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Synthesis of palladium(II) and platinum(II) *N,N*-dialkyldithiocarbamates starting from hydroxo-halophenyl complexes

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Abstract

In dichloromethane, the hydroxo-complexes $[NBu_4]_2[\{M(C_6X_5)_2(\mu\text{-}OH)\}_2]$ [M = Pd (X = F or Cl) or Pt (X = F)] and $[\{Pd(C_5X_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (X = F or Cl) react with amines in the presence of carbon disulfide to give the corresponding dithiocarbamate complexes $[NBu_4][M(C_6X_5)_2(S_2CNR_2)]$ [M = Pd, X = F and R = Me (**I**), Et (**II**), or C_4H_8 (**III**); M = Pd, X = Cl and R = Me (**IV**) or Et (**V**); M = Pt, X = F and R = Me (**VI**) or Et (**VII**)] and $[Pd(C_6X_5)(PPh_3)(S_2CNR_2)]$ [X = F and R = Me (**VIII**) or Et (**IX**); X = Cl and R = Me (**X**) or Et (**XI**)]. Conductance measurements and spectroscopic (IR, ^1H and ^{19}F NMR) methods have been used for structural assignments.

Introduction

A general method for the preparation of dithiocarbamato-complexes is based on the reaction of a transition-metal halocomplex with the alkali dithiocarbamate [1–3] and some organometallic dithiocarbamato-complexes of palladium(II) and platinum(II) have recently been synthesised through the reaction between the corresponding halodithiocarbamato-complex and the organolithium or Grignard reagent [4].

On the other hand, we have recently reported the preparation of some dithiocarbamato-complexes of nickel(II) [5] based on a different synthetic strategy: the reaction of the binuclear organohydroxo-complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with an amine in the presence of carbon disulfide. The experimental results reported in this paper demonstrate that this method is of general application and some dithiocarbamato-palladium(II) and platinum(II) complexes have been obtained starting from $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Pd or Pt and R = C_6F_5 or C_6Cl_5). Similar results are obtained with $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$.

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Experimental

C, H, N and S analyses were performed with a Carlo Erba Model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance. Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Philips PW 9501/01 conductimeter. The spectroscopic instruments were a Perkin–Elmer Model 1430 for IR spectra (as Nujol mulls) and a Varian Unity 300 for NMR spectra, with $SiMe_4$, 85% H_3PO_4 and $CFCl_3$ as external references for ^1H, ^{31}P and ^{19}F, respectively.

The starting compounds $[NBu_4]_2[\{M(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd, X = F [6] or Cl [7]; M = Pt, X = F [8]) and $[\{Pd(C_6X_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (X = F or Cl [9]) were prepared as described elsewhere.

Bis(pentafluorophenyl)dithiocarbamato-complexes (I–III, VI and VII)

In separate experiments, the stoichiometric amount (0.128 mmol) of the corresponding amine was added to a solution or suspension of $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.0634 mmol) in methanol (5 cm^3) and carbon disulfide (0.128 mmol). The solution was stirred at room temperature for 1 h, then concentrated under reduced pressure. Addition of water caused the precipitation of the desired complex which was filtered off and air-dried. Yield: 70–80%.

NMR data [solvent $(CD_3)_2CO$]. Complex **I**: ^1H δ 3.23 (s, 6H, CH_3); ^{19}F δ −111.1 (d, $4F_o$, $J_{om} = 26.8$ Hz), −165.8 (t, $2F_p$, $J_{mp} = 19.8$ Hz), −166.5 (m, $4F_m$). Complex **II**: ^1H δ 3.73 (q, 4H, CH_2, $J = 7.1$ Hz), 1.20 (t, 6H, CH_3, $J = 7.1$ Hz); ^{19}F δ −111.0 (d, $4F_o$, $J_{om} = 24.8$ Hz), −165.9 (t, $2F_p$, $J_{mp} = 19.8$ Hz), −166.6 (m, $4F_m$). Complex **III**: ^1H δ 3.59 (t, 4H, $J = 6.8$ Hz), 2.05 (4H overlapped); ^{19}F δ −111.1 (d, $4F_o$, $J_{om} = 27.9$ Hz), −165.9 (t, $2F_p$, $J_{mp} = 19.6$ Hz), −166.1 (m, $4F_m$). Complex **VI**: ^1H δ 3.17 (s, 6H, CH_3); ^{19}F δ −115.1 (d, $4F_o$, J_{om} 26.5 Hz; $J(Pt\text{–}F_o) = 478$ Hz), −167.8 (m, $2F_p + 4F_m$). Complex **VII**: ^1H δ 3.63 (q, 4H, CH_2, $J = 8.0$ Hz), 1.23 (t, 6H, CH_3, $J = 8.0$ Hz); ^{19}F δ −115.1 (d, $4F_o$, $J_{om} = 26.5$ Hz; $J(Pt\text{–}F_o) = 477$ Hz), −167.8 (m, $2F_p + 4F_m$). Additional peaks from $[NBu_4]^+$ are found in the ^1H spectra of **I–III**, **VI** and **VII**.

Bis(pentachlorophenyl)dithiocarbamato-complexes (IV and V)

To a solution of $[NBu_4]_2[\{Pd(C_6Cl_5)_2(\mu\text{-}OH)\}_2]$ (0.079 mmol) in dichloromethane (10 cm^3) was added the corresponding amine (0.158 mmol) and carbon disulfide (0.158 mmol). The solution was stirred for 1 h and then evaporated to dryness *in vacuo*. The residue was treated with hexane, filtered off and air-dried. Yield: 75–85%.

NMR data (solvent $CDCl_3$). Complex **IV**: ^1H δ 3.23 (s, 6H, CH_3). Complex **V**: ^1H δ 3.69 (q, 4H, CH_2, $J = 7.1$ Hz), 1.20 (3H, CH_3, overlapped). Additional peaks from $[NBu_4]^+$ are found in the ^1H spectra of **IV** and **V**.

Mono(halophenyl)dithiocarbamato-complexes (VIII–XI)

Carbon disulfide (0.181 mmol) was added to a dichloromethane solution (10 cm^3) containing $[\{Pd(C_6X_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (0.0905 mmol) and the corresponding amine (0.181 mmol). After stirring the solution for 30 min, the solvent was partly evaporated under reduced pressure. Addition of hexane caused the precipitation of the complex which was filtered off and air-dried. Yield: 70–85%.

NMR data. Complex VIII (solvent CDCI3): lH ~ 7.6-7.4 (m, 15H, Ph), 3.33 (s, 3H, CH3), 3.28 (s, 3H, CH3); 31p t~ 30.3 (s); 19F ~ - 114.4 (d, 2Fo, *Join* = 23.1 Hz), -163.0 (t, Fp, *Jmp* = 19.5 Hz), -164.2 (m, 2F,,). Complex IX (solvent (CD3)2CO): IH ~ 7.6-7.4 (m, 15H, Ph), 3.70 (m, 4H, CH2), 1.27 (t, 3H, CH3, J = 7.2 Hz), 1.23 (t, 3H, CH3, J = 7.2 Hz); 31p t~ 30.1 (s); 19F t~ -114.4 (d, 2Fo, *Join* = 27.4 Hz), - 163.0 (t, Fp, *Jmp* = 19.5 Hz), - 164.2 (m, 2Fro). Complex X (solvent CDCI3): tH t5 7.6-7.3 (m, 15H, Ph), 3.30 (s, 3H, CH3), 3.24 (s, 3H, CH3); 31p t~ 29.6 (s). Complex XI (solvent CDCI3): IH ~ 7.6-7.2 (m, 15H, Ph), 3.69 (m, 4H, CH2), 1.23 (t, 3H, CH3, J = 7.1 Hz), 1.18 (t, 3H, CH3, J = 7.1 Hz); 31p t~ 29.4 (s).

Results and discussion

The formation of the bis(pentahalophenyl)dithiocarbamato-complexes I-VII takes place in dichloromethane or methanol according to eq. 1.

[NBU4]E[(C6X5)2M(/~-OH)2M(C6X5)2] + 2RENH + 2CS2)

[C6X 5~ / S..-~]
2[NBu4] | /M~ ~C--NR2| +2H20 (1)
LC6X5 S" J

M = Pd; X = F; R = Me (I), Et (II) or C4H 8 (HI)
M =Pd; X -- Cl; R = Me (IV) or Et (¥)
M=Pt;X--F; R=Me(VI) orEt(VII)

The neutral complexes VIII-XI are likewise obtained in dichloromethane when the mono(pentahalophenyl)di-/~-hydroxo-complex is used as starting material (eq. 2).

[(C6Xs)(PPha)Pd(/~-OH)EPO(PPh3)(C6Xs)] + 2R2NH + 2CS2)

2[C6X5~ Pd/ S.~,...]
[PPh3/ ~S "~'C-NR2] + 2H20 (2/

X = F; R = Me (VIII) or Et (IX)
X = CI; R = Me (X) or Et (XI)

Recent work has demonstrated the ability of the complexes [{M(C6Xs)2(~-OH)2]2- [X = F (M = Ni [10], Pd [6], or Pt [8]) or CI (M = Pd [7]) to act as deprotonating agents towards some protic electrophiles. Most probably the reaction of these hydroxo-complexes with the amine R2NH generates R2N- with concommitant release of water, and the carbon disulfide present in the reaction medium should undergo nucleophilic attack by R2N- to give the dithiocarbamate anion which is subsequently trapped by the organometallic moiety M(C6Xs) 2 to form complexes l-XI.

Partial elemental analyses and decomposition temperatures for all the complexes are given in Table 1. In acetone solution, they behave as 1:1 electrolytes [11] (complexes I-VII) or non-conducting (complexes VII-XI) compounds, in agreement with the proposed formulae. The pentafluorophenyl derivatives (I-III and VI-IX) show IR absorptions characteristic of the C6F5 group (1630m, 1490vs,

Table 1

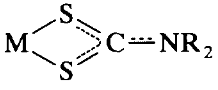
Analyses, decomposition temperatures, conductances and IR data for the dithiocarbamato complexes

	Complex [a]	Analysis (%) [b]				M.p. [c] (°C)	Λ_M [d]	IR bands (cm^{-1})	
		C	H	N	S			ν(C=N)	ν(C=S)
I	Q[Pd(C_6F_5)$_2$(S_2CNMe_2)]	46.2 (46.4)	5.4 (5.3)	3.4 (3.5)	7.8 (8.0)	247	93	1530s	970m
II	Q[Pd(C_6F_5)$_2$(S_2CNEt_2)]	47.6 (47.7)	5.6 (5.6)	3.2 (3.4)	7.6 (7.7)	247	94	1500sh	990m
III	Q[Pd(C_6F_5)$_2$($S_2CN(CH_2)_4$)]	47.5 (47.8)	5.4 (5.3)	3.5 (3.4)	7.5 (7.7)	247	95	1500sh	990m
IV	Q[Pd(C_6Cl_5)$_2$(S_2CNMe_2)]	38.5 (38.5)	4.6 (4.4)	3.0 (2.9)	6.3 (6.6)	224	96	1510s	980m
V	Q[Pd(C_6Cl_5)$_2$(S_2CNEt_2)]	39.5 (39.8)	5.0 (4.7)	3.0 (2.8)	6.5 (6.4)	226	91	1500sh	990m
VI	Q[Pt(C_6F_5)$_2$(S_2CNMe_2)]	41.8 (41.7)	4.7 (4.7)	3.0 (3.1)	7.0 (7.2)	261	98	1530s	975m
VII	Q[Pt(C_6F_5)$_2$(S_2CNEt_2)]	43.0 (43.1)	5.1 (5.0)	2.9 (3.0)	6.7 (7.0)	277	102	1500sh	990m
VIII	[Pd(C_6F_5)(PPh_3)(S_2CNMe_2)]	49.1 (49.4)	3.3 (3.2)	2.0 (2.1)	9.8 (9.8)	311		1535s	970m
IX	[Pd(C_6F_5)(PPh_3)(S_2CNEt_2)]	50.8 (50.9)	3.8 (3.7)	1.9 (2.0)	9.2 (9.4)	293		1510s	995m
X	[Pd(C_6Cl_5)(PPh_3)(S_2CNMe_2)]	44.0 (43.9)	2.9 (2.9)	2.1 (1.9)	8.8 (8.7)	296		1530s	970m
XI	[Pd(C_6Cl_5)(PPh_3)(S_2CNEt_2)]	45.2 (45.5)	3.4 (3.3)	1.6 (1.8)	8.2 (8.4)	304		1510s	995m

[a] Q = NBu_4. [b] Calculated values in parentheses. [c] With decomposition. [d] Ohm^{-1} mol^{-1} cm^2.

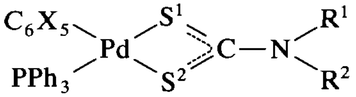
1050s, 950vs and 790–770s cm^{-1}) [12] and the pentachlorophenyl derivatives (**IV**, **V**, **X**, **XI**) those attributed to the C_6Cl_5 group (1315vs, 1285vs, 1220s, 830–820m, 670s and 610–600m cm^{-1}) [13]. The IR absorption at approx. 780 (**I–III**) or 790 (**VI**, **VII**) cm^{-1} is a split band characteristic of the *cis* geometry of the $M(C_6F_5)_2$ fragment [14]. Similarly, the *cis*-$Pd(C_6Cl_5)_2$ moiety must also be present in complexes **IV** and **V** because of the split bands at 830 and 610 cm^{-1} [13]. As expected, no splitting of these bands is observed for the mono(pentahalophenyl) derivatives.

The most relevant IR absorptions of coordinated dithiocarbamate are those originating from the thioureide group. The stretching vibration of the C–S bonds [15–19] in the complexes reported here are at 1535–1500 and 995–970 cm^{-1} (Table 1). The presence of only one band for ν(C–S) is consistent with bidentate coordination of the dithiocarbamate [20,21]. Since the ν(C=N) and ν(C–N) modes are usually found at 1690–1640 and 1350–1250 cm^{-1} [22], the thioureide band at 1535–1500 cm^{-1} indicates that the C–N bond in the coordinated $(S_2CNR_2)^-$ has considerable double bond character, as represented by structure **A**.

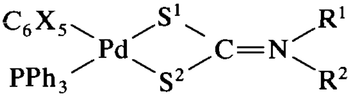


(**A**)

The ^{19}F spectra of the bis(pentafluorophenyl)palladium derivatives are consistent with two equivalent C_6F_5 rings freely rotating around the carbon–metal bond, which supports the assignment of bidentate dithiocarbamate. The same is true of the corresponding platinum complexes but in this case the *para*- and *meta*-fluorine signals overlap and the *ortho*-fluorine resonance shows ^{19}F–^{195}Pt satellites. As a consequence of the different ligands C_6F_5 and PPh_3 in the mono(pentahalophenyl)complexes **VIII–XI** the sulfur atoms are not equivalent (S^1 and S^2 in structures **B** and **C**).



(**B**)



(**C**)

The two R groups (R^1 and R^2) are magnetically inequivalent only if rotation of the NR^1R^2 group around the C–N bond is hindered, as in **C**. Complexes **VIII–XI** show different ^1H resonances for the Me groups, indicating that there is a significant contribution of the Lewis structure **C** to the resonance hybrid. The same is observed for the CH_2 groups in complexes **IX** and **XI** but the small differences between the chemical shifts cause overlapping of the expected two quartets.

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