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Several derivatives of cyclopalladated *N,N*-dimethylferrocenecarbothioamide

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Abstract

N,N-Dimethylferrocenecarbothioamide (Hfct) was prepared from ferrocenecarboxaldehyde by reaction with elemental sulphur and dimethylamine hydrochloride in the presence of sodium acetate in *N,N*-dimethylformamide. Reaction of Hfct with lithium tetrachloropalladate in methanol resulted by cyclopalladation in $[PdCl(fct)]_2$, which reacted with some monodentate ligands to give the adduct PdCl(fct)L (L = triphenylarsine, triphenylphosphine, tri-*p*-tolylphosphine, tri-*n*-butylphosphine, pyridine, and 4-t-butylpyridine). It also reacted with an acetylacetonate ion (acac) to give Pd(fct)(acac). A few iodo analogues were also prepared. These complexes were characterized spectroscopically. The substituted cyclopentadienyl ring of ferrocene is cyclopalladated at the position adjacent to the substituent and the sulphur atom of the thioamide group is coordinated to the palladium atom to form a five membered palladathiaheterocycle. Geometrical isomers (*trans*- and *cis*-(C,X); C represents a palladated carbon atom) were found for some of PdX(fct)L (X = Cl, I) in $CDCl_3$ solutions.

Introduction

The *N,N*-dimethylthiocarbamoyl group is an auxiliary substituent which facilitates cyclometallation of furan and thiophene rings with lithium tetrachloropalladate in methanol [1,2]. Ring-cyclopalladation of the heterocycles is quite different from the cyclopalladation of the benzene analogue substituted with the same *N,N*-dimethylthiocarbamoyl group, in that under similar conditions the benzene derivative is cyclopalladated not at the benzene ring but at the *N*-methyl substituent [3]. We are therefore interested in studying further the auxiliary ability of the *N,N*-dimethylthiocarbamoyl group when bonded to some other aromatic compounds. *N,N*-Dimethylferrocenecarbothioamide (abbreviated as Hfct) has been chosen as a candidate since ferrocene survives, in many cases, the reaction conditions involved in aromatic substitution and similar reactions [4]. Hfct is, as expected, cyclopalladated with lithium tetrachloropalladate in methanol and in this paper the resulting palladium–iron heterobimetallic complexes are described.

Results and discussion

N,N-Dimethylferrocenecarbothioamide (Hfct) was conveniently prepared in moderate yield from commercial ferrocenecarboxaldehyde by the method reported for the synthesis of *N,N*-dimethylbenzcarbothioamide [5]. Hfct was characterized

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Table 1

Yield, melting points, analytical results, and ν(C–N) and ν(Pd–Cl) bands

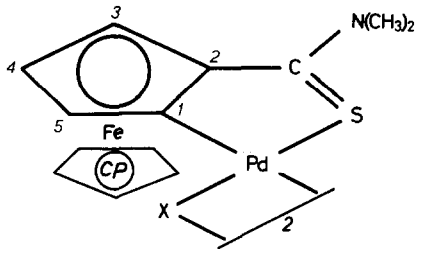
Compound [a]	Yield (%)	M.p. [b] (°C)	Anal. (Found (calcd.) (%))			ν(C–N) (cm^{-1})	ν(Pd–Cl) [c] (cm^{-1})
			C	H	N		
Hfct	40	90–91	57.05 (57.16)	5.66 (5.53)	5.17 (5.13)	1509	
$[PdCl(fct)]_2$	52	230 (dec.)	37.66 (37.71)	3.52 (3.41)	3.47 (3.38)	1563	300 217
$[PdI(fct)]_2$	76	220 (dec.)	30.99 (30.89)	2.67 (2.79)	2.60 (2.77)	1554	
$PdCl(fct)(AsPh_3)$	59	210 (dec.)	51.70 (51.69)	4.10 (4.06)	2.15 (1.94)	1556	296
$PdCl(fct)(PPh_3)$	78	200 (dec.)	55.10 (55.10)	4.32 (4.30)	1.98 (2.10)	1554	298
$PdCl(fct)(Ptol_3)$	69	210 (dec.)	56.92 (56.84)	4.89 (4.91)	1.80 (1.95)	1553	297
$PdCl(fct)(PBu_3)$	67	148–150	48.68 (48.72)	6.74 (6.71)	2.26 (2.27)	1552	284
$PdI(fct)(PBu_3)$	80	136–139	42.36 (42.42)	5.86 (5.84)	1.97 (1.98)	1553	
PdCl(fct)(py)	80	215 (dec.)	43.62) (43.84)	3.94 (3.88)	5.59 (5.68)	1556	297
PdCl(fct)(tbp)	85	154–164	48.08 (48.10)	5.08 (5.00)	4.93 (5.10)	1555	306
PdI(fct)(tbp)	66	193–196	41.37 (41.24)	4.16 (4.25)	4.38 (4.37)	1554	
Pd(fct)(acac)	68	182–186	45.21 (45.26)	4.36 (4.43)	3.00 (2.93)	1564	437 [d] 212

[a] Abbreviations: Hfct = *N*,*N*-dimethylferrocenecarbothioamide, $AsPh_3$ = triphenylarsine, PPh_3 = triphenylphosphine, $Ptol_3$ = tri-*p*-tolylphosphine, PBu_3 = tri-n-butylphosphine, py = pyridine, tbp = 4-t-butylpyridine, and acac = acetylacetonate ion. [b] dec. = decomposed. [c] Nujol mulls. [d] ν(Pd–O) bands.

by elemental analysis and by infrared (IR) and ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra; in the ^{13}C NMR spectrum the signal characteristic of a thioamide group [6] is observed at 199.7 ppm and the IR spectrum shows a strong band at 1509 cm^{-1} assignable to ν(C–N) of the group [7].

Hfct reacted with lithium tetrachloropalladate in methanol to give $[PdCl(fct)]_2$, which was converted to the iodo analogue upon metathesis with excess lithium iodide in acetone. The IR spectra (Table 1) of the two show a higher frequency shift of the ν(C–N) bands to indicate S-coordination of the thioamide group [7]. In the far infrared (far-IR) region (the lower limit of our spectrometer is 200 cm^{-1}), $[PdCl(fct)]_2$ shows ν(Pd–Cl) bands (Table 1) which are missing from the spectrum of $[PdI(fct)]_2$. The two complexes are not soluble in most common solvents but only sparingly soluble in dimethylsulphoxide (DMSO). The ^1H NMR spectra of the two in deuterated DMSO (DMSO-d_6) are shown in Table 2 but no ^{13}C NMR spectra are available. The two triplets (at 4.35 and 4.70 ppm; each intensity of 2H) of free Hfct are converted into three separate peaks (each intensity of 1H) in the ^1H NMR spectra of the complexes (Table 2). Integration of the ^1H spectra indicates clearly that one hydrogen atom is removed from the substituted cyclopentadienyl ring and

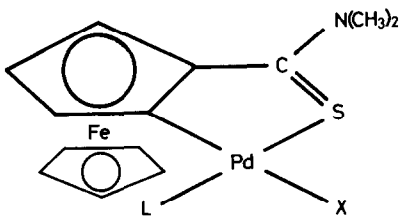
that the *N,N*-dimethylthiocarbamoyl group is intact. The following structure I is proposed:



I (X=Cl, I)

$[PdCl(fct)]_2$ reacted with some monodentate ligands (L) (abbreviations are given in Table 1) to give the adduct PdCl(fct)L and with an acetylacetonate ion to form Pd(fct)(acac) like other cyclopalladated complexes [8]. These derivatives (Table 1) have been characterized spectroscopically (Table 2 and 3). The IR spectra of all the complexes show ν(C–N) at frequencies higher by 43–55 cm^{-1} than that of free Hfct (Table 1). *S*-coordination of the thioamide group is evident [7] and an increase in double bond character of the C–N bond is suggested in the complexes. In the ^1H and ^{13}C NMR spectra (Tables 2 and 3), inequivalence of the two methyl groups of the thioamide group [9] results from the restricted rotation of the C–N bond with the increase of double bond character.

The IR spectrum of Pd(fct)(acac) shows that two bands at 1513 and 1577 cm^{-1} characteristic of normal acetylacetonato-*O,O'* complexes [10] and ν(Pd–O) bands (Table 1) are at lower frequencies than those of $Pd(acac)_2$ (463 and 294 cm^{-1}) to suggest that the *trans* influence of both the cyclopentadienyl-C and thioamide-S atoms of fct is greater than that of acac-O atoms. The ^1H NMR spectrum of Pd(fct)(acac) shows the signals due to the acac moiety at 1.96, 2.06, and 5.32 ppm and those due to the ^{13}C one at 27.8, 28.0, 99.5, 186.1, and 186.8 ppm also suggesting a normal *O,O'*-coordination mode. Of the proton signals of the substituted cyclopentadienyl (Cp) ring of fct, the chemical shifts of 3-H and 4-H coincide accidentally and the two protons give a doublet. The signal of 5-H is a triplet (Table 2) due apparently to ^3J(4-H–5-H) approximating to ^4J(3-H–5-H). In the ^{13}C NMR spectrum (Table 3) the most significant feature is a large downfield shift (more than 20 ppm) of 1-C upon palladation. Similar downfield shifts have also been observed for cyclopalladated carbon atoms of other substrates such as azobenzene, benzo[h]quinoline, and triphenylphosphite [11]. Structure II (X, L = acac-*O,O'*) is most probable.



II *trans*-(C,X)

Table 2

^{1}H (90 MHz) and ^{31}P{^{1}H} (36.4 MHz) NMR spectra of the ligand and complexes

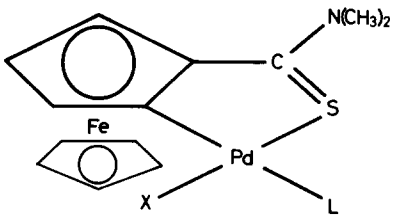
Compound	Solvent	δ(^{1}H) ppm (J(H–H) in Hz) [a]					δ(^{31}P)
		3-H	4-H	5-H	Cp	N–CH_3	
Hfct	$CDCl_3$	4.35t [b] (2.0)	4.70t (2.0)	4.70t (2.0)	4.22s	3.44br	
$[PdCl(fct)]_2$	DMSO-d_6	4.89dd (1.0, 2.7)	4.65t (2.7)	5.53br	4.32s	3.50br	
$[PdI(fct)]_2$	DMSO-d_6	4.90dd (0.9, 2.7)	4.66t (2.6)	5.55dd (0.9, 2.4)	4.32s	3.50	
$PdCl(fct)(AsPh_3)$	$CDCl_3$	4.55d (2.6)	4.25t (2.7)	3.86d (2.4)	3.97s	3.48, 3.57	
$PdCl(fct)(PPh_3)$	$CDCl_3$	4.55d (2.4)	4.23br	3.76br	3.87s	3.49, 3.56	32.9
$PdCl(fct)(Ptol_3)$	$CDCl_3$	4.58d (2.4)	4.20br	3.79br	3.87s	3.44, 3.53	31.7
$PdCl(fct)(PBu_3)$	$CDCl_3$	4.47br, d (2.0)	4.55td (2.6) [c]	4.65br, d (2.6)	4.18s	3.49, 3.54	15.7
$PdI(fct)(PBu_3)$	$CDCl_3$						
trans-(C,I)		[d]	[d]	[d]	4.17s	3.49, 3.52	14.5
cis-(C,I)		[d]	[d]	5.88m	4.22s	3.55	−1.3
PdCl(fct)(py)	$CDCl_3$						
trans-(C,Cl)		[e]	[e]	3.90br	4.26s	3.56	
cis-(C,Cl)		[e]	[e]	5.57br	4.33s	3.48, 3.50	
PdCl(fct)(tbp)	$CDCl_3$						
trans-(X,Cl)		[f]	4.43t (2.3)	3.97d (2.3)	4.25s	[f]	
cis-(C,Cl)		4.57d (1.5)	4.57d (1.5)	5.53t (1.5)	4.31s	3.49	
PdI(fct)(tbp)	$CDCl_3$						
trans-(C,I)		[g]	[g]	[g]	4.26s	3.55	
cis-(C,I)		4.54d (1.5)	4.54d (1.5)	5.83t (1.5)	4.33s	3.47	
Pd(fct)(acac)	$CDCl_3$	4.53d	4.53d	5.18t	4.24s	3.44, 3.50	

[a] Only the signals due to Hfct are given in this Table. The numbering system follows structure I. Abbreviations: Cp = unsubstituted cyclopentadienyl ring, br = broad, s = singlet, d = doublet, t = triplet, and m = multiplet. [b] 1-H is at 4.35 ppm (t, J = 2.0 Hz). [c] J(P–H) = 1.1 Hz. [d] These protons gave a complex multiplet between 4.5 and 4.7 ppm. [e] These protons gave a broad resonance at 4.59 ppm. [f] Obscured by the signals of the *cis* isomer. [g] Could not be identified owing to a low concentration of the trans isomer and obscuration by the signals of the *cis* isomer.

Marked features of the ^{1}H NMR spectra of PdCl(fct)L (L = $AsPh_3$, PPh_3, and $Ptol_3$) are upfield shifts of the signals of 5-H and the unsubstituted Cp ring protons as compared with those of the above discussed complexes. The three ligands (L) have common benzene rings and the anisotropic shielding effect of the ring operates upon 5-H and the Cp ring protons when PdCl(fct)L has *trans*-(C,X) structure II (L locates near 5-H and the Cp ring). No ^{13}C NMR spectrum of $PdCl(fct)(PPh_3)$ is available because of low solubility. The ^{13}C NMR spectra of PdCl(fct)L (L = $AsPh_3$ and $Ptol_3$) are very similar except for ^{31}P-^{13}C couplings (Table 3). The small J(P–C) value (1.4 Hz) for 1-C (which is linked directly to Pd) of the latter supports structure II where the P and the 1-C atoms are in *cis* relation. The presence of ν(Pd–Cl) in the far-IR spectra (Table 1) is evidence of coordination of Cl.

In the ^{1}H NMR spectrum of PdCl(fct)(PBu_3) (Table 2), 5-H is deshielded in contrast to those of the above three: in this complex no anisotropic aromatic shielding effect is expected. The small J(P–C) value (2.4 Hz) for 1-C (Table 3) supports a *cis* P and 1-C arrangement (structure II). The other ^{1}H and ^{13}C signals are less informative. For broadening of some ^{1}H signals of the phosphine-containing complexes (Table 2) small ^{1}H–^{31}P couplings are probably responsible, but these are unresolved in our ^{1}H NMR (90 MHz) spectra.

The ^{1}H and ^{13}C NMR spectra of the remaining complexes are complicated (Tables 2 and 3) and this indicates the presence of isomers. Their relative abundances were established on the basis of integration intensities of the ^{1}H NMR spectra of $CDCl_3$ solutions. The major isomer of PdI(fct)(PBu_3) exists in a proportion of 75% and the minor one in a proportion of 25%. The spectral properties of the major isomer resemble those of the above mentioned *trans*-(C,Cl)-PdCl(fct)(PBu_3) to suggest that the isomer also has structure II. On the contrary, the deshielding of 5-H and the conspicuously large J(P–C) for 1-C (149.6 Hz) of the minor isomer indicate an isomeric *cis*-(C,I) geometry (structure III): the 5-H proton is located in the proximity of the iodide ligand experiencing its local anisotropic effect [11] and the 1-C atom is held *trans* to the PBu_3 ligand resulting in a large ^{31}P–^{13}C coupling constant [11]. The ^{31}P NMR spectrum confirms the assignment of the isomers: the chemical shift of the major isomer is close to that of the above mentioned *trans*-(C,Cl)-PdCl(fct)(PBu_3) and the resonance of the minor isomer (*cis*-(C,I)) shows a shielding of 15.8 ppm with reference to that of the major one (*trans*-(C,I)), a similar relationship having been reported for the isomers of PdX(att)(PBu_3) (X = Cl, I; att = cyclopalladated *N*,*N*-dimethyl-2-thiophenecarbothioamide) [2].



III *cis*-(C, X)

The ratio of isomers for PdX (fct)(tbp) is 33/67 (X = Cl) and 20/80 (X = I), and the fraction of the minor isomer of PdCl(fct)(py) is less than 15%. The chemical shifts of 5-H are markedly different between the isomers. The 5-H shielding of the minor isomers is caused by the aromatic ring current of the pyridine ring coordinated perpendicular to a coordination plane because of the steric restraint of the ring. Structure II, where the 5-H is situated in the shielding region, is acceptable for the minor isomers. The X dependent deshielding of 5-H of the major isomers is due to the same cause as that of *cis*-(C,I)-PdI(fct)(PBu_3). The major isomers of PdX(fct)(tbp) (X = Cl, I) and PdCl(fct)(py) thus have *cis*-(C,X) structure III. The ^{1}H NMR spectral pattern of the substituted Cp ring of the major isomer of PdX(fct)(tbp) is similar to that of Pd(fct)(acac): it consists of one triplet (an intensity of 1H) and one doublet (an intensity of 2H) (Table 2).

An *N*,*N*-dimethylthiocarbamoyl group is a good auxiliary substituent to promote cyclopalladation of ferrocene. The cyclopalladated ferrocene derivatives are as stable in air as other cyclopalladated complexes [8]. Isomerism is found for PdX(fct)L

Table 3

$^{13}C\{^1H\}$ NMR (22.6 MHz) spectra of the ligand and some complexes

Compound	$\delta(^{13}C)$ ppm (J(P–C) in Hz) [a]							
	1-C	2-C	3-C	4-C	5-C	Cp	C(=S)	$(CH_3)_2N$
Hfct	72.0 [b]	87.2	72.0 [b]	69.1 [b]	69.1 [b]	71.0	199.7	44.5br
PdCl(fct)($AsPh_3$) [c]	94.4	87.5	71.3	69.6	80.5	71.5	201.8	46.5, 44.7
PdCl(fct)($Ptol_3$)	96.4	87.8	71.1	69.5	80.2	71.6	200.9	46.5, 45.0
	(1.4)	(0.7)	(4.5)		(13.1)		(2.8)	(3.1)
PdCl(fct)(PBu_3)	94.8	88.7	71.5	70.0	77.9	71.5	201.5	46.5, 45.0
	(2.4)		(7.3)		(11.1)		(3.1)	(2.8)
PdI(fct)(PBu_3)								
trans-(C,I)	100.5	87.7	72.1	69.3	77.5	71.6	202.8	46.7, 45.3
	(0.7)	(0.7)	(4.5)		(10.7)		(2.8)	(3.1)
cis-(C,I)	101.6	86.4	71.8 [b]	71.4 [b]	74.9	70.9	202.8 [d]	46.3, 45.2
	(149.6)				(8.6)			(2.4)
PdCl(fct)(tbp) [c]								
trans-(C,Cl)	95.8	86.1	70.7	69.8	[e]	70.9	202.5	[e]
cis-(C,Cl)	94.7	85.7	71.6	70.0	80.4	71.3	202.1	46.1, 44.9
PdI(fct)(tbp) [c]								
trans-(C,I)						70.9 [f]		
cis-(C,I)	92.6	86.7	73.7	70.3	88.2	71.5	202.6	46.2, 44.7
Pd(fct)(acac)	94.7	85.2	70.1	69.6	74.8	70.9	202.6	45.6, 44.5

[a] Only the signals of Hfct are given in this Table. The numbering system follows structure I. Solvent is $CDCl_3$. [b] Tentative assignment. [c] Measured in the presence of $Cr(acac)_3$ as a relaxation reagent. [d] Uncertain. [e] Coincident with the signals of the *cis* isomer. [f] Signals of the other carbon atoms were not identified.

in $CDCl_3$ solutions and the ratio of the isomers (*trans*-(C,X)/*cis*-(C,X)) is affected by X and L. Almost all are *trans* (X = Cl; L = $AsPh_3$, PPh_3, $Ptol_3$, PBu_3) but the ratio is 75/25 (X = I; L = PBu_3), 33/67 (X = Cl, L = tbp), and 20/80 (X = I; L = tbp). The proportion of the *trans* isomer is less than 15% (X = Cl; L = py). The *trans*-(C,X) arrangement (structure II) is, therefore, more favourable to X = Cl than I and to L = PBu_3 than tbp. A similar tendency has been found for the isomerism of the cyclopalladated *N*,*N*-dimethyl-2-thiophenecarbothioamide derivatives PdX(att)L [2] and the proportion of *trans*-(C,X) isomers of PdX(att)L is always smaller than that of PdX(fct)L with respect to the same L and X. A dominant factor governing the isomerism will be mutual relationship of the *trans* influences of four donors around a Pd atom. Further discussion will require detailed structural and/or thermodynamic characterization.

Experimental

Measurements

Measurements were carried out by the methods reported previously [2].

Synthesis

Elemental analysis, yields, and melting points are given in Table 1 and NMR spectra in Tables 2 and 3.

N,N-*Dimethylferrocenecarbothioamide (Hfct).* Hfct was prepared according to the method reported for *N*,*N*-dimethylbenzthioamide [5]. A mixture of commercial ferrocenecarboxaldehyde (Aldrich) (10.7 g), dimethylamine hydrochloride (6.12 g),

elemental sulphur (2.40 g), and anhydrous sodium acetate (6.15 g) in *N,N*-dimethylformamide (40 cm^3) was gradually heated to 100 °C over 30 min and the temperature was maintained for 3 h in an oil bath. After cooling, the mixture was poured into icewater (200 cm^3) with stirring and external cooling, and the stirring was continued until a dark brown substance had solidified. The substance was filtered, washed with water, dried in air, and recrystallized from ethanol to remove the unreacted sulphur. The crude crystals were further recrystallized from petroleum ether to give brownish orange crystals. Some characteristic IR bands (Nujol mulls): 3112, 3077, 1509, 1387, 1377, 1273, 1133, 1061, 837, 510, 497, amd 484 cm^{-1}. Absorption maxima (ethanol): 462 nm ($\epsilon = 598$ $mol^{-1}\,dm^3\,cm^{-1}$) and 276 nm (1.04×10^4).

[PdCl(fct)]$_2$. To a solution of lithium tetrachloropalladate (262 mg, 1 mmol) in methanol (30 cm^3), prepared *in situ* from palladium(II) chloride (177 mg, 1 mmol) and lithium chloride (85 mg, 2 mmol), was added Hfct (273 mg, 1 mmol). The solution developed a dark colour and was stirred overnight at room temperature to form a yellow brown precipitate. The precipitate was filtered, washed with methanol, and dried in air. $[PdI(fct)]_2$ was prepared by metathesis of $[PdCl(fct)]_2$ with a large excess of lithium iodide in acetone.

PdCl(fct)(PBu$_3$). To a suspension of $[PdCl(fct)]_2$ (414 mg, 0.5 mmol) in dichloromethane (30 cm^3) was added PBu_3 (202 mg, 1 mmol) and the mixture was stirred until it became clear. To the concentrated filtrate was cautiously added n-hexane little by little and a dark brown precipitate appeared initially, which was filtered off. This process was repeated until no more dark brown precipitate appeared. Further addition of n-hexane gave PdCl(fct)(PBu_3) as a red precipitate, which was filtered, washed with n-hexane, and dried in air. PdCl(fct)L (L = $AsPh_3$, PPh_3, $Ptol_3$, tbp, and py) was similarly prepared (tbp and py were added in twofold excess). PdI(fct)L was prepared by metathesis of PdCl(fct)L with excess lithium iodide in acetone (a few drops of tbp were added in case of PdI(fct)(tbp)).

Pd(fct)(acac). To a solution of sodium acetylacetonate (122 mg, 1 mmol) in a mixture of methanol (25 cm^3) and dichloromethane (50 cm^3) was added $[PdCl(fct)]_2$ (414 mg, 0.5 mmol) and the mixture was stirred for a few hours. The filtered solution was evaporated to dryness, the residue was dissolved in dichloromethane, and undissolved material was removed by filtration. The filtrate was concentrated to a small volume and treated with n-hexane as described above to afford a red precipitate, which was washed with n-hexane and dried in air.

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