Inorganica Chimica Acta, 24 (1977) 261–267

Mixed Ligand Monothio- and Dithiocarbamato Complexes of Palladium(II)

J. G. M. VAN DER LINDEN, W. BLOMMERDE, A. H. DIX and F. W. PIJPERS

Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

Received February 15, 1977

The complexes $[(Ph_2dtc)Pd(R_2mtc)_2Pd(Ph_2dtc)]$, $Pd(R_2mtc)(R'_2dtc)(PPh_3)$ *and* $Pd(az)(R_2mtc)$ *have been prepared (az = azobenzene-2-C,N; R = methyl,* R_2 *= pyrrolidyl, piperidyl and R′ = phenyl, ethyl, butyl). Infrared data reveal that in the solid state the* $[(Ph_2dtc)Pd(R_2mtc)_2Pd(Ph_2dtc)]$ *complexes are dimers, bridged by the sulfur atoms of the monothiocarbamate ligand. In organic solvents these complexes dissociate giving a monomer–dimer equilibrium, which is studied by* ^1H *and* ^{13}C *nmr spectroscopy. The equilibrium constants and the dissociation enthalpies were calculated from these measurements. In the monomers* $Pd(R_2mtc)(Ph_2dtc)$ *and in the* $Pd(az)(R_2mtc)$ *complexes the thiocarbamate ligand is bidentate bonded with the palladium ion through the oxygen and the sulfur atom, whereas in the compounds* $Pd(R_2mtc)(R_2dtc)PPh_3)$ *the monothiocarbamate acts as a monodentate ligand bonded through the sulfur atom only. The activation energy and activation entropy of the hindered rotation around the C*$\simeq$*N bond of the thiocarbamate ligand have also been determined from* ^1H *nmr measurements. It is shown that the alkyl substituent of the thiocarbamate ligand has a much larger influence on the values of the activation energies than the coordination mode of this ligand,* i.e. *whether the ligand is monodentate or bidentate bonded with the metal ion.*

Introduction

Marked differences between sulfur and oxygen as ligating donor atoms can be well demonstrated by studying the differences in chemical and structural properties of thio- and dithiocarbamato complexes.

The dithiocarbamates form in most cases simple bis, tris and tetrakis chelate complexes and they are remarkable in the way they can stabilize metals in high oxidation states [1].

Contrary to this the thiocarbamate ligand generally coordinates with metals in low oxidation states and can act (i) as a monodentate ligand*, *e.g.* in $Zn(R_2mtc)_2(R_2NH)_2$ [2], $Mn(CO)_5(R_2mtc)$ [3], $(Ph_3P)_2Rh(CO)(R_2mtc)$ [4, 5], $(Ph_3P)_2Pd(R_2mtc)_2$ [6], $Me_3Sn(Me_2mtc)$ [7], $Ph_3PAg(R_2mtc)$ [8], $Ph_3PAu(R_2mtc)$ [4], and recently in $Co(acac)_2(R_2mtc)(R_2NH)$ [9], in which complexes the thiocarbamate is bonded through the sulfur atom. Only in $Me_3Si(R_2mtc)$ it is supposed that the monothiocarbamate is monodentate bonded through the oxygen [10]. (ii) as a bidentate ligand in $Ti(Et_2mtc)_4$ [11], $Co(R_2mtc)_2(NHR_2)_2$ [12] and $Mn(CO)_4(R_2mtc)$ [3]. (iii) as a bidentate ligand with the sulfur atom bridging adjacent metal ions giving dimeric complexes as $[(R_2mtc)Mn(CO)_3]_2$ [3, 13], hexameric complexes as $[Ni(R_2mtc)_2]_6$ [14, 15] and oligomers of Zn(II), Cd(II) and Hg(II) [16]. (iv) and as a sulfur bridged monodentate ligand in $[(R_2mtc)Rh(CO)_2]_2$ [5].

The various possibilities for these different types of ligand bonding have been confirmed by crystal and molecular structure determinations of thiocarbamato complexes of Zn [2], Ti [11], Co [12], Ni [14], Cu [17] and Ag [18].

As an indication of the type of bonding the values of the coupled carbon–oxygen and carbon–nitrogen stretching vibrations have been used, appearing in the infrared spectra in the region 1525–1650 cm^{-1}. From the collected values (Table I) it may be concluded that this criterion should be handled with great care.

Recently we reported values for the free energy of activation for the hindered rotation around the C$\simeq$N bond for triphenylphosphine goldthio- and selenocarbamates [4]. This parameter may be also a criterion to decide between monodentate or bidentate coordination of the thiocarbamate ligand. It is therefore of interest to extend these investigations. This paper describes the preparation of some thiocarbamato complexes of palladium(II). Infrared data and kinetic parameters of the hindered rotation around the C$\simeq$N bond of the monothiocarbamate ligand are also presented.

---

*Abbreviations used in this paper: Me, methyl; Et, ethyl; pyr, pyrrolidine; pip, piperidine; py, pyridine; Ph, phenyl; R_2mtc, N,N-di-alkylthiocarbamate; R_2dtc, N,N-di-alkyldithiocarbamate; AzH, azobenzene; bzaH, benzylidene aniline; benzH, N,N-dimethylaniline.

TABLE I. ν (C$\stackrel{\cdots}{-}$O), (C$\stackrel{\cdots}{-}$N) Frequencies at Thiocarbamate Complexes.

Complex		References
Monodentate Coordinated Thiocarbamates		
Zn(pipmtc)$_2$(pipH)$_2$	1575, 1565	2
Mn(CO)$_5$(R$_2$mtc)	1600	3
Co(acac)$_2$(R$_2$mtc)(R$_2$NH)	1575	9
Rh(CO)(PPh$_3$)$_2$(R$_2$mtc)	1565	4, 5
Pd(R$_2$mtc)(PPh$_3$)$_2$	1580, 1570	6
Pd(R$_2$mtc)(R$_2$dtc)(PPh$_3$)	1585	this work
Me$_3$Sn(Me$_2$mtc)	1621	7
Ag(R$_2$mtc)(PPh$_3$)	1590	8
Au(R$_2$mtc)(PPh$_3$)	1595, 1590	4
Au(Ph$_2$mtc)(PPh$_3$)	1620, 1590	4
Bidentate Coordinated Thiocarbamate		
Ti(Et$_2$mtc)$_4$	1547, 1530	11
Co(pyrmtc)$_2$(pyrH)$_2$	1565, 1515	12
Mn(CO)$_4$(R$_2$mtc)	1540	3
Pd(az)(R$_2$mtc)	1550	this work
Bidentate Coordinated and Sulfur Bridged Thiocarbamate		
[Mn(CO)$_3$(R$_2$mtc)]$_2$	1585	3, 13
[Ni(R$_2$mtc)$_2$]$_6$	1525–1566	14, 15
Monodentate Sulfur-bridged Thiocarbamate		
[(R$_2$mtc)Rh(CO)$_2$]$_2$	1660	5
[(R$_2$mtc)Pd(Ph$_2$dtc)]$_2$	1650	this work

Results and Discussion

Pd(az)(R$_2$mtc) Complexes

The reaction in tetrahydrofuran of the thiocarbamate ligand with the chloro bridged complexes of the type [ClPd(C–N)]$_2$ [20] (N–C = chelating ligands with nitrogen and carbon donor atoms) depends on the nature of the chelating ligand. With [ClPd(az)]$_2$ (az = azobenzene-2-C,N) monomeric complexes Pd(az)(R$_2$mtc) (R = methyl, pyrrolidyl and piperidyl) were obtained.

The complexes Pd(az)R$_2$mtc) are monomeric with the thiocarbamate ligand bidentate coordinated. This conclusion is drawn from the molecular weight determinations (Table VII) and the relatively low (1550 cm^{-1}) coupled ν(C$\stackrel{\cdots}{-}$O), (C$\stackrel{\cdots}{-}$N) (Table II). The same value has been reported recently for Co(R$_2$mtc)$_2$-(NHR$_2$)$_2$ in which complex the bidentate coordination is proven by a crystal structure determination [12]. Furthermore an intense band appeared around 550 cm^{-1} in the infrared spectrum which is assigned to the palladium–oxygen stretching vibration [15a]. Palladium–sulfur stretching vibrations are located at 380 cm^{-1} as is usually found.

In the ^{1}H nmr spectrum at –30 °C the methyl groups of the thiocarbamate ligand in the Pd(az)-(Me$_2$mtc) complex show two signals of equal intensity 10 Hz apart (Table III). Upon increasing the temperature the two signals coalesce and at about 85 °C only one signal is observed due to rapid rotation of the –N(CH$_3$)$_2$ group around the partially double C$\stackrel{\cdots}{-}$N bond.

The ^{1}H nmr spectra for the Pd(az)(R$_2$mtc) complexes, R$_2$ = pyr, pip, have been measured in the temperature range –60 °C–+150 °C in CDCl$_3$ and C$_6$-D$_5$Br solutions. However, no fluxional behaviour could be observed for these complexes, because of the unobservable small difference in chemical shift between the α-protons of the ring. In the ^{13}C spectra two signals for these α-CH$_2$ groups are observed at room temperature in CDCl$_3$ solutions (Table IV), which indicates that slow rotation occurs at this temperature.

TABLE II. Infrared Spectral Data, cm^{-1}.

Complex	ν (C$\stackrel{\cdots}{-}$O) (C$\stackrel{\cdots}{-}$N) mtc	ν (C$\stackrel{\cdots}{-}$N) dtc	ν (C$\stackrel{\cdots}{-}$S) mtc	ν (Pd–S) dtc	ν (Pd–Cl)
[ClPdaz]$_2$	–				263
[ClPdEt$_2$dtc]$_2$	–	1536	–	374, 350	310
[ClPdPh$_2$dtc]$_2$	–	1428, 1394	–	363, 347	275
[Me$_2$mtcPdPh$_2$dtc]$_2$	1647	1410	678	350, 332	
[pyrmtcPdPh$_2$dtc]$_2$	1655	1390	665	375, 348	
[pipmtcPdPh$_2$dtc]$_2$	1648	1395	669	365, 349	
[Ph$_2$mtcPdPh$_2$dtc]$_2$	1668	1402	660	346	
[Me$_2$mtcPdEt$_2$dtc]$_2$	1645	1514	675, 660	390	
[pipmtcPdEt$_2$dtc]$_2$	1640	1528	665, 653	370	
[MeBenzmtcPdEt$_2$dtc]$_2$	1653	1530	660	372, 345	
Pd(az)(Me$_2$mtc)	1550	–	654	381	
Pd(az)(pyrmtc)	1540	–	656	380	
Pd(az)(pipmtc)	1550	–	653	378	
Pd(Ph$_2$dtc)(Me$_2$mtc)(PPh$_3$)	1593	1385	–	336	
Pd(Ph$_2$dtc)(pyrmtc)(PPh$_3$)	1582	1380	–	336	
Pd(Ph$_2$dtc)(pipmtc)(PPh$_3$)	1586	1410	–	328	
Pd(Ph$_2$dtc)(Ph$_2$mtc)(PPh$_3$)	1581	1390	–	330	

TABLE III. Proton Nmr Data[a].

Complex	Solvent	δ_{arom} (ppm)		δCH_3 or αCH_2 (ppm)		T (°C)	$1/T_{2,0}$ (rad sec^{-1})
$Pd(PPh_3)(Ph_2dtc)(Me_2mtc)$	$CDCl_3$	7.26		2.84	2.70	−30	9.4
$[(Me_2mtc)Pd(Ph_2dtc)]_2$	$CDCl_3$	7.26	3.30	2.98	2.76[b]	+30	9.4
	C_6H_5Br	–	3.26	3.02	2.73[b]	+30	12.6
$[(pyrmtc)Pd(Ph_2dtc)]_2$	$CDCl_3$	7.29	3.85	3.38	3.23[b]	+30	9.4
$[(pipmtc)Pd(Ph_2dtc)]_2$	$CDCl_3$	7.33	3.99	3.64	3.38[b]	+30	9.4
$Pd(az)(Me_2mtc)$	$CDCl_3$	8.3–7.2		3.07	2.97	+30	9.4
	C_2Cl_4	8.3–7.2		3.10	3.00	+30	9.4
$Pd(az)(pyrmtc)$	C_2Cl_4	8.6–7.4		3.97		+24.5	9.4
$Pd(az)(pipmtc)$	$CDCl_3$	8.3–7.1		3.61		+30	9.4

[a] TMS was the internal standard; $\delta = (H_{complex} - H_{ref})/H_{ref} \times 10^6$, shift accuracy is about 0.01 ppm; measured at 100 Mc.
[b] Strongly overlapping two peak signal.

In the reaction of the thiocarbamate ligand with some other chloro bridged complexes, *i.e.* with the complexes $[Cl(Pd(bza)]_2$ and $[ClPd(benz)]_2$ (bza = benzylidene aniline-2-C,N; benz = N,N-dimethylbenzylamine-2-C,N) the aromatic ligand is split off completely and polymeric products with the composition $[Pd(R_2mtc)_2]_n$ were formed. Similar red brown products with analogous composition $[Pd(pipmtc)_2]_n$ were also obtained when K_2PdCl_4 was reacted with one equivalent Na(pipmtc) in ethanol. In the infrared spectra ν(C–O), (C–N) frequencies were found at 1635 and 1620 cm^{-1} as well as at 1580 and 1570 cm^{-1}. This may indicate that some monothiocarbamate ligands in these complexes are monodentate and others bidentate bonded with the metal atom. Due to the insolubility of these products in all common organic solvents no further attempts to gain more structural information were undertaken.

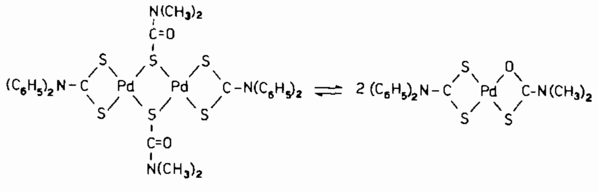
$[(R_2mtc)Pd(R'_2dtc)]_2$ Complexes

The preparation of the dimeric (*vide infra*) palladium complexes is readily achieved by the reaction of the chloro bridged dimers $[ClPd(R'_2dtc)]_2$ [19] with the freshly prepared di-alkylammonium thiocarbamates, $[R_2NH_2][R_2mtc]$.

When triphenylphosphine is added to solutions containing the $[(R_2mtc)Pd(Ph_2dtc)]_2$ complexes yellow products are obtained having compositions corresponding to $Pd(R_2mtc)(Ph_2dtc)(PPh_3)$. Molecular weight determinations in chloroform indicate that these last complexes are monomeric in solution, although some dissociation seems to occur (Table VII). The infrared spectra show intense absorption bands at 1585 cm^{-1} which are assigned to ν(C$\cdots$O), (C$\cdots$N) and indicate that the monothiocarbamate ligand is bonded as a monodentate ligand through the sulfur atom.

For the crystalline $[(R_2mtc)Pd(Ph_2dtc)]_2$ complexes a dimeric structure is proposed in which the sulfur atoms of the monothiocarbamate ligand bridge the two palladium ions. In the infrared spectra of these complexes an intense band in the 1650 cm^{-1} region appeared, which is assigned to ν (C=O) in the $-S-C(=O)NR_2$ system. The same high frequency was recently reported for $[(R_2mtc)Rh(CO)_2]_2$, for which complex a dimeric structure was suggested with the sulfur atoms bridging the two rhodium ions [5].

^1H and ^{13}C nmr spectra show a somewhat complicated picture. At low temperatures in the ^1H nmr spectrum in $CDCl_3$ as well as in C_6H_5Br four methyl signals are observed; the two high field signals are strongly overlapping. Upon increasing the temperature the intensity of two signals increases while those of the other decrease. At temperatures around +50 °C depending on solvent and concentration only two signals of equal intensity are observed; a further increase in temperature leads to the coalescence of these two signals. We think that between room temperature and 50 °C the dissociation of the dimer to monomer proceeds as:



and that above 50 °C only the monomer is present in solution. At higher temperatures the rotation around the C$\cdots$N bond becomes so rapid that the methyl signals coalesce.

The data of the ^{13}C spectra (Table IV) confirm the occurrence of a monomer–dimer equilibrium. On increasing the temperature from −40 °C–+30 °C the intensities of the signals of the methyl carbon atoms of the monomer centered around 40 ppm clearly increase and are thus easily assigned (Fig. 1).

TABLE IV. ^{13}C Chemical Shifts (ppm relative to TMS) for Palladium Complexes in CDCl$_3$ at 30 °C.

Complex		Pd–C	N–C=O	NCS$_2$	CH$_3$ or αCH$_2$	β and γ CH$_2$	C$_{arom}$–N	C$_{aromatic}$^{c}
[(Me$_2$mtc)Pd(Ph$_2$dtc)]$_2$	dimer		167.1	140.2	40.8 36.9		128.2	128.5(*p*) 127.0(*m*) 129.4(*o*)
	monomer		165.2	139.8	40.1 36.5		128.2	128.5(*p*) 127.0(*m*) 129.4(*o*)
Pd(az)(Me$_2$mtc)		a	164.3		36.9 34.5		151.8 a	125.2(*p*) 123.4(*m*) 129.2(*o*) 135.9 131.4 131.1 130.0
Pd(az)(pyrmtc)		b	164.5		47.3 46.3	25.0 25.0	151.7 154.3	125.6(*p*) 123.6(*m*) 129.3(*o*) 135.9 133.6 131.3 130.1
Pd(az)(pipmtc)		185.5	164.0		46.5 43.4	25.6 25.4 24.5	151.6 154.7	125.5(*p*) 123.5(*m*) 129.3(*o*) 135.9 131.6 131.1 130.0

[a] Not observed, due to the poor solubility of the compound. [b] Not observed, probably due to enhanced relaxation. [c] *p* = *para*; *m* = *meta* and *o* = *ortho* positions in the not-metallated ring.

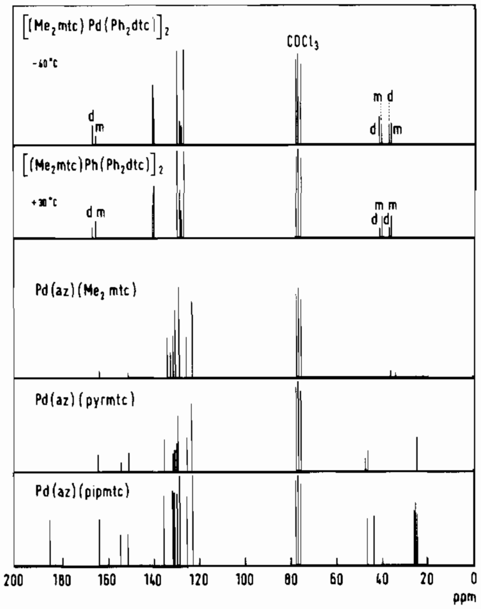


Figure 1. ^{13}C spectra of Palladium complexes.

In the same way the assignments are made for the two signals of the carbon atom of the carbonyl group, NC(=O)S, which group is bidentate bonded with the palladium ion in the monomer (δ = 165.2 ppm) and monodentate in the dimer (δ = 167.1 ppm).

For another bidentate bonded thiocarbamate, *i.e.* Pd(az)(R$_2$mtc), about the same value is observed (δ = 164.0) (Table IV and Fig. 2).

By integrating the methyl proton nmr signals the ratio of the concentrations of the monomer and

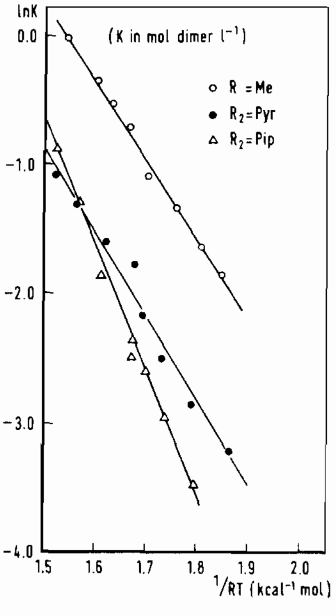


Figure 2. Equilibrium constant K *versus* 1/RT for the dimer–monomer equilibrium of Pd(R$_2$mtc)(Ph$_2$dtc) complexes.

TABLE V. Equilibrium Constants and Thermodynamic Data for Dimer–monomer Equilibria of $[(R_2mtc)Pd(Ph_2dtc)]_2$ Complexes at 27 °C.

Monomeric Complex	Equilibrium Constant, K (mol l^{-1})	ΔH (kcal mol^{-1})	ΔS (e.u.)
$Pd(Me_2mtc)(Ph_2dtc)$	0.44 ± 0.02	6.18 ± 0.06	19 ± 2
$Pd(pyrmtc)(Ph_2dtc)$	0.22 ± 0.01	6.65 ± 0.3	19 ± 2
$Pd(pipmtc)(Ph_2dtc)$	0.18 ± 0.015	9.90 ± 0.1	30 ± 2

dimer species is measured as a function of temperature and concentration in $CDCl_3$ solution.

In the same way the varying intensities of the α-CH_2 group protons of the pyrrolidyl and piperidyl rings were used to calculate monomer/dimer concentration ratios.

The values of the equilibrium constants $K = [Monomer]^2/[Dimer]$ (mol l^{-1}) calculated from these measurements (at 27 °C) are given in Table V.

The heats of formation of the dimer from the monomers (ΔH) were calculated from the plots of lnK *versus* 1/RT (Fig. 2) and are given in Table V.

Thermodynamic Data for the Hindered Rotation

From the temperature dependence of the signals of the α-protons the values of the kinetic parameters for C$\overset{\cdot\cdot\cdot}{-}$N bond rotation in the monothiocarbamate ligand were calculated. For the complexes $Pd(R_2mtc)(Ph_2dtc)(PPh_3)$ and $Pd(az)(R_2mtc)$ in which R_2 = pyrrolidyl and piperidyl the coupling of the β-protons with the α-protons prevents the observation of fluxional behaviour.

From the data summarised in Table VI it can be concluded that there is a distinct effect of the alkyl substituent of the thiocarbamate ligand on the activation energy. For $Au(R_2mtc)(PPh_3)$ and for $Pd(R_2mtc)(Ph_2dtc)$ $\Delta H^{\ddagger}$ is 4–5 kcal/mol higher for R = methyl than for R_2 = piperidyl.

In the temperature range where the dimer $[(R_2mtc)Pd(Ph_2dtc)]_2$ could be observed the hindred rotation is slow on the nmr time scale. At higher temperatures the rotation in the monomer speeds up. Thus the energy of activation found pertains to the monomer $Pd(R_2mtc)(Ph_2dtc)$ in which a bidentate bonded thiocarbamate is thought to be present. For the other bidentate bonded thiocarbamate complex $Pd(az)(Me_2mtc)$ also a somewhat higher value for the activation energy is found. The data in Table VI show that the alkyl substituent of the thiocarbamate ligand has a larger influence on the values of $\Delta H^{\ddagger}$ than the coordination mode of this ligand.

Experimental

Infrared spectra were measured on a Perkin–Elmer 257, Perkin–Elmer 283 and a Hitachi EPI-L spectrofotometers. ^1H nmr spectra were recorded on a Varian HA 100 or a Bruker WH 90 spectrometer equipped with a variable temperature unit. ^{13}C nmr spectra were measured on a Varian XL 100 FT and a Bruker WP 60 spectrometer. The activation energies were obtained from the usual least squares Arrhenius plots. The rotation rates were found from the dynamic proton nmr pattern by full line shape analysis.

Molecular weights were measured in chloroform solutions (approximately 5 g compound per 1 solvent) using a Hewlett–Packard 302B vapour phase osmometer.

Analyses were carried out in the microanalytical department of this university by Mr. P. J. Koonen. Analytical data are given in Table VII.

Ligands and Starting Materials

Di-alkylammonium N,N-di-alkylthiocarbamates, $[R_2NH_2][R_2mtc]$, were prepared from the amines and carbonyl sulfide as described previously [4].

TABLE VI. Kinetic Constants for the C$\overset{\cdot\cdot\cdot}{-}$N Bond Rotation in Thiocarbamate Complexes.

Complex	Solvent	$\Delta H^{\ddagger}_{300}$ °K (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
$Pd(Me_2mtc)(Ph_2dtc)(PPh_3)$	$CDCl_3$	14.9 ± 0.8	2.6 ± 2
$Pd(pyrmtc)(Ph_2dtc)(PPh_3)$	$CDCl_3$	no splitting observed in ^1H NMR	
$Pd(pipmtc)(Ph_2dtc)(PPh_3)$	$CDCl_3$	no splitting observed in ^1H NMR	
$Au(Me_2mtc)(PPh_3)$[a]		15.8	0
$Au(pipmtc)(PPh_3)$[a]		10.8	−14.7
$Pd(Me_2mtc)(Ph_2dtc)$	C_6H_5Br	16.4 ± 0.8	−5.0 ± 2
$Pd(pipmtc)(Ph_2dtc)$	C_6D_5Br	12.4 ± 1.0	−14.4 ± 1.6
$Pd(az)(Me_2mtc)$	C_2Cl_4	20.9 ± 1.8	3.5 ± 3
$Pd(az)(pyrmtc)$	$CDCl_3$	no splitting observed in ^1H NMR	
$Pd(az)(pipmtc)$	$CDCl_3$	no splitting observed in ^1H NMR	

[a] Values from ref. 4.

TABLE VII. Analytical and Molecular Weight Data.

	%C	%H	HN	Mol. wt.
$[(Me_2mtc)Pd(Et_2dtc)]_2$	27.1(26.8)	4.7(4.5)	7.9(7.8)	
$[(pipmtc)Pd(Et_2dtc)]_2$	33.4(33.1)	5.2(5.1)	7.4(7.0)	800(798)
$[(MeBzmtc)Pd(Et_2dtc)]_2$	38.0(38.7)	4.6(4.6)	6.3(6.4)	
$[(pipmtc)Pd(Bu_2dtc)]_2$	40.2(40.2)	6.3(6.3)	6.2(6.1)	
$[(Me_2mtc)Pd(Ph_2dtc)]_2$	42.5(42.2)	3.7(3.6)	6.1(6.2)	828(910)
$[(pyrmtc)Pd(Ph_2dtc)]_2$	45.7(45.0)	3.8(3.8)	5.9(5.8)	
$[(pipmtc)Pd(Ph_2dtc)]_2$	46.2(46.1)	4.2(4.1)	5.6(5.7)	990(990)
$Pd(az)(Me_2mtc)$	46.0(46.0)	3.9(3.9)	10.6(10.7)	365(392)
Pd(az)(pyrmtc)	49.0(48.9)	4.2(4.1)	10.1(10.1)	431(418)
Pd(az)(pipmtc)	50.5(50.1)	4.5(4.4)	9.8(9.7)	430(432)
$Ph_3PPd(Bu_2dtc)(pipmtc)$	55.3(55.4)	6.1(6.0)	3.9(3.9)	
$Ph_3PPd(Ph_2dtc)(Me_2mtc)$	57.7(58.2)	4.6(4.5)	3.6(3.8)	584(717)
$Ph_3PPd(Ph_2dtc)(pyrmtc)$	57.0(56.9)	4.4(4.4)	3.7(3.9)	627(743)
$Ph_3PPd(Ph_2dtc)(pipmtc)$	58.1(58.7)	4.8(4.7)	3.6(3.7)	662(757)
$Ph_3PPd(Ph_2dtc)(Ph_2mtc)$	58.7(58.7)	4.8(4.7)	3.5(3.7)	
$[(pipmtc)Pd(pipmtc)]_n$	35.8(36.5)	5.1(5.1)	7.1(7.1)	

[a] Theoretical values in parenthesis. Molecular weight determinations in chloroform.

$[ClPd(C–N)]_2$ [20] and $[ClPd(R_2dtc)]_2$ [19] were prepared as described.

$[ClPd(R_2dtc)]_2$ complexes were prepared as described by shaking $Pd(R_2dtc)_2$ in chloroform with K_2PdCl_4 (in a slight excess) dissolved in a small volume of water slightly acidified with 0.1 *M* sulfuric acid. After a change in colour from yellow to orange the chloroform layer was evaporated and the product was recrystallised from chloroform–diethyl ether mixtures.

Complexes

The procedures used to prepare the various palladium complexes were basically the same and the following procedures are typical examples.

Di-μ-(N,N-di-methylthiocarbamato)-bis(N,N-diphenyldithiocarbamatopalladium(II)), $[(Me_2mtc)Pd(Ph_2dtc)]_2$

In 700 ml of absolute alcohol was dissolved 0.53 g (0.7 mmol) of $[ClPd(R_2dtc)]_2$ and to this solution was added 0.21 g (1.4 mmol) of freshly prepared $[Me_2NH_2]$ $[Me_2mtc]$. The solution was stirred for an hour, the precipitate filtered off, washed with ethanol and diethyl ether and the product was recrystallised from chloroform–diethyl ether mixtures. M.p.: all complexes decompose above 200 °C.

Azobenzene-2-C,N, N,N-di-alkylthiocarbamato palladium(II), Pd(az)(R₂mtc)

To 0.32 g (0.5 mmol) of $[ClPd(az)]_2$ in 200 ml ethanol was added in excess 2 mmol of freshly prepared $[R_2NH_2]$ $[R_2mtc]$. The orange–red $[ClPd(az)]_2$ dissolved slowly and the colour changed from orange–red to brown–red. After stirring for 1.5 hour another 2 mmol of the thiocarbamate ligand was added to the reaction mixture and stirring was continued for another 1.5 hour. The solution was filtered and after adding 25 ml of water to the filtrate most of the solvent was removed *in vacuo*. The precipitated complex was filtered off, washed thoroughly with water and dried *in vacuo* over P_2O_5. The product was recrystallised from ethanol. A red–brown crystalline product was obtained. $Pd(az)(Me_2mtc)$, m.p. 151–152.5 °C; Pd(az)(pyrmtc), m.p. 186–187.5 °C; Pd(az)(pipmtc), m.p. 157–159 °C.

Acknowledgments

We thank Professor Dr. Ir. J. J. Steggerda for his interest in this work, Mr. C. Kruk (University of Amsterdam) and Mr. H. Brinkhof for the recording of the nmr spectra and Mr. P. J. Koonen for his experimental assistance.

References

1 J. Willemse, J. A. Cras, J. J. Steggerda and C. P. Keijzers, *Struct. and Bonding, 28,* 84 (1976).

2 D. L. Green, B. J. McGormick and C. G. Pierpont, *Inorg. Chem., 12,* 2148 (1973).

3 K. Tanaka, Y. Miya-Uchi and T. Tanaka, *Inorg. Chem., 14,* 1545 (1975).

4 F. W. Pijpers, A. H. Dix and J. G. M. van der Linden, *Inorg. Chim. Acta, 11,* 41 (1974).

5 E. M. Krankovits, R. J. Magee and M. J. O'Connor, *Inorg. Chim. Acta, 7,* 528 (1973).

6 E. M. Krankovits, R. J. Magee and M. J. O'Connor, *Austr. J. Chem., 26,* 1645 (1973).

7 R. F. Dalton and K. Jones, *J. Chem. Soc.,* 590 (1970).

8 S. Araki, K. Matsumoto, K. Tanaka and T. Tanaka, *J. Inorg. Nucl. Chem.*, *38*, 727 (1976).

9 B. Annuar and R. J. Magee, *J. Inorg. Nucl. Chem.*, *38*, 2195 (1976).

10 C. H. Yoder, A. Komoriya, J. E. Kochanowski and F. H. Suydam, *J. Am. Chem. Soc.*, *93*, 6515 (1971).

11 W. L. Steffen. S. L. Hawthorne and R. C. Fay, *J. Am. Chem. Soc.*, *98*, 6757 (1976).

12 C. G. Pierpont, R. C. Dickinson and B. J. McGormick, *Inorg. Chem.*, *13*, 1674 (1974).

13 E. W. Abel and M. O. Dunster, *J. Chem. Soc. Dalton*, 98 (1973).

14 B. F. Hoskins and C. D. Pannan, *Inorg. Nucl. Chem. Letters*, *10*, 229 (1974).

15 a) J. Willemse, *Inorg. Nucl. Chem. Letters*, *8*, 45 (1972).
b) B. J. McCormick and B. J. Stormer, *Inorg. Chem.*, *11*, 729 (1972).

16 B. J. McCormick and D. L. Green, *Inorg. Nucl. Chem. Letters*, *8*, 599 (1972).

17 R. Hesse and A. Aava, *Acta Chem. Scand.*, *25*, 423 (1971).

18 P. Jennische and R. Hesse, *Acta Chem. Scand.*, *25*, 423 (1971).

19 J. Willemse, *Thesis*, Nijmegen, 1974.

20 B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, *J. Chem. Soc. A*, 531 (1970).