

Cyclopalladation and Cycloplatination of the Furan Ring of *N,N*-Dimethyl-2-furancarbothioamide

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Abstract

N,N-Dimethyl-2-furancarbothioamide (abbreviated as Haft) was cyclometallated with lithium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) to give, respectively, [PdCl(aft)] and [PtCl(aft)]. These reacted with a donor (L) to give [MCl(aft)L] (M = Pd, L = tri-*n*-butylphosphine (PBU₃), di-*n*-butylsulphide (SBU₂), triphenylarsine and tri-*o*-tolylphosphine; M = Pt, L = PBU₃ and SBU₂). Some of the bromo and iodo analogues of the palladium complexes were also prepared. These new complexes were characterized spectroscopically. Metallation occurs at position 3 of the furan ring and the thioamide group is coordinated through the S atom to form a five-membered metallathiaheterocycle. In [MCl(aft)L] the Cl donor is coordinated *trans* to the σ -bonded 3-C atom of the furan ring. The furan ring cyclometallation of Haft is in contrast to the fact that the corresponding benzene derivative, *N,N*-dimethylbenzthioamide, is cyclo-metallated at the thioamide N-methyl group under similar conditions.

Introduction

Benzene is a representative of aromatic compounds and cyclometallation occurs very often for a benzene ring when it is substituted by a suitable donor group [1]. Furan is also an aromatic compound but the properties are not necessarily similar to those of benzene [2]. The possibility of cyclometallation of a furan ring is intriguing and we are investigating the subject. In due course we have found that the furan ring of *N,N*-dimethyl-2-furancarbothioamide is cyclometallated with lithium tetrachloropalladate(II) and potassium tetrachloroplatinate(II). This observation is in great contrast to the fact that the corresponding benzene derivative, *N,N*-dimethylbenzthioamide, is, under similar conditions, cyclopalladated not at the benzene ring but at the N-methyl group [3]. The difference should reflect the general trend that a furan ring is more reactive than a benzene ring [2].

Results and Discussion

N,N-Dimethyl-2-furancarbothioamide (abbreviated as Haft) is reported to be obtained in a yield of 22% by thiation of *N,N*-dimethyl-2-furancarbothioamide with phosphorus pentasulphide [4] but the yield can be improved to 65% with Lawesson's reagent. Haft was cyclopalladated with lithium tetrachloropalladate(II) in methanol at room temperature (Table 1). The product with the composition [PdCl(aft)] is insoluble in common organic solvents except dimethylsulphoxide (abbreviated as dmsO) in which it is slightly soluble. The ¹H NMR spectrum in dmsO-d₆ shows two signals (each with an intensity of 1 H) in the region of aromatic ring proton resonances: a broad peak at 7.09 ppm* and a doublet at 7.91 ppm (*J* = 1.8 Hz) (Table 2). The latter doublet becomes a singlet upon irradiation of the former peak. Thus one hydrogen atom must have been removed from the furan ring because free Haft shows three signals in that region (Table 2). The coupling constant (1.8 Hz) of [PdCl(aft)] is typical of ³*J*((4-H)–(5-H)) for a 2,3-disubstituted furan [2]. The methyl signal of the thioamide group is observed as two singlets each with an intensity of 3 H at 3.54 and 3.72 ppm.

In the ¹³C{¹H} NMR spectra of [PdX(aft)] (X = Cl, Br, I) (Table 3) the signals expected for 3-C are missing because of their limited solubilities and the poor quality of the spectra. In the higher field spectrum (100.5 MHz) of [PdCl(aft)] it was found at 144.3 ppm**. Upon palladation the 3-C atom is significantly deshielded. Similar deshielding has been reported for cyclopalladated benzene derivatives [5]. In conformity with the ¹H NMR spectrum, the ¹³C chemical shifts of CH₃ of the thioamide group are inequivalent. Metallation is supposed to occur at a furan ring and Structure I is tentatively pro-

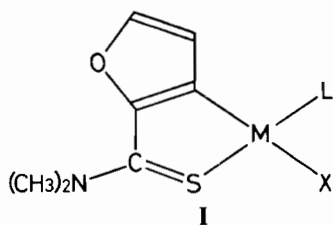
*The broad peak at 7.09 ppm (4-H) became a sharp doublet at about 100 °C. The broadness may originate in slow exchange of a donor at the adjacent coordination site at room temperature. At ca. 100 °C the exchange is sufficiently faster than a NMR time scale so that the 4-H signal is sharp.

**The high field ¹³C{¹H} NMR spectra were measured by a JEOL GX 400 spectrometer.

TABLE 1. Melting points, Yields, Analytical Results and $\nu(\text{M}-\text{Cl})$ Bands of the Complexes

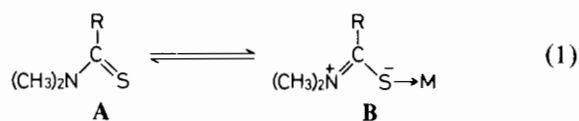
Complex ^a	Yield (%)	Melting point ^b (°C)	Analysis: found(calc.) (%)			$\nu(\text{M}-\text{Cl})^c$ (cm ⁻¹)
			C	H	N	
[PdCl(aft)]	93	252(dec)	28.52 (28.40)	2.71 (2.72)	4.77 (4.73)	219 241
[PdBr(aft)]	95	255(dec)	24.82 (24.69)	2.37 (2.37)	4.18 (4.11)	
[PdI(aft)]	80	244(dec)	21.70 (21.70)	2.07 (2.08)	3.61 (3.61)	
[PdCl(aft)(PBU ₃)]	51	149–151	45.81 (45.79)	7.13 (7.08)	2.87 (2.81)	252
[PdBr(aft)(PBU ₃)]	71	123–124	42.09 (42.04)	6.19 (6.50)	2.58 (2.58)	
[PdI(aft)(PBU ₃)]	69	114–117	38.85 (38.69)	6.08 (5.98)	2.40 (2.37)	
[PdCl(aft)(SBU ₂)]	79	248(dec)	40.70 (40.73)	5.89 (5.92)	3.28 (3.17)	241
[PdBr(aft)(SBU ₂)]	75	247(dec)	37.26 (37.01)	5.48 (5.38)	2.90 (2.88)	
[PdCl(aft)(Ptol ₃)]	73	170–172	55.92 (56.01)	4.89 (4.87)	2.45 (2.33)	240
[PdCl(aft)(AsPh ₃)]	76	255(dec)	50.00 (49.85)	3.88 (3.85)	2.33 (2.33)	243
[PtCl(aft)]	68	256(dec)	21.89 (21.85)	2.04 (2.10)	3.56 (3.64)	312br
[PtCl(aft)(Haft)]	10	209(dec)	31.10 (31.14)	3.24 (3.17)	5.08 (5.19)	287
[PdCl(aft)(PBU ₃)]	52	153–154	38.65 (38.87)	6.03 (6.01)	2.39 (2.39)	297
[PtCl(aft)(SBU ₂)]	68	257(dec)	33.87 (33.93)	4.97 (4.97)	2.62 (2.64)	288

^aAbbreviations: Haft = *N,N*-dimethyl-2-furancarbothioamide, PBU₃ = tri-*n*-butylphosphine, SBU₂ = di-*n*-butylsulphide, Ptol₃ = tri-*p*-tolylphosphine, and AsPh₃ = triphenylarsine. ^bdec = decomposition. ^cM = Pd or Pt; measured of nujol mull and down to 200 cm⁻¹; br = broad.



posed. The structure is further confirmed by the spectral data discussed below.

The IR spectrum of [PdCl(aft)] (nujol mull) shows a very strong band at 1592 cm⁻¹ assignable to the thioamide group C–N bond [6]. The increase in frequency from 1511 cm⁻¹ of free Haft suggests that upon coordination the C–N bond gains more double bond character (eqn. (1)) [6]. This interpre-



tation is consistent with the NMR spectra: free Haft shows a single peak due to the N(CH₃)₂ group because of free rotation about the C–N bond [7] but in the complex the signal separates into two peaks because the restricted rotation of the C–N bond with a partially double bond character results in inequivalence of the two methyl groups [7]. In the far IR spectral region there are two strong bands at 219 and 241 cm⁻¹ which are assigned to $\nu(\text{Pd}-\text{Cl})$: these bands are absent in the spectra of [PdX(aft)] (X = Br and I). The low frequencies imply the

TABLE 2. ^1H (90 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (36.4 MHz) NMR Spectra of the Complexes

Complex	Solvent	$\delta(^1\text{H})$ (ppm) ($J(\text{H}-\text{H})$ (Hz) ^a			$\delta(^{31}\text{P})$
		4-H	5-H	N-CH ₃	
Haft	CDCl_3	6.44dd(1.8)(3.5)	7.46dd(0.9)(1.8)	3.47s ^b	
	dmsO-d_6	6.61dd	7.82dd	3.43s ^b	
[PdCl(aft)]	dmsO-d_6	7.09br	7.91d(1.8)	3.54s, 3.72s	
[PdBr(aft)]	dmsO-d_6	7.10br	7.93d(1.8)	3.53s, 3.71s	
[PdI(aft)]	dmsO-d_6	7.14d(1.8)	7.90d(1.8)	3.53s, 3.71s	
[PdCl(aft)(PBU ₃)]	CDCl_3	6.43d(1.8)	7.53t(1.9) ^c	3.56s, 3.72s	16.6
[PdBr(aft)(PBU ₃)]	CDCl_3	6.45d(1.8)	7.54t(1.9) ^c	3.56s, 3.70s	15.9
[PdI(aft)(PBU ₃)]	CDCl_3	6.47d(1.8)	7.60t(1.8) ^c	3.57s, 3.67s	15.4
[PdCl(aft)(SBU ₂)] ^d	CDCl_3	6.71br	7.52d(1.5)	3.56s, 3.83s	
[PdCl(aft)(Ptol ₃)]	CDCl_3	5.38dd(1.8)($J(\text{PH})$ 0.7)	^e	3.56s, 3.66s	32.0
[PdCl(aft)(AsPh ₃)]	CDCl_3	5.49d(1.5)	7.12d(1.5)	3.60s, 3.69s	
[PtCl(aft)]	dmsO-d_6	7.06d(1.8)[25.9] ^f	7.97d(1.8)	3.55s, 3.76s	
[PtCl(aft)(Haft)]	CDCl_3	6.61d(1.8)[32.1] 6.52dd(3.7)(1.8)	7.56d(1.8) 7.61dd(1.8)(0.8)	3.51s, 3.69s 3.40s, 3.81s ^g	
[PtCl(aft)(PBU ₃)]	CDCl_3	6.39d(1.8)[28.2]	7.55dd(1.8)($J(\text{PH})$ 1.0)	3.55s, 3.72s	3.95[3575] ^h
[PtCl(aft)(SBU ₂)]	CDCl_3	6.66d(1.6)[29.7]	7.62d(1.6)	3.54s, 3.74s	

^aOnly the signals due to aft are given in this Table. Figures in parentheses are coupling constants, $J(\text{H}-\text{H})$, in Hz unless otherwise noted. Abbreviations: br = broad, s = singlet, d = doublet, t = triplet. ^b3-H signal is at 7.04 ppm (dd, 3.5, 0.9) (CDCl_3) or at 6.99 (dmsO-d_6). Coupling constants are identical for the two spectra in CDCl_3 and dmsO-d_6 . ^c $J(\text{P}-\text{H})$ is comparable to $J(\text{H}-\text{H})$. ^dA precipitate appeared during the measurement and the quality of the spectrum is poor. ^eObscured by the signals of Ptol₃. ^fFigures in square brackets are $J(\text{Pt}-\text{H})$ in Hz. ^g3-H signal is at 7.76 ppm (dd, 3.7, 0.8). ^hThis value is $J(\text{Pt}-\text{P})$ in Hz.

strong *trans* influence of the σ -coordinated furan ring C atom.

The reaction of potassium tetrachloroplatinate(II) with Haft did not give pure [PtCl(aft)] but a mixture of the complex and [PtCl(aft)(Haft)]. The solubility difference in dichloromethane permitted their separation (Table 1). The ^1H NMR spectrum of [PtCl(aft)] in dmsO-d_6 shows two signals due to furan ring protons like that of [PdCl(aft)] (Table 2). For the higher field a $J(\text{Pt}-\text{H})$ value of 25.9 Hz is observed and the signal is assigned to 4-H *ortho* to the metallated carbon (3-C). The signal is sharp in contrast to the broad signal of 4-H of [PdCl(aft)]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is also similar to that of [PdCl(aft)] (Table 3). Because of its low solubility, $J(\text{Pt}-\text{C})$ is detected only for 4-C and 5-C which bear a proton. In the IR spectrum (nujol mull) $\nu(\text{C}-\text{N})$ of the thioamide group is observed at 1601 cm^{-1} and in the ^1H NMR spectrum the thioamide group gives two peaks like in that of [PdCl(aft)]. A very broad band at 312 cm^{-1} in the far IR region may be $\nu(\text{Pt}-\text{Cl})$ (Table 1). Structure I is assigned to [PtCl(aft)].

Reactions of [MCl(aft)] with monodentate ligands (L) easily gave the adducts [MCl(aft)L] (Table 1)

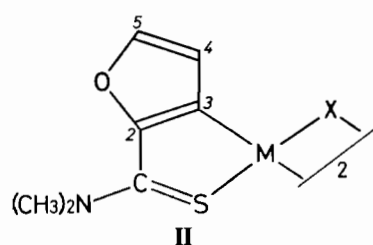
as usually observed for halogen bridged cyclopalladated or cycloplatinated complexes [1]. Some bromo and iodo analogues were also prepared by metathesis of halide ions. The chloro complexes show $\nu(\text{M}-\text{Cl})$ at appreciably low frequencies (Table 1) where the bromo and iodo analogues show no corresponding band. This fact indicates that Cl is coordinated *trans* to a donor with a strong *trans* influence [8]. For these adducts $\nu(\text{C}-\text{N})$ of the thioamide group appears in a similar region to that of the parent [MCl(aft)], and consistently in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the two methyl groups are magnetically inequivalent (Tables 2 and 3). In the ^1H NMR spectra in CDCl_3 the chemical shifts of 4-H of [PdCl(aft)L] are markedly influenced by L. For L = PBU₃ and SBU₂ the chemical shifts are similar to that of free Haft. However for L = Ptol₃ and AsPh₃ the signals of 4-H are shielded by about 1 ppm compared with those for L = PBU₃ and SBU₂. The shielding should arise by an aromatic ring current of Ptol₃ and AsPh₃, since in the proposed Structure II 4-H is favourably situated in the shielding region of the aromatic rings of Ptol₃ and AsPh₃.

The signals of 5-H of [MX(aft)(PBU₃)] are a triplet (M = Pd) or a doublet of doublets (M = Pt)

TABLE 3. $^{13}\text{C}\{^1\text{H}\}$ NMR (22.6 MHz) Spectra of the Complexes

Complex	Solvent	^{13}C (ppm) ^a					
		2-C	3-C	4-C	5-C	C(=S)	CH ₃ (N)
Haft	CDCl ₃	152.1	117.1	111.7	143.0	185.3	44.2
[PdCl(aft)]	dms _o -d ₆	148.6	b	116.9	145.4	175.9	44.0, 42.8
[PdBr(aft)]	dms _o -d ₆	148.3	b	117.6	145.6	176.0	44.1, 42.9
[PdI(aft)]	dms _o -d ₆	148.5	b	121.1	145.8	176.3	44.2, 42.8
[PdCl(aft)(PBU ₃)]	CDCl ₃	152.4(1.4)	143.4(4.8)	118.8(8.3)	144.6(2.8)	180.2(2.8)	44.9(2.8), 43.0
[PdBr(aft)(PBU ₃)]	CDCl ₃	152.4(1.4)	145.0(4.1)	118.7(8.3)	144.7(2.8)	180.1(3.5)	44.9(2.8), 42.9
[PdI(aft)(PBU ₃)]	CDCl ₃	152.0(1.4)	146.9(2.8)	118.3(8.3)	145.3(2.8)	181.1(2.8)	45.2(3.5), 43.1
[PdCl(aft)(SBU ₂)] ^c	CDCl ₃	149.8	143.6	117.0	144.9	179.1	44.4, 42.9
[PdCl(aft)(Ptol ₃)]	CDCl ₃	151.7(1.4)	143.6(3.5)	120.2(10.4)	144.5(2.8)	179.9(3.5)	44.9(2.8), 42.9
[PdCl(aft)(AsPh ₃)]	CDCl ₃ ^d	151.3	142.1	120.2	143.9	179.9	44.7, 42.8
[PtCl(aft)]	dms _o -d ₆ ^d	151.3	135.8	117.6[42.8] ^e	148.2[39.4]	174.9	44.5[15.9], 42.9
[PtCl(aft)(PBU ₃)]	CDCl ₃	154.2[116] (2.8)	134.0[1102] (7.6)	118.8[86.0] (4.1)	147.4[53.2]	179.3[30.4] (2.8)	45.2[9.0], 42.9 (2.8)
[PtCl(aft)(SBU ₂)]	CDCl ₃	152.1[158]	136.0[1065]	116.0[51.1]	147.8[40.8]	178.6[29.7]	44.6[17.3], 42.8

^aOnly the signals due to aft are given in this table. Figures in parentheses are $J(\text{P}-\text{C})$ and those in square brackets $J(\text{Pt}-\text{C})$ in Hz. ^bCould not be detected. ^cIn the presence of excess free SBU₂ to prevent precipitation. ^dIn the presence of tris(acetylacetonato)chromium(III) as a relaxation reagent. ^eFor carbons bearing no proton $J(\text{Pt}-\text{C})$ could not be identified because of low quality of the spectrum.



and both signals become a simple doublet upon irradiation of 4-H. The $^5J(\text{P}-\text{H})$ values are then obtained (Table 2). The appreciably long range coupling may result from an extended W-conformation pathway [2]: (5-H)–(5-C)–(4-C)–(3-C)–M(P).

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{MX}(\text{aft})\text{L}]$ are similar to those of the parent $[\text{MX}(\text{aft})]$ (Table 3). To ascertain the assignment of signals $^1J(\text{C}-\text{H})$ values were measured for $[\text{PdCl}(\text{aft})(\text{PBU}_3)]$. The values are 173 Hz for 4-C and 204 Hz for 5-C as usually observed [2]. When L is a phosphine ligand, $J(\text{P}-\text{C})$ is observed for the $^{13}\text{C}\{^1\text{H}\}$ signals of aft except for one of the signals of the $(\text{CH}_3)_2\text{N}$ group. The coupled methyl signals are always at a lower field than the uncoupled ones. For $\text{M} = \text{Pt}$, $J(\text{Pt}-\text{C})$ is similarly observed except the same one is again absent. These appreciably long range $^5J(\text{P}-\text{C})$ and $^4J(\text{Pt}-\text{C})$ of the methyl group may be due to the fact that one methyl group gratifies an extended W-conformation pathway: $\text{CH}_3-\text{N}=\text{C}=\text{S}-\text{Pt}(\text{P})$, while the other is directed differently. The value $^1J(\text{Pt}-\text{C})$ of 3-C (Table 3) is similar to those reported for cycloplatinated carbon atoms situated *trans* to a Cl donor [5] and $^1J(\text{Pt}-\text{P})$ of $[\text{PtCl}(\text{aft})(\text{PBU}_3)]$

suggests that PBU₃ is coordinated *trans* to a donor with moderate *trans* influence [5]. This further supports Structure II.

The byproduct $[\text{PtCl}(\text{aft})(\text{Haft})]$ is characterized by ^1H and IR spectra. The ^1H NMR spectrum (Table 2) reveals the presence of both aft and Haft. The IR spectrum shows two strong bands at 1532 and 1572 cm^{-1} assignable to $\nu(\text{C}-\text{N})$ and in the region of aromatic ring C–H out-of-plane deformation vibrations two characteristic bands at 758 and 774 cm^{-1} are observed. Free Haft shows the band at 752 and $[\text{PtCl}(\text{aft})(\text{SBU}_2)]$ at 795 cm^{-1} to support the presence of both aft and Haft. In the far IR region a strong band at 287 cm^{-1} is assigned to $\nu(\text{Pt}-\text{Cl})$. The byproduct has Structure II where L is Haft which is coordinated through the thioamide-S atom alone.

Experimental

Synthesis of *N,N*-Dimethyl-2-furancarbothioamide-(Haft)

Haft was obtained by thiation of *N,N*-dimethyl-2-furancarbothioamide with Lawesson's reagent as in the literature method [9]. Boiling point 159–162 °C/18 mmHg. Yield 65%. *Anal.* Found: C, 54.10; H, 5.92; N, 9.10. Calc. for $\text{C}_7\text{H}_9\text{NOS}$: C, 54.17; H, 5.84; N, 9.02%. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data are given in Tables 2 and 3. IR (nujol mull): 1511s, 1389s, 1380s, 1292s, 1280m, 1144s, 1027m, 752s, 594m cm^{-1} (s = strong and m = medium).

Synthesis of the Complexes

Melting points, yields and analytical results of the complexes are given in Table 1.

[PdCl(aft)]

To a solution of 1 mmol of lithium tetrachloropalladate in 30 ml of methanol, prepared *in situ* from 2 mmol of lithium chloride and 1 mmol of palladium(II) chloride, was added 1 mmol of Haft and the mixture was stirred for 1 day at room temperature. A yellow precipitate was collected, washed with methanol and dried in air. *[PdBr(aft)]* was similarly prepared by use of 4 mmol of lithium bromide instead of lithium chloride and *[PdI(aft)]* was obtained by metathesis of *[PdCl(aft)]* with a four-fold excess of lithium iodide in acetone.

[PtCl(aft)]

To a solution of 1 mmol of potassium tetrachloroplatinate(II) in 20 ml of water was added a solution of 1 mmol of Haft in 20 ml of methanol and processed as above. The product, a mixture of *[PtCl(aft)]* and *[PtCl(aft)(Haft)]*, was suspended in 100 ml of dichloromethane and stirred for several hours at room temperature. The undissolved solid was collected, washed with dichloromethane, and dried in air to give pure *[PtCl(aft)]*. The mother liquor was concentrated to a few ml and mixed with about ten times the volume of methanol to precipitate *[PtCl(aft)(Haft)]*, which was washed with methanol and dried in air.

[MCl(aft)L]

Reaction of *[MCl(aft)]* with a stoichiometric amount of L (in the case of SBU_2 , a two-fold excess was used) in dichloromethane gave *[MCl(aft)L]*, which was precipitated by addition of hexane to a concentrated solution. Metathesis of *[MCl(aft)L]* with lithium bromide or lithium iodide in acetone gave the corresponding bromo and iodo complexes, respectively.

Measurements

NMR spectra (^1H , ^{13}C , ^{31}P) were recorded on a Hitachi R-90H spectrometer. Chemical shifts in δ ppm are given relative to tetramethylsilane (^1H , ^{13}C) or 85% H_3PO_4 (^{31}P). Other measurements were carried out by the methods reported previously [10].

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