Dialkylcarbamato Complexes of Palladium(II). Crystal Structure of *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$ *

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The reaction of $[Pd(MeCN)_4][BF_4]_2$ with NHR_2 (R = Et or Pr^i) and carbon dioxide in toluene led to the dialkylcarbamato complexes $[Pd(O_2CNR_2)_2(NHR_2)_2]$. The derivative *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$ was studied by X-ray diffraction methods. The square-planar geometry of the palladium atom involves one oxygen atom of each monodentate carbamato group and two amine nitrogen atoms. An intramolecular N–H • • • O bond is probably responsible for a further stabilization within the molecule, for the features of the IR bands associated with the carbamato ligand and for the ^{1}H NMR non-equivalence observed within the amine alkyl group at room temperature.

Previous work from these laboratories has shown that anhydrous metal halides react with secondary amines and CO_2 to give dialkylcarbamato complexes. However, until now, 3d, 4f and 5f systems, see refs. 1, 2 and 3, respectively, have been investigated and it was therefore of interest to extend this preparative procedure to 4d metals. We thus turned our attention to palladium, mainly because of the still limited number of palladium(II) complexes containing oxygen as donor ligands and their labile character.[4] It was anticipated that, in view of the relatively high palladium–halogen bond energy, palladium(II) compounds other than halides had to be used as starting substrates. This paper reports the synthesis of palladium(II) dialkylcarbamato complexes obtained by using $[Pd(MeCN)_4]^{2+}$ as starting material, the study of their reactivity and the crystal and molecular structure of the ethyl derivative, *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$. Part of this work was reported in a preliminary communication.[5]

Experimental

Unless otherwise stated, all operations were carried out under an atmosphere of prepurified dinitrogen. Solvents were dried according to conventional methods. Carbon dioxide (Rivoira, Chivasso, Torino) and H_2S (Matheson) were dried over $CaCl_2$. Nitrosyl tetrafluoroborate was a commercial product (Aldrich) purified by sublimation. The following compounds were prepared according to literature procedures: $[Pd(MeCN)_4][BF_4]_2$,[6] $[Pd(PPh_3)_4]$,[7] palladium black[8] and PdI_2.[9] Palladium(II) chloride was obtained by concentrating an aqueous solution of $[PdCl_4]^{2-}$ to a syrup and then adding $SOCl_2$; after stirring for several hours at room temperature the suspension was filtered and the anhydrous palladium chloride dried *in vacuo*. The secondary amines were distilled from sodium prior to use.

The IR spectra were measured with a Perkin-Elmer model 283 instrument equipped with a grating, NMR spectra with a Varian XL 100 instrument. Palladium analyses were carried out by combustion; the carbon dioxide content of the products was determined by decomposition of the compounds with a 20% aqueous solution of H_2SO_4.

Preparation of trans-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$ **1** *and* $[Pd(O_2CNPr^i_2)_2(NHPr^i_2)_2]$ **2**.—Diethylamine (63.0 mmol) in toluene (50 cm^3) was treated with carbon dioxide at room temperature. The complex $[Pd(MeCN)_4][BF_4]_2$ (2.82 g, 6.3 mmol) was then added at room temperature. A fast reaction was observed as indicated by the precipitation of $[NH_2Et_2][BF_4]$. The suspension was stirred at room temperature for about 12 h. After partial evaporation of the solvent, the reaction mixture was filtered, the filtrate evaporated to dryness and compound **1** was obtained as yellow microcrystals (2.82 g, 92% yield) (Found: C, 44.5; H, 8.8; N, 11.5; Pd, 21.6; CO_2, 18.0. Calc. for $C_{18}H_{42}N_4O_4Pd$: C, 44.6; H, 8.7; N, 11.6; Pd, 21.9; CO_2, 18.1%); *M*, 493 (485) by cryoscopy in benzene. The product is soluble in the common organic solvents and is apparently stable in air for short periods of time. IR spectrum [poly(chlorotrifluoroethylene) mull]: 3060m, 2985s, 2935s, 2870s, 1590m, 1555s, 1475s, 1455m, 1440w, 1410s, 1375s and 1325m cm^{-1}. ^{1}H NMR (25 °C, C_6D_6 with respect to $SiMe_4$): δ 1.04 (t, *J* = 7), 1.71 (m), 2.37 (m), 3.25 (q, *J* = 7 Hz) and 8.67 (s, br); at 60 °C the low-field resonance shifts to 8.51.

Compound **2**, somewhat contaminated with $[NH_2Pr^i_2][BF_4]$, was prepared in a similar way (45% yield) (Found: Pd, 16.6; CO_2, 13.2. Calc. for $C_{26}H_{58}N_4O_4Pd$: Pd, 17.8; CO_2, 14.7%); CO_2:Pd molar ratio = 2.0:1.

Unsuccessful attempts to prepare **1** were made with the following palladium substrates: $PdCl_2$, yield 74% $[PdCl_2(NHEt_2)_2]$; PdI_2, 83% $[PdI_2(NHEt_2)_2]$; $[Pd(PPh_3)_4]$ or palladium black, no reaction at room temperature or at 60–90 °C.

X-Ray Crystal Structure Determination of Complex **1**.—The compound was recrystallized from heptane at a temperature gradient from 40 to 0 °C. A crystal of approximate dimensions 0.47 × 0.59 × 0.62 mm was sealed in a glass capillary under an inert atmosphere. A computer-controlled Siemens AED single-crystal diffractometer was employed. Automatic peak-search

* *trans*-Bis(diethylamine)bis(diethylcarbamato-κ*O*)palladium(II).

Supplementary data available (No. SUP 56845, 5 pp.). Plots of potential energy *vs.* angle of rotation: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: cal = 4.184 J.

and indexing procedures in conjunction with a cell-reduction program yielded a monoclinic primitive cell and the systematic absences unambiguously established the space group as $P2_1/c$. The θ–2θ scan technique and Mo-Kα radiation were used to measure the intensity of 3176 reflections ($\pm h + k + l$) within the limits $3 < \theta < 27.5°$; equivalent reflections were averaged and those having $I < 2\sigma(I)$ were considered as unobserved leaving 1822 independent observed reflections for structure analysis. No loss of intensity of standard reflections was detected during the data collection. A modification of the Lehmann and Larsen procedure[10] was used to calculate the intensities from profile analysis. The data were corrected for Lorentz and polarization factors. During the refinement correction for absorption effects was made by the method of Walker and Stuart.[11,12]

Crystal data. $C_{18}H_{42}N_4O_4Pd$, M 484.96, monoclinic, space group $P2_1/c$, $a = 8.331(2)$, $b = 15.828(5)$, $c = 9.222(3)$ Å, $\beta = 93.43(2)°$, $U = 1213.9(6)$ Å^3, $Z = 2$, $D_c = 1.327$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 7.79 cm^{-1}, $F(000) = 512$; scan speed 0.04–0.2° s^{-1}; absorption correction (minimum, maximum) 0.7046, 1.1879; extinction correction (minimum, maximum), 0.9719, 1.1133. The experimental density of the compound was found to be between that of $ClCH_2CH_2Cl$ (1.26 g cm^{-3}) and that of $CHCl_3$ (1.48 g cm^{-3}).

The structure was solved by the conventional heavy-atom technique. Since there are two molecules in the unit cell and the space group $P2_1/c$ has four-fold general positions, the molecule is required to have a crystallographically imposed C_i symmetry with the palladium atom occupying the inversion centre. Such a situation is well reflected in the weakness of the hkl reflections with $k + l$ odd. A Fourier difference map phased on the position of the metal atom led to the location of all non-hydrogen atoms. Refinement was by full-matrix least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were allowed to vibrate anisotropically, the hydrogen atoms being placed at calculated riding positions and refined isotropically. A weighting scheme of the type $w = k/[\sigma^2(F_o) + gF_o^2)]$ with $k = 0.6508$ and $g = 0.001\,25$ was applied. Refinement converged to $R = 0.0320$ ($R' = 0.0426$, goodness of fit = 0.7315) for 145 variables refined, with the final cycle having all shift-to-error ratios less than 0.02:1. The final Fourier difference map contained two residual peaks of about 0.7 e Å^{-3} near the palladium atom, but was devoid of any other significant feature.

Neutral scattering factors were employed and the heavy atoms were corrected for anomalous dispersion effects, both real and imaginary.[13] Computing was performed on a 6040 Gould computer. Programs used were SHELX 76,[14] PARST[15a] and ORTEP.[15b] Fractional atomic coordinates of the non-hydrogen atoms are in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

The atom–atom non-bonded potential-energy calculations were carried out using a function of the exp-6-1 type: $E_{jk} = B_{jk}\exp(-C_{jk}r_{jk}) - A_{jk}r_{jk}^{-6}$, disregarding the coulombic energy and assuming the H atoms to be in calculated positions (C–H 1.07 Å). The ROTENER program[15c] was used.

Reactions of Complex **1**.—*With* CS_2. To a solution of complex **1** (0.70 g, 1.4 mmol) in toluene (50 cm^3) was added CS_2 (16.6 mmol) at room temperature. After a few minutes the colour turned from yellow to orange and a yellow microcrystalline solid precipitated. The IR spectrum of the supernatant had bands due to dissolved CO_2 (2340 cm^{-1}), while the bands of the starting palladium complex had disappeared. After stirring for 12 h the suspension was filtered, and the solid was dried *in vacuo*. A second crop of the product $[Pd(S_2CNEt_2)_2]$ was obtained by addition of heptane to the filtered solution (overall yield 72%). The product was characterized by IR spectroscopy, in comparison with an authentic sample.[16]

With H_2S. A toluene solution of complex **1** (50 cm^3), obtained from $[Pd(MeCN)_4][BF_4]_2$ (0.94 g, 2.1 mmol), $NHEt_2$ (21.3 mmol) and CO_2 in toluene (50 cm^3) at room temperature, after filtration of $[NH_2Et_2][BF_4]$ and removal of the excess of amine by evaporating 2/3 of the solution under reduced pressure, was treated with dry H_2S. After stirring for about 6 h the brick-red precipitate was collected by filtration (yield 78%). The product analysed correctly as $C_8H_{24}N_2PdS_2$ (calculated values in parentheses): C, 30.2 (30.1); H, 7.6 (7.6); N, 8.7 (8.8); Pd, 31.5 (33.4); S, 19.4 (20.1%). IR spectrum (Nujol mull): 3180m, 1260m, 1210m, 1150m, 1105m, 1070m, 1050(sh), 1045ms, 860m, 820m, 800(sh) (br) and 720m cm^{-1}.

With acetic anhydride. A solution of complex **1** (0.46 g, 0.95 mmol) in toluene (40 cm^3) was treated with acetic anhydride (2.1 mmol). After some minutes the progress of the reaction was monitored by IR spectroscopy, which showed the presence of CO_2 and *N*,*N*-diethylacetamide (1650 cm^{-1}), whereas the bands of the anhydride and of the starting palladium complex had disappeared. An excess of acetic anhydride (2 cm^3) was then added and the mixture was stirred for 12 h at room temperature. The solution was then completely evaporated *in vacuo*. To the oily brown residue heptane (30 cm^3) was added and the resulting solution was heated at 40 °C; by slow cooling to room temperature, yellow crystals of $[Pd(O_2CMe_2)(NHEt_2)_2]$ (yield 10%) were obtained, with a correct elemental analysis (C,H,N), and with an IR spectrum in agreement with that reported in the literature for the same substance obtained by a different route.[17] ^{1}H NMR (25 °C, C_6D_6, $SiMe_4$ as reference): δ 1.61 (m, 12 H), 1.95 (s, 6 H), 2.65 (m) and 7.35 (br s).

Results and Discussion

Displacement of the weak acetonitrile ligand from $[Pd(MeCN)_4][BF_4]_2$ led to *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$, according to equation (1). The best results were obtained by

$$[Pd(MeCN)_4][BF_4]_2 + 2CO_2 + 6NHEt_2 \longrightarrow trans\text{-}[Pd(O_2CNEt_2)_2(NHEt_2)_2] + 2[NH_2Et_2][BF_4] + 4MeCN \quad (1)$$

introducing the palladium–acetonitrile complex into a toluene solution of the amine presaturated with CO_2. On the other hand, if the palladium complex was contacted with diethylamine prior to the introduction of CO_2 some palladium metal was formed, presumably due to the reduction of palladium(II) to palladium(0) by the amine, in agreement with the literature.[18] On the contrary, in the presence of CO_2, the concentration of amine in equilibrium with $[NH_2Et_2][O_2CNEt_2]$ is reduced to a minimum and the secondary reaction is minimized.

The yellow diethylcarbamato complex of equation (1) shows a N–H stretching vibration at 3060 cm^{-1} attributed to co-ordinated amine. However, the lower wavenumber of this band with respect to both the free or co-ordinated amine[19] suggested that some hydrogen-bond interaction was involved. The compound was found to be monomeric in benzene and, moreover, the vibrations due to the co-ordinated carbamato group were found below 1600 cm^{-1}. This should be compared with the strong band observed at about 1710 cm^{-1} assigned to the C=O stretching vibration of the monodentate dialkylcarbamato group in $Si(O_2CNR_2)_4$.[20]

All these observations can be rationalized by assuming that the amine and the O_2CNEt_2 groups around palladium are involved in an intramolecular hydrogen bond, thus implying that the two groups occupy mutually *cis* co-ordination positions. In order to establish conclusively the molecular structure of compound **1**, an X-ray structural investigation was undertaken. The molecular structure is shown in Fig. 1, while Table 2 reports selected bond distances and angles.

Palladium has the usual square-planar co-ordination with the ligands in a *trans* centrosymmetric arrangement, with

Table 1 Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Pd	0	0	0
O(1)	666(3)	−1032(2)	1181(3)
O(2)	3328(4)	−1097(2)	921(3)
N(1)	2180(4)	−1930(2)	2549(4)
N(2)	2309(3)	429(2)	−194(4)
C(1)	2093(5)	−1320(2)	1495(4)
C(2)	3759(5)	−2230(3)	3091(5)
C(3)	4577(6)	−1691(4)	4252(5)
C(4)	740(5)	−2209(3)	3253(5)
C(5)	316(7)	−1655(4)	4506(6)
C(6)	2713(5)	1173(3)	710(5)
C(7)	2594(7)	989(4)	2304(6)
C(8)	2729(5)	583(3)	−1718(5)
C(9)	2497(8)	−197(3)	−2653(6)

Table 2 Selected bond distances (Å) and angles (°) for $[Pd(O_2CNEt_2)_2(NHEt_2)_2]$

Pd–O(1)	2.022(3)	C(2)–C(3)	1.501(7)
Pd–N(2)	2.058(3)	C(4)–C(5)	1.509(7)
O(1)–C(1)	1.290(5)	N(2)–C(6)	1.471(6)
O(2)–C(1)	1.236(5)	N(2)–C(8)	1.488(6)
C(1)–N(1)	1.370(5)	C(6)–C(7)	1.508(7)
N(1)–C(2)	1.459(5)	C(8)–C(9)	1.512(7)
N(1)–C(4)	1.467(6)		
O(1)–Pd–N(2)	94.9(1)	N(1)–C(2)–C(3)	114.9(4)
Pd–O(1)–C(1)	128.7(2)	N(1)–C(4)–C(5)	113.6(4)
O(1)–C(1)–O(2)	125.6(4)	Pd–N(2)–C(6)	113.5(2)
O(1)–C(1)–N(1)	114.7(4)	Pd–N(2)–C(8)	114.2(2)
O(2)–C(1)–N(1)	119.7(4)	C(6)–N(2)–C(8)	110.2(3)
C(1)–N(1)–C(2)	118.8(3)	N(2)–C(6)–C(7)	111.8(4)
C(1)–N(1)–C(4)	121.1(3)	N(2)–C(8)–C(9)	112.1(4)
C(2)–N(1)–C(4)	119.7(3)		

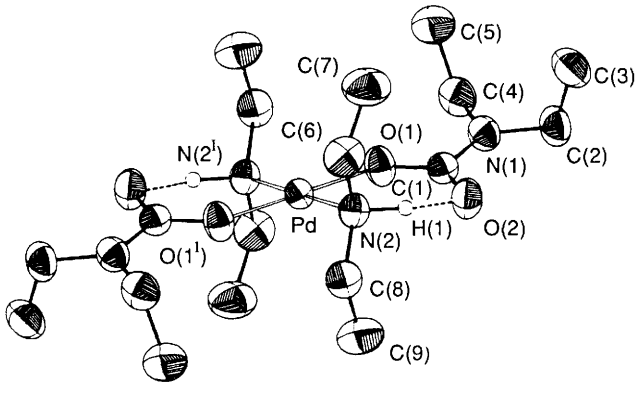


Fig. 1 An ORTEP view of *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$ with the numbering scheme used

monodentate diethylcarbamato groups. Extensive electron delocalization within the O(1)–C(1)–O(2)–N(1)–C(4)–C(2) system is clearly evidenced by the observation that the first five atoms of the sequence lie on the same plane, C(2) deviating only by about 0.15 Å, corresponding to a rotation of 6.5(4)° of the O(1)–C(1)–O(2) plane with respect to N(1)–C(4)–C(2). Also the C(1)–N(1) distance of 1.370(5) Å is considerably shorter than the single C–N bonds of the co-ordinated amine [N(2)–C(6) 1.471(6), N(2)–C(8) 1.488(6) Å], thus suggesting electron delocalization to some extent within the carbamato group.

The crystals are built up from discrete molecules, the shortest non-hydrogen intermolecular distance being O(2)···C(8) $(1-x, -y, -z)$ 3.421(5) Å.

The bonding situation between the *cis* diethylcarbamato and diethylamine ligands is of considerable interest. The distance between the unco-ordinated oxygen of the monodentate carbamato group and the nitrogen atom of the co-ordinated amine, *i.e.* N(2)···O(2), is 2.740(4) Å, which is shorter than the sum of the van der Waals radii (2.90 Å)[21] and similar to the N···O distances found in $[NH_4]_2[H_3IO_6]$ (2.86 Å)[22] or in cyanuric acid (1,3,5-triazine-2,4,6-trione) (2.79 Å),[23] where hydrogen bonding is suggested to occur. In the present compound the N(2)–H···O(2) angle is 154°. The Pd–O distance of 2.022(3) Å is among the longest found in oxygen-co-ordinated palladium(II) square-planar complexes. As shown by a literature search carried out by means of the Cambridge Crystallographic Database Files, the ranges of Pd–O and Pd–N bond distances in square-planar palladium(II) complexes having two oxygen and two nitrogen donor atoms are 1.961–2.029 and 1.960–2.071 Å, respectively. The Pd–O distances in $Pd(O_2CMe)_2$ range[24] from 1.973(9) to 2.014(9) Å. The unco-ordinated carbamato oxygen atom is far away from the palladium atom, the O(2)···Pd contact amounting to 3.338(3) Å. Accordingly, O(2) has slightly larger thermal ellipsoids than O(1), and the O(2)–C(1) distance is shorter than O(1)–C(1) by a significant 0.05 Å. Both the short N···O distance and the long Pd–O distances are believed to be consistent with the presence of an intramolecular hydrogen bond. A useful comparison can be made with the parameters found[25] for the somewhat related complex $[Pd(SOCNPr_2)_2(NHPr_2)_2]$: in this case the sulphur-bonded monodentate thiocarbamato ligand is part of a Pd–S–C=O···H–N sequence forming a substantially planar six-membered ring system. A similar situation can be observed in our compound for the corresponding Pd–O–C=O···H–N sequence. The ring system is relatively rigid. It shows some degree of puckering, the maximum deviation from the plane of best fit being 0.19 Å.

The van der Waals potential-energy profile for rotation of the diethylcarbamato group around the C(1)–O(1) bond shows that the minimum does not correspond to the observed conformation in the crystal, but is shifted by about 30°, see SUP 56845. This is probably due to the fact that the calculation does not take into consideration the presence of the intramolecular hydrogen bond, which should sensibly lower the energy minimum.

The IR and the ^1H NMR data can be interpreted on the basis of the solid-state parameters. The diethylcarbamato complex has IR vibrations, associated with the O_2CNEt_2 moiety, between 1590 and 1325 cm^{-1}. The absence of bands above 1600 cm^{-1} is consistent with the presence of the intramolecular hydrogen bond: the upper limit of a substantially pure C=O stretching vibration for a monodentate diethylcarbamato group is represented by the compound $Si(O_2CNEt_2)_4$ which shows a strong absorption at 1710 cm^{-1}.

The ^1H NMR spectrum of *trans*-$[Pd(O_2CNEt_2)_2(NHEt_2)_2]$ in C_6D_6 at room temperature shows four resonances centred at δ 1.04, 1.71 (multiplet), 2.37 (multiplet) and 3.25 besides one at δ 8.67 (NH), as specified in the Experimental section. The triplet at δ 1.04 and the quartet at δ 3.25 can easily be attributed to equivalent methyl and methylene groups, respectively. In order to assign the proton resonances of the carbamato complex, the ^1H NMR spectrum of *trans*-$[Pd(O_2CMe)_2(NHEt_2)_2]$[17] was also measured under comparable conditions [δ 1.61 (m), 1.95 (s), 2.65 (m) and 7.35 (s) (NH)]. The multiplets at δ 1.61 and 2.65 must originate from the ethyl groups, respectively, of the amino ligand, thus implying that in our carbamato complex the multiplets at δ 1.71 and 2.37 should be due to the methyl and methylene groups, respectively, of the amino ligand. We believe that the observed NMR spectrum of complex **1** can be accommodated by the rather rigid situation within the hydrogen-bonded six-membered ring system: the hydrogen bond presumably prevents free rotation around the Pd–N(2) bond, thus making the methyl and the methylene groups diastereotopic.[26] On the other hand, the rotation around the

O_2C–NEt_2 bond should be relatively fast at room temperature, thus making the methyl and methylene protons of the carbamato ligand equivalent on the NMR time-scale. *Calculation of* the van der Waals potential energy for rotation of the NEt_2 fragment around the C(1)–N(1) bond shows the presence of two minima, symmetrical at $\pm 90°$ with respect to the conformation observed in the solid state, see SUP 56845. The corresponding energy barrier is about 12 kJ mol^{-1}, which can easily be overcome, in agreement with the NMR data.

Attempts were also made to prepare the isopropyl derivative *trans*-$[Pd(O_2CNPr^i_2)_2(NHPr^i_2)_2]$ by a reaction similar to (1), using $NHPr^i_2$ instead of $NHEt_2$. In this case, owing to the relatively higher solubility of $[NH_2Pr^i_2][BF_4]$, the palladium(II) complex was contaminated by the co-product. However, the analytical and IR data leave little doubt as to the nature of the isopropyl derivative.

The preparation of the diethylcarbamate was unsuccessfully attempted by several other routes, starting from other palladium(II) or palladium(0) materials. Of particular significance is the failure of the $PdCl_2$–$NHEt_2$–CO_2 system, the amine adduct $[PdCl_2(NHEt_2)_2]$ being the only observed product. This contrasts with the smooth reaction observed in the $PdCl_2$–$NHEt_2$–CS_2 system which gave the known[16] diethyldithiocarbamato complex $[Pd(S_2CNEt_2)_2]$. The latter has been prepared[16] by treating $PdCl_2$ with $NHEt_2$ and CS_2 in an aqueous medium. An X-ray diffractometric experiment showed the compound to be monomeric with bidentate terminal dithiocarbamato groups. The larger bite of the S_2CNEt_2 group with respect to O_2CNEt_2 should explain the different stoichiometries in the two cases.

The different behaviour observed in the $PdCl_2$–$NHEt_2$–CX_2 system on going from X = O to X = S is believed to be due to purely thermodynamic factors. In this connection, it is important to realize that the $\Delta G_f°$ of CX_2[27] is −94.3 and +15.6 kcal mol^{-1} for X = O and S respectively, thus making the tendency for the oxygen-containing species to undergo reaction much lower.

The diethyldithiocarbamato complex $[Pd(S_2CNEt_2)_2]$ can be prepared by the exchange reaction (2), which is believed to occur through the intermediate formation of the diethyldithiocarbamato anion, see equation (3), followed by O_2CNR_2/

$$[Pd(O_2CNR_2)_2(NHR_2)_2] + 2CS_2 \longrightarrow [Pd(S_2CNR_2)_2] + 2NHR_2 + 2CO_2 \quad (2)$$

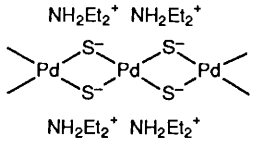
$$CS_2 + 2NHR_2 \rightleftharpoons [NH_2R_2][S_2CNR_2] \quad (3)$$

S_2CNR_2 exchange. This is confirmed by the observation that reaction (2), R = Pr^i, is considerably accelerated by the addition of $NHPr^i_2$. When free amine is not added, some may become available by partial hydrolysis due to adventitious water or by dissociation from the starting palladium complex.

In agreement with the general reactivity pattern observed with dialkylcarbamato complexes studied earlier,[28,29] compound **1** reacts with a number of electrophilic reagents with evolution of CO_2. The reaction with dry H_2S produces a red compound analysing as $[Pd(SH)_2(NHEt_2)_2]$ or, alternatively $[NH_2Et_2]_2[PdS_2]$, obtained according to equation (4). Two

$$[Pd(O_2CNEt_2)_2(NHEt_2)_2] + 4H_2S \longrightarrow 2CO_2 + C_8H_{21}N_2PdS_2 + 2[NH_2Et_2][HS] \quad (4)$$

structures are possible for this compound, **A** or **B**, an anionic sulphido-bridged aggregate and a monomeric hydrogensulphido complex, respectively. The IR spectrum of this new palladium(II) compound shows an intense band at 3180 cm^{-1} attributed to the N–H stretching vibration of co-ordinated amine. On the other hand, the intense bands of the $[NH_2Et_2]^+$ cation at 2780, 2770, 2480 and 2395 cm^{-1} were not observed. On



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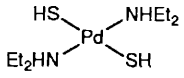

B

the basis of the spectroscopic data and of the moderate solubility in some organic solvents, structure **B** is preferred. The failure to observe the S–H stretching vibration of the co-ordinated SH groups at about 2550 cm^{-1} is not considered to invalidate the structural proposal because these bands are usually very weak and sometimes not observed.[30] A confirmation of the presence of SH groups in the complex came from its ^1H NMR spectrum (freshly prepared solutions in CD_2Cl_2), showing a signal at δ −1.69.[30b,31] Some hydrogensulphido complexes of transition elements containing either terminal[32] or bridging[33] SH groups have been reported.

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