halide with the sulphur atom of the coordinated thiocarboxamido group and subsequent transfer of the ligand PPh_3 with breakage of the metal–sulphur bond. A complex like (3) and (4) was obtained [15] from the reaction of $[Pd\{P(OMe)_3\}_4]$ with $ClC(S)NMe_2$, but using $[Pd(PPh_3)_4]$ or $[Pt(PPh_3)_4]$, in the same reaction, (1) and (2) are the only products. The attempt to obtain (3) and (4) by refluxing benzene solution of (1) and (2) failed although (3) and (4) are nearly insoluble in this solvent. Thus, formation of (3) and (4) by loss, under equilibrium conditions, of one PPh_3 ligand from (1) and (2) and dimerization of the resulting three-coordinated species, seems unlikely. The course of the reaction of (1) with $PdCl_2$ or Na_2PdCl_4, described below, supports the view that the formation of (3) and (4) occurs by initial interaction of the metal halide with the sulphur atom of the complexes (1) and (2). It is noteworthy that the very strong Lewis acid $HgCl_2$ does not react with (1) and (2) to give the dicationic complexes $[M_2L_4(\mu\text{-}CSNMe_2)_2]^{2+}$, as do $FeCl_3$, $AlCl_3$ and $ZnCl_2$.

The compounds (3) and (4) are orange solids, soluble in chlorinated solvents and sparingly soluble in acetone. When they are obtained from this solvent they crystallise with one acetone molecule (ν(CO) 1710 cm^{-1}). The IR spectra of (3) and (4) show the ν(CS) at 938 cm^{-1} (vs) and the ν(CN) at 1515 cm^{-1} (vs,br); the far-infrared of (3) and (4) are quite different with ν(M–Cl) at 305 and 270 cm^{-1} respectively. Thus compounds (3) and (4) have a structure with the thiocarboxamido groups μ-coordinated but probably differ in the positions of the chloro atoms. Owing to the greater labilizing *trans*-influence of the σ-bonded carbon atom with respect to sulphur, the chloro atoms could take a position *trans* to carbon in (4) and *trans* to sulphur in (3).

Reaction of (1) with $PdCl_2$ or Na_2PdCl_4

On mixing equimolar amounts of (1) and $PdCl_2$, in acetone, at room temperature, the yellow colour of the solution changes to orange while the $PdCl_2$ slowly dissolves. On letting the solution stand for about two days orange crystals which analyse for $Pd_2Cl_3(PPh_3)_2(CSNMe_2)CH_3COCH_3$ (5) are formed. Additional product was obtained by adding diethyl ether to the acetone solution. Compound (5) can be obtained in a similar way using Na_2PdCl_4 as the palladium(II) salt. While compound (5) is stable in

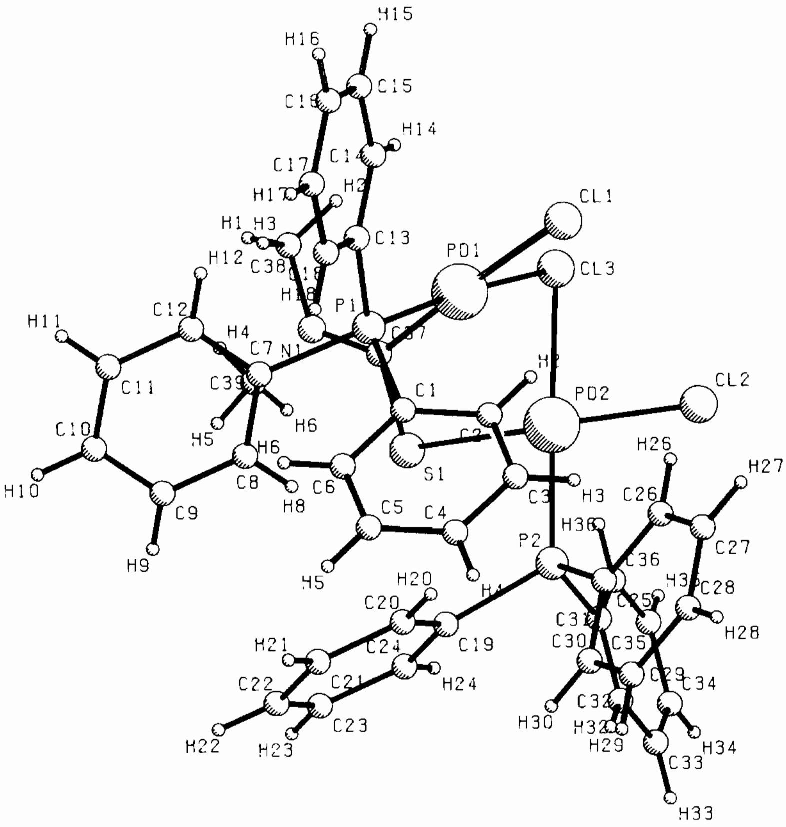

Fig. 1. Projection of a dimeric unit down *a*.

the solid state over long periods of time, it decomposes in chlorinated solvents. This and the low solubility in acetone prevented the taking of satisfactory ^{1}H NMR spectra. In the IR spectrum, a strong ν(CS) band at 922 cm^{-1}, namely at lower frequency than the starting material, and the ν(CN) at 1540 cm^{-1} indicate μ-coordination of the thiocarboxamido ligand; in the far-infrared spectrum, bands of medium intensity at 333, 310 cm^{-1}, which can be assigned to terminal ν(Pd–Cl), and at 275 cm^{-1}, assignable to bridged ν(Pd–Cl), are observed. On this basis compound (**5**) can be assigned a structure in which the thiocarboxamido group and a chloride ligand are bridging two palladium atoms. An X-ray structural investigation undertaken on a single crystal of (**5**) confirmed the proposed structure (see below).

Compound (**5**) presumably results from a reaction involving initial coordination of the sulphur or the coordinated thiocarboxamido group to the palladium(II) atom of the halide; a subsequent intramolecular rearrangement process with transfer of PPh$_3$ and formation of the halide bridge yields the product.

A product like (**5**), $[Pd_2Br_2(\mu\text{-}Br)(\mu\text{-}CSNMe_2)(PPh_3)_2]CH_3COCH_3$ (**6**), was obtained by reacting (**1**) in acetone with Na_2PdBr_4. Compound (**6**) is a red orange solid, insoluble in acetone or benzene and very unstable in chlorinated solvents. Apart from the lack of the ν(Pd–Cl) bands, the IR spectrum of (**6**) closely resembles the spectrum of (**5**).

The attempts to obtain a dinuclear heterometallic product like (**5**) by reacting (**2**) with $PdCl_2$ or Na_2PdCl_4 failed and the reaction products are the dimer complexes $[Pt_2(PPh_3)_2Cl_2(\mu\text{-}CSNMe_2)_2]$ (**4**) and $[Pd_2(PPh_3)_2Cl_4]$. As described above, also from the reaction of (**2**) with $PtCl_2$ or Na_2PtCl_4 we did not get a compound like (**5**).

Thus, formation of (**5**) comes about as the result of a balance of various factors, among which the electronic structure and the ionic radii to the metals involved assume overriding importance.

Description of the Structure

The crystal of the title compounds consists of the packing of discrete dimeric molecules $[Pd_2(PPh_3)_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SCNMe_2)]$ and of disordered acetone molecules of crystallization separated by normal Van der Waals contacts. The molecular structure is shown in Fig. 1 together with the atom numbering scheme. Selected bond distances and angles for the structure

TABLE III. Selected Interatomic Distances and Angles.

Pd(1)–Cl(1)	2.356(3)	Pd(2)–Cl(2)	2.330(2)
Pd(1)–Cl(3)	2.453(2)	Pd(2)–Cl(3)	2.495(2)
Pd(1)–P(1)	2.266(2)	Pd(2)–P(2)	2.244(2)
Pd(1)–C(37)	1.963(8)	Pd(2)–S	2.294(2)
P(1)–C(1)	1.831(6)	P(2)–C(19)	1.821(6)
P(1)–C(7)	1.829(6)	P(2)–C(25)	1.824(6)
P(1)–C(13)	1.811(6)	P(2)–C(31)	1.807(7)
N–C(37)	1.296(10)	C(37)–S	1.723(9)
N–C(38)	1.462(12)	N–C(39)	1.466(12)
	Pd(1)–Pd(2)	3.122(1)	
P(1)–Pd(1)–Cl(3)	174.1(1)	P(2)–Pd(2)–Cl(3)	176.6(1)
C(37)–Pd(1)–Cl(1)	176.4(3)	S–Pd(2)–Cl(2)	169.1(1)
P(1)–Pd(1)–C(37)	91.8(3)	P(2)–Pd(2)–S	90.6(1)
C(37)–Pd(1)–Cl(3)	84.6(3)	S–Pd(2)–Cl(3)	91.3(1)
Cl(3)–Pd(1)–Cl(1)	92.4(1)	Cl(3)–Pd(2)–Cl(2)	88.9(1)
Cl(1)–Pd(1)–P(1)	91.0(1)	Cl(2)–Pd(2)–P(2)	89.8(1)
Pd(1)–C(37)–S	112.1(4)	Pd(2)–S–C(37)	102.0(3)
Pd(1)–C(37)–N	128.0(7)	C(37)–N–C(38)	121.6(9)
S–C(37)–N	119.9(7)	C(37)–N–C(39)	123.6(8)
C(7)–P(1)–C(1)	103.0(3)	C(38)–N–C(39)	114.8(8)
C(13)–P(1)–C(1)	106.6(3)	C(25)–P(2)–C(19)	103.7(3)
C(13)–P(1)–C(7)	104.3(3)	C(31)–P(2)–C(19)	103.8(3)
		C(31)–P(2)–C(25)	108.5(3)

TABLE IV. Least-squares Planes with Deviations (Å) of the Relevant Atoms in Square Brackets. The Equation of the Plane in the Direct Space is Given by PX + QY + RZ = S.

	P	Q	R	S
Plane 1 C(37), Cl(1), P(1), Cl(3) [C(37) 0.032, Cl(1) 0.025, P(1) −0.029, Cl(3) −0.028, Pd(1) 0.069]	−3.7711	−6.0944	10.0452	3.3637
Plane 2 S, Cl(2), P(2), Cl(3) [S −0.140, Cl(2) −0.141, P(2) 0.148, Cl(3) 0.133, Pd(2) 0.079]	15.2108	−1.0333	1.6910	2.3911
Plane 3 C(39), C(38), N, C(37), S [C(39) 0.008, C(38) −0.023, N 0.007, C(37) 0.033, S −0.025]	15.6496	−6.4383	−3.8858	0.1080

Angles (°)

1–2	88.8	1–3	75.4	2–3	45.0

are reported in Table III and important least-squares planes are presented in Table IV. The unit cell content viewed down c* is shown in Fig. 2.

The coordination geometry about the two palladium atoms of each dimeric unit is approximately square-planar. Palladium(I) is planarly surrounded by two *cis* chlorine atoms, a phosphorus atom of the PPh_3 ligand and a σ-bonded carbon of the thiocarboxazimido ligand; whereas the atoms coordinated at Palladium(2) *i.e.* P(2) of the second PPh_3 ligand, Cl(2), Cl(3) and S of the thiocarboxamide ligand deviate remarkably from planarity towards a tetrahedral arrangement: the four donor atoms being alternately above and below the mean plane (Table

TABLE V. Comparison between Pd–S and Pd–C Bond Distances (Å) in Different Compounds.

Compound	Pd–S	Pd–C	Reference
$Pd_2(PPh_3)_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SCNMe_2)$	2.294(2)	1.963(8)	this work
$[(MeO)_3P]_2Pd_2Cl_2(CSNMe_2)_2$	2.382(2)	1.99(1)	29
trans-Pd(COPr-n)Cl$(PPh_3)_2$		1.974(10)	35
trans-Pd$(SCN)_2(MTC)_2$[a]	2.319(1)		36
trans-Pd$(COCO_2CH_3)Cl(PPh_3)_2$		1.97	34
trans-$PdBr_2(DTMC)_2$[b]	2.327(1)		37
trans-$PdCl_2(DTMC)_2$[b]	2.330		38
trans-PdClC(=N–p-C_6H_4OMe)C(Me=N-p-C_6H_4OMe)$(PPh_3)_2$		1.98	32

[a] MTC = O-ethyl-N-methylthiocarbamate. [b] DMTC = O-ethyl-N,N-dimethylthiocarbamate.

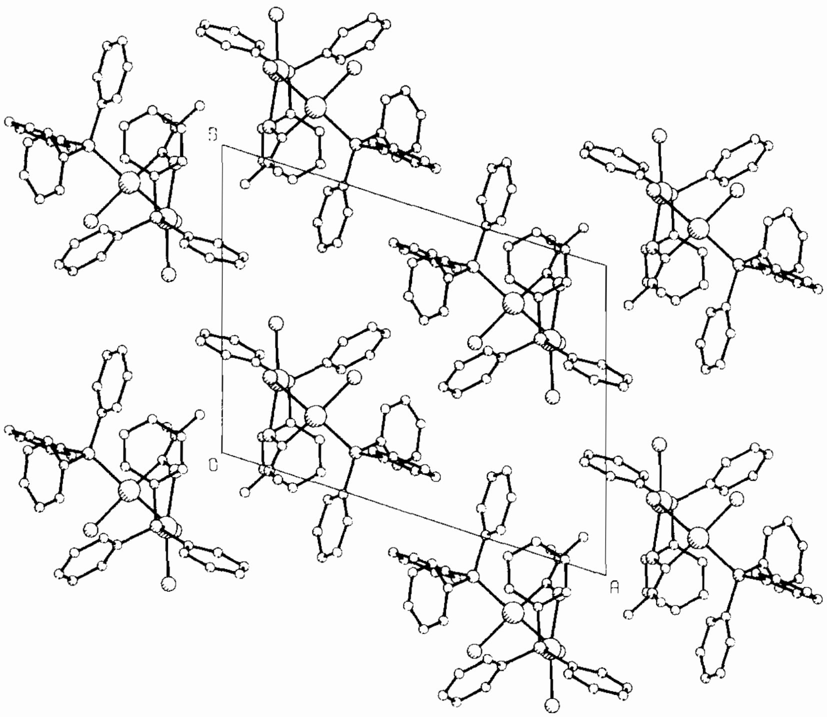

Fig. 2. The unit cell content viewed down c*.

IV) passing through them. The dihedral angle between the two coordination planes is about 89°.

The two palladium atoms are connected together at a distance of 3.122 Å through a bridging chlorine and the thiocarboxamido ligand bonded with C(37) to palladium(1) and with the sulphur to palladium(2). The chlorine bridge is asymmetric being Pd(1)–Cl(3) 2.453 Å and Pd(2)–Cl(3) 2.495 Å.

The $SCNMe_2$ ligand is essentially planar and it is more bent (75.4°) with respect to the Pd(1) coordination plane than with the Pd(2) coordination plane (45.0°). Its distances C–S 1.723(9) Å ad C–N 1.296(10) Å involving the trigonal carbon atom C(37) have a partial double bond character which can be estimated to about 20% and 75% respectively [26–28].

These distances as well as the N–Me distances (1.462(12) and 1.466(12) Å) agree with those found in $[(MeO)_3P]_2Pd_2(Cl)_2(SCNMe_2)_2$ [29] and in other palladium complexes with thiocarbamic esters where a high double bond character has been postulated for these bonds [30, 31].

The Pd–S bond distance (2.294(2) Å) is significantly shorter than that found in the dimer $[(MeO)_3P)_2Pd_2Cl_2(CSNMe_2)_2]$ [29] (2.382(2) Å) where the two thiocarboxamido ligands bridge the two Pd through the C and S atoms and is also shorter than th sum of covalent radii 2.35 Å [28] but is in agreement with those reported for palladium complexes with thiocarbamic esters (see Table V).

The Pd(1)–C(37) bond distance (1.963(8) Å) is shorter than the sum of covalent radii for a Pd–C-(sp^2) (2.05 Å) [28] but falls within the range of the observed Pd–C(sp^2) distances in other palladium complexes [32] hence considering also the dihedral angle between the thiocarboxamido ligand and the coordination plane (75.4°) it appears that a π-bonding interaction between palladium and the σ-bonded ligand is small if at all.

The Pd(1)–P(1) and Pd(2)–P(2) bond lengths 2.266(3) and 2.244(2) Å respectively are among the shorter found in other Pd–PPh_3 complexes (2.23–2.35 Å) [32]. The triphenylphosphine geometry as judged by P–C distances and C–P–C angles ranging from 1.807(7) to 1.831(6) Å for the distances and from 103.0(3)° to 108.5(3)° for the angles, agrees with those found in many other complexes containing this ligand.

The palladium–(terminal chlorine) bond lengths are, as expected, significantly shorter than the palladium–(bridging chlorine) distances. Appropriate values are Pd(1)–Cl(1)T 2.356(3) Å, Pd(2)–Cl(2)T 2.330(2) Å and Pd(1)–Cl(3)B 2.453(2) Å Pd(2)–Cl(3)B 2.495 Å. In addition the Pd(1)–Cl(1)T distance *trans* to the C(37) carbon is slightly but significantly longer than Pd(2)–Cl(2)T *trans* to the sulphur, suggesting a higher *trans* influence of the carbon respect to the sulphur for this kind of ligand. We notice also that the chloro bridge is asymmetric, and a different *trans* effect on the two bond distances cannot be invoked as the Cl(3) is *trans* to both the triphenylphosphine ligands; but the Pd(1)–Cl(3) distance (2.453(2) Å) is shorter on the side where the *trans* influence of the carbon C(37) on Pd(1)–Cl(1)T is higher in comparison to the *trans* influence of the sulphur on the Pd(2)–Cl(2)T. This means that the carbon having a higher *trans*-influence has a lower *cis* influence and the reverse is valid for the sulphur. This ideal recalls the Syrkin's original *trans*-influence theory predicting that ligands of strong *trans* influence should yield a slight strengthening of the *cis* bond by rehybridization of the σ-bond framework [33].

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