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METAL-THIOPHEN DERIVATIVES. ORGANOMETALLIC COMPOUNDS OF PALLADIUM AND PLATINUM

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Summary

Thienylmercury(II)chloride reacts with $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, $[\text{Pd}(\text{PPh}_3)_4]$ and $[\text{Pt}(\text{PPh}_3)_4]$ to afford new compounds containing a metal-2-thienyl linkage. The compound $[\text{Pd}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{Cl}]$ probably has *trans* stereochemistry.

2-Bromothiophen undergoes oxidative addition with $[\text{Pd}(\text{PPh}_3)_4]$ and $[\text{Pt}(\text{PPh}_3)_4]$, probably via a radical mechanism. With $[\text{Pd}(\text{CO})(\text{PPh}_3)_3]$, a carbonyl inserted product is obtained. The bromo-metal(II) complexes have *trans* stereochemistry. The course of the reaction between 3-methyl-2-bromothiophen and $\text{Pd}(\text{PPh}_3)_4$ is more complex. Thus, there is evidence of some *cis* bromopalladium(II) compounds amongst the products, also there is good evidence to support the view that some isomerisation of 3-methyl-2-thienyl to 4-methyl-2-thienyl occurs during the reaction, thus giving greater molar quantities of $[\text{Pd}(\text{PPh}_3)_2(4\text{-CH}_3\text{-2-C}_4\text{H}_2\text{S})\text{Br}]$ than can be accounted for from any initial 4-methyl-2-bromothiophen impurity.

The metallation of the thiophen ring, probably in the 4-position, with palladium(II) is described for 3-thienylidene-4-methylaniline.

Introduction

Thiophen derivatives are of some pharmaceutical interest [1], and this prompted us to investigate new ways of introducing a 2-aldehyde group to a thiophen ring. Our work included a survey of methods of forming some transition metal to thiophen bonds involving the 2-carbon atom of the thiophen nucleus. This paper reports experiments carried out with palladium and platinum.

We are prompted to communicate our results by the appearance of two recent papers. Thus, Nonoyama [2] reports the cyclopalladation of 2-acetylthiophenacetylhydrazone, which is the only such compound to be reported

apart from Giordano and Rasmussen's successful metallation of 2-(2-pyridyl) thiophen [3]. Maitlis and his co-workers [4] have recently reported some tetramethylthiophen derivatives of noble metals following their observation [5] that thiophen was an efficient poison for an alkene hydrogenation catalyst. Also Eaborn and co-workers have reported the synthesis of one compound considered here [6].

During the course of our work, Heck demonstrated the carbonylation [7] and amidation [8] of 2-thienylpalladium systems. We do not therefore stress related parts of our work.

Experimental

All thiophen derivatives were supplied by Croda Synthetic Chemicals Limited, and their purity was checked by GLC. $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ [9], *cis*- [10] and *trans*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ [11], $[\text{Pd}(\text{PPh}_3)_4]$ [12] and $[\text{Pt}(\text{PPh}_3)_4]$ [13] were prepared by the indicated literature methods. $[\text{Pd}(\text{PPh}_3)_2\text{Br}_2]$ was prepared from the dichloro-compound by metathesis with excess potassium bromide. $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ was prepared following the method of Doyle [14] and 3-thienylidene-4-methylaniline [15] and 3-thiophen aldehyde [16] were synthesised via established routes.

Preparation of complexes

Reactions with 2-thienylmercury(II) chloride:

(a) with $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$. 2-Thienylmercury(II)chloride (3.18 g, 10 mmol) was dissolved in benzene/dioxane (1/2, 100 ml). $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (7.01 g, 10 mmol) was added to the solution, followed by an excess of triphenylphosphine (5.24 g, 20 mmol). The mixture was heated under reflux for 3 h and filtered hot (to remove the precipitate of $\text{HgCl}_2 \cdot 2 \text{PPh}_3$). The filtrate afforded a yellow precipitate on cooling ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$). Evaporation of solvent gave a yellow material, which was triturated with ether and re-crystallised from benzene (1/1) to give pure chloro-2-thienylbis(triphenylphosphine)palladium (II) in 68% yield (m.p. 184°C). Found: C, 62.2; H, 4.52; P, 7.69; S, 4.47. $\text{C}_{40}\text{H}_{33}\text{ClP}_2\text{PdS}$ calcd.: C, 64.07; H, 4.44; P, 8.26; S, 4.27%.

(b) with *cis* and *trans*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$. The conditions described above were used. No reaction was noted with the *cis* isomer. The *trans* isomer is isomerised to the *cis* isomer over 24 h. No reaction with the mercury(II) compound was observed.

(c) with $[\text{Pd}(\text{PPh}_3)_4]$. $[\text{Pd}(\text{PPh}_3)_4]$ (1.15 g, 1 mmol) was suspended in benzene (50 ml) and treated with 2 thienylmercury(II) chloride (0.32 g, 1 mmol). The resulting green suspension was stirred overnight. A grey precipitate (mercury) was removed and the filtrate treated with n-hexane to give a pale yellow material of m.p. 184°C . Spectroscopic analysis showed this to be chloro-2-thienylbis(triphenylphosphine)palladium(II).

(d) with $[\text{Pt}(\text{PPh}_3)_4]$. An procedure identical to that for the palladium compound gave, after removal of mercury and dilution with n-hexane, yellow chloro-2-thienylbis(triphenylphosphine)platinum(II) in 65% yield, m.p. $144\text{--}146^\circ\text{C}$. Found: S, 3.70. $\text{C}_{40}\text{H}_{33}\text{ClP}_2\text{Pt}$ calcd.: S, 3.82%. (This compound has been prepared previously [6] when a m.p. of $158\text{--}160^\circ\text{C}$ was reported.)

Reactions with various 2-bromothiophens:

(a) *With [Pd(PPh₃)₄].* [Pd(PPh₃)₄] (2.89 mmol) was added to deaerated benzene (50 ml) containing 2-bromothiophen (6 ml). The mixture was refluxed for 4 h. The yellow solution was cooled and treated with ether to afford a yellow solid which was recrystallised from dichloromethane/n-hexane (1/1) to m.p. 186° C. (Yield 51%).

The reaction was repeated under identical conditions in the presence of galvinoxyl, benzoyl peroxide, or oxygen. In no case was the yield influenced by more than a few per cent. However, when the reflux time was reduced to 0.5 h, some product was still obtained, but when galvinoxyl was present no reaction had occurred after 30 minutes. Found: C, 59.9; H, 4.96; P, 7.14; S, 4.30. C₄₀H₃₃BrP₂PdS calcd.: C, 60.5; H, 4.16; P, 7.81; S, 4.03%.

(b) *With [Pt(PPh₃)₄].* [Pt(PPh₃)₄] (12.49 g, 2 mmol) was added to deaerated benzene (50 ml) followed by 2-bromothiophen (6 ml). The mixture was heated under reflux for 4 h, cooled and finally treated with ether to give a white material (m.p. 246° C) in 74% yield. Evaporation of the filtrate afforded the remaining starting material.

In this case, addition of galvinoxyl caused a significant reduction in yield despite the 4 h reflux period, e.g. the presence of 10–15 mol % galvinoxyl under the above conditions reduced the yield by over 10%. Found: C, 54.5; H, 3.83; P, 6.88; S, 3.85. C₄₀H₃₃BrP₂PtS calcd.: C, 54.4; H, 3.63; P, 7.03; S, 3.63%.

(c) *With [Pd(CO)(PPh₃)₃].* [Pd(CO)(PPh₃)₃] (0.92 g, 1 mmol) was dissolved in toluene (30 ml) at –40° C under an atmosphere of carbon monoxide and treated with 2-bromothiophen (3 ml). The solution was stirred at –40° C for 3 h, and then allowed to warm to ambient temperature. Hexane was added to afford a yellow product in 73% yield which subsequent examination showed to be [2-C₄H₃S · CO · Pd(PPh₃)₂Br]. Found: C, 57.8; H, 4.56; S, 3.90. C₄₁H₃₃BrOP₂PdS calcd.: C, 59.9; H, 4.56; S, 3.98%.

(d) *Reactions of 2-bromo-3-methylthiophen were carried out with Pd(PPh₃)₄ under various conditions:* (i) Use of purified 2-bromo-2-methylthiophen and the conditions described above for 2-bromothiophen afforded a yellow product of m.p. 172–174° C. Found: C, 59.5; H, 4.55; P, 6.34; S, 3.93. C₄₁H₃₅BrP₂PdS calcd.: C, 60.8; H, 4.45; P, 7.67; S, 3.96%. (ii) If the reactions were repeated using crude 2-bromo-3-methylthiophen, shown by GLC to be slightly contaminated with 2-bromo-4-methylthiophen, a yellow product having the same elemental analysis is obtained. However, ¹H NMR spectroscopy showed there to be a greater molar proportion of 4-methylthienyl in the palladium containing product than in the original sample of “3-substituted” thiophen. (iii) The reaction with crude 2-bromo-3-methylthiophen was repeated using ethylene glycol as solvent. The product contained a marginally smaller amount of the 4-methyl isomer (see Table 1).

(e) Reaction of 2-bromo-3-methyl thiophen with [Pt(PPh₃)₄] in benzene gives a yellow product in 72% yield which, when the initial thiophen is contaminated with the 4-methyl isomer, contains both Pt(PPh₃)₂(3-MeC₄H₂S)Br and [Pt(PPh₃)₂(4-MeC₄H₂S)Br].

(f) *Preparation of 2-bromo-3-methylthiophen-2-aldehyde.* 2-Bromo-3-methylthiophen (59 g, 333 mmol), dichlorobis(triphenylphosphine)palladium(II) (3.5 g,

TABLE 1

PROPORTION OF $[\text{Pd}(\text{PPh}_3)_2(3\text{-MeC}_4\text{H}_2\text{S})\text{Br}]$ AND $[\text{Pd}(\text{PPh}_3)_2(4\text{-MeC}_4\text{H}_2\text{S})\text{Br}]$ IN PRODUCTS OBTAINED FROM REACTION OF $[\text{Pd}(\text{PPh}_3)_4]$ WITH CRUDE 2-BROMO-3-METHYL THIOPHEN (CONTAMINATED WITH 2-BROMO-4-METHYLTHIOPHEN)

Solvent	Yield (overall)	Proportion of isomers in Pd complex	
		3-Methyl	4-Methyl
Benzene	74%	79%	21%
Ethylene glycol	85%	84%	16%

5 mmol), triethylamine (41 g, 400 mmol) and benzene (200 ml) were sealed in a Baskerville and Lindsay autoclave of 1 litre capacity. The vessel was purged twice with nitrogen, and once with carbon monoxide and finally charged with 20 atm of carbon monoxide and to 40 atm with hydrogen. The temperature was raised to 130°C and the reaction was allowed to continue until no further uptake of gases occurred.

At the completion of the reaction the gases were vented, and the reaction mixture was filtered to give crystalline triethylamine hydrobromide (49 g). Removal of benzene afforded a red oil (37 g) shown to contain 3-methylthiophen-2-aldehyde (54%) and 4-methylthiophen-2-aldehyde (18%). In molar terms, the yield of the 4-methyl-isomer is greater than can be accounted for by the quantity of 2-bromo-4-methylthiophen originally present. An analogous reaction could be carried out using dibromobis(triphenylphosphine)palladium(II).

(g) *Attempts to directly metallate a thiophen nucleus with palladium.* One successful experiment is described:

3-Thenylidene-4-methylaniline was prepared from 3-thiophenaldehyde and *p*-toluidine, m.p. 60°C (lit. [15], 60–61°C).

Metallation of 3-thenylidene-4-methylaniline

3-Thenylidene-4-methylaniline (1 g, 5 mmol) was dissolved in benzene (100 ml) under nitrogen and $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (0.96 g, 2.5 mmol) was added. The solution was stirred overnight, the yellow precipitate was filtered under nitrogen washed with ether and dried in vacuo. Yield: 91%. m.p. 200°C. Found: C, 56.3; H, 4.0; Cl, 6.2; N, 4.4; S, 11.0%. $\text{C}_{27}\text{H}_{23}\text{ClN}_2\text{PdS}_2$ calcd.: C, 55.8; H, 4.0; Cl, 6.1; N, 4.8; S, 11.0%.

From analysis the yellow product is formulated as $[\text{Pd}(\text{L} - \text{H})\text{L} \cdot \text{Cl}] \frac{1}{2} \text{C}_6\text{H}_6$ when $\text{L} = 3\text{-C}_4\text{H}_3\text{S} \cdot \text{CH}=\text{N} \cdot \text{C}_6\text{H}_4\text{-}p\text{-CH}_3$.

Physical Measurements

Mass spectra were recorded at 70 eV with an AEI MS9 instrument. ^1H NMR spectra were obtained with Varian HA 100D (100 MHz) or Perkin Elmer R10 (60 MHz) instruments. TMS was used as internal standard. (Two ^{31}P NMR spectra were obtained courtesy of Mr. E. Hartland).

Infra-red spectra (400–250 cm^{-1}) were recorded with a Perkin Elmer 457 instrument and the range 400–200 cm^{-1} was covered using a Perkin Elmer 225

instrument. Some spectra were recorded in the range $400\text{--}40\text{ cm}^{-1}$ using a RHC FS720 Interferometer. Conductivity measurements were made with a Mullard bridge using a standard cell (type E7591/B). GLC analyses of bromothiophens were provided by Croda Synthetic Chemicals Limited.

Results and discussion

(a) Reactions of 2-thienylmercury(II) chloride

The reaction of $[(2\text{-C}_4\text{H}_3\text{S})\text{HgCl}]$ with *trans* $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ went to completion only in the presence of excess triphenylphosphine despite the use of dioxane as solvent. The product of the reaction was $[\text{Pd}(2\text{-C}_4\text{H}_3\text{S})\text{Cl}(\text{PPh}_3)_2]$ which is assigned *trans* stereochemistry since it shows isomorphism with $[\text{Pt}(2\text{-C}_4\text{H}_3\text{S})\text{Br}(\text{PPh}_3)_2]$, which is rather convincingly shown to be *trans* by ^{31}P NMR spectroscopy (vide infra). The palladium–chlorine stretch is assigned at 302 cm^{-1} (by comparison with the bromo-complex). This enables us to place the $2\text{-C}_4\text{H}_3\text{S}$ -group in a *trans* influence series [17,18]:



No reaction was observed between $[(2\text{-C}_4\text{H}_3\text{S})\text{HgCl}]$ and *cis*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$. When *trans*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ was used, the only reaction was the isomerisation to the *cis* compound. The mercury(II) compound did however react with the tetrakis(triphenylphosphine)metal(0) derivatives for both palladium and platinum. For palladium the product was identical with that obtained by the *trans* metallation procedure above, namely $[\text{Pd}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{Cl}]$. The platinum compound is stoichiometrically similar (see also ref. 6). It is likely, following Sokolov [19] that these products arise via intermediates containing palladium or platinum to mercury bonds.

The assignment of $\nu(\text{MC})$ in these compounds is a matter of some interest. Given the similar mass of iodine and palladium the work of Horak and coworkers with 2-iodothiophen [20] provides a useful starting point. The band most closely corresponding to $\nu(\text{CI})$ is located at 277 cm^{-1} , hence we may well scan the $200\text{--}300\text{ cm}^{-1}$ region for $\nu(\text{PdC})$ and $\nu(\text{PtCl})$. Without resort to isotopic substitution work [21,22] we are hesitant to speculate on a particular assignment, but suffice it to say that coupling between $\nu(\text{MC})$ and $\nu(\text{MCl})$ seems very possible, thus the use of $\nu(\text{MCl})$ to establish a *trans*-influence series is only likely to be valid if $\nu(\text{PdCl})$ and $\nu(\text{PdC})$ differ considerably in energy. Following Nakamoto [21], bands located at 191 cm^{-1} for $\text{Pd}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) are assigned as $\nu(\text{PdP})$.

(b) Reaction of 2-bromothiophen and related compounds

2-Bromothiophen reacted with both $[\text{Pd}(\text{PPh}_3)_4]$ and $[\text{Pt}(\text{PPh}_3)_4]$ in refluxing benzene to give the expected products of oxidative addition in good yield. Using a long reaction time (4 h) for the palladium system, it was found that the ultimate yield was uninfluenced by the initial presence of galvinoxyl, benzoyl peroxide or oxygen. However, when the influence of these materials was investigated over a shorter time scale (0.5 h), it was observed that galvinoxyl totally inhibited the reaction. In the case of $[\text{Pt}(\text{PPh}_3)_4]$ yields of product were noticeably less in the presence of galvinoxyl.

Thus, as Osborn [23] has observed for several alkyl halides, radical pathways are possible. The influence of galvinoxyl might argue for a radical chain mechanism [23], however, great care must be exercised in the interpretation of this observation since galvinoxyl may react with $[\text{Pd}(\text{PPh}_3)_4]$. Thus, a non-chain process is also possible [24], but in the absence of serious mechanistic study no distinction can be made between these routes. Also, we cannot assume that the radical mechanism is the only one operative.

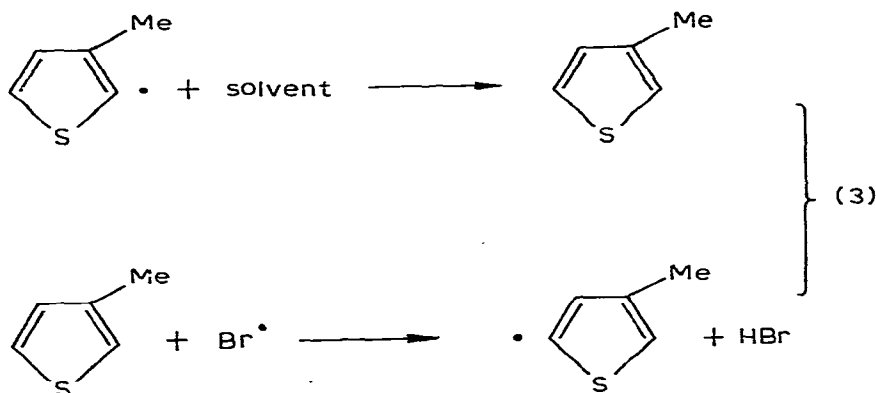
The ^{31}P NMR spectrum of $[\text{Pt}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{Br}]$ shows a single chemical shift with $^1J(\text{Pt}-\text{P}) = 1870$ Hz. This is entirely consistent with *trans* stereochemistry and X-ray powder photography shows $[\text{Pd}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) to be isomorphous with *trans* $[\text{Pt}(\text{PPh}_3)_2(2\text{-C}_4\text{H}_3\text{S})\text{Br}]$.

$[\text{Pd}(\text{CO})(\text{PPh}_3)_3]$ will react with 2-bromothiophen to give the carbonyl-inserted product, $[\text{Pd}(2\text{-C}_4\text{H}_3\text{S} \cdot \text{CO})(\text{PPh}_3)_2\text{Br}]$ which is consistent with the view of Heck that such species are intermediates in this carbonylation studies of a range of organic halides [7].

Given the importance of 3-methylthiophen-2-aldehyde, the reactions of 3-methyl-2-bromothiophen with $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) were of some interest to us. As supplied, the compound contains some 4-methyl-2-bromothiophen. Reaction of pure (GLC) 3-methyl-2-bromothiophen with $[\text{Pd}(\text{PPh}_3)_4]$ affords a material giving a single methyl resonance in CDCl_3 solutions (δ 1.51 ppm vs. TMS) and formulated as $[\text{Pd}(\text{PPh}_3)_2(3\text{-Me-2-C}_4\text{H}_2\text{S})\text{Br}]$. Examination of the ^{31}P NMR spectrum (CHCl_3) reveals a more complex picture. Thus four distinct resonances are seen; a single intense signal and a grouping of three weaker signals (1/3/2 with a total separation of 33 Hz) to lower field. A possible interpretation is that we have a *trans* isomer as the main component, together with two *cis* isomers in approximately 2/1 ratio showing small, but differing $^2J(\text{P}-\text{P})$ of ~ 22 Hz and ~ 11 Hz. Hence it would appear that the stereochemical course of this reaction differs from that with 2-bromothiophen, also that a small quantity of another product (probably $[\text{Pd}(\text{PPh}_3)_2(4\text{-Me-2-C}_4\text{H}_2\text{S})\text{Br}]$ in the light of subsequent work) has been produced.

Further experiments were carried out with specimens of 3-methyl-2-bromothiophen used as obtained. Stoichiometrically all products from the reaction of this material with $[\text{Pd}(\text{PPh}_3)_4]$ were $[\text{Pd}(\text{PPh}_3)_2(\text{C}_5\text{H}_5\text{S})\text{Br}]$, however, in chloroform solution two methyl resonances (δ 1.51 and 1.26 ppm) are seen. The latter may be shown to arise from a 4-methyl-2-thienyl residue. 3- and 4-methyl-2-bromothiophen show methyl resonances at δ 2.13 and 2.03 ppm respectively, thus substitution of the electronegative bromo group by palladium(II) causes the methyl proton to become more shielded. An interesting observation is that, in molar terms, the organometallic complexes contain a greater proportion of the 4-methyl-2-thienyl residue (NMR) than was present in the initial bromothiophen (GLC, NMR). Thus, some isomerisation of the thiophen residue has occurred. A rather smaller proportion of the 4-methyl compound was formed when the more viscous ethylene glycol replaced benzene as the solvent for oxidative addition (see experimental section). Similar observations are made for $[\text{Pt}(\text{PPh}_3)_4]$. Clearly, a rather complex reaction has been discovered. The indication, from our limited access to ^{31}P NMR facilities, that some *cis* isomer might be involved need not imply a fundamentally different mechanism for the oxidative addition compared with 2-bromothiophen. More

probably we are simply observing the beginning of a slow isomerisation of the kinetically formed *trans* isomer to the thermodynamically preferred *cis* isomer. In the absence of a rigorous kinetic study excessive mechanistic speculation is not justified. We may, however, suggest that, if radical processes are operative, after the initial capture of a bromine atom by a palladium(0) species subsequent reaction with a less sterically hindered 4-methyl-2-thienyl radical may be more rapid than with a 3-methyl-2-thienyl radical. The 3-methyl-2-thienyl radical may have a larger average lifetime and, hence, may enter into side reactions leading to the generation of further 4-methyl-2-thienyl radicals, e.g.:



The use of a more viscous solvent such as ethylene glycol should reduce the concentration of solvent separated free radicals and reduce the importance of processes such as reaction 3. This is in accord with observation, but the effect is by no means dramatic.

A synthesis of 3-methylthiophen-2-aldehyde based on the above chemistry was developed (experimental section). The observed formation of a greater than expected proportion of 4-methylthiophen-2-aldehyde may be interpreted in terms of faster attack on 4-methylthienyl radicals during the oxidative addition stage and also in terms of isomerisation of the 3-methyl to 4-methyl through radicals.

(c) Direct metallation of the thiophen nucleus

The direct metallation of the thiophen ring with metals such as palladium or platinum was of some interest to us. In benzene chemistry, the presence of a donor group as substituent in the ring will often promote metallation of a position *ortho* to the substituent. The two reported examples of metallation of the thiophen ring [3,4] are of this type. We examined a fairly wide range of materials in which a donor group was a 3-substituent in the thiophen ring, but only in one case did we obtain reasonably convincing evidence that metallation had occurred. The reaction of 3-C₄H₃S · CH=N · C₆H₄ · CH₃ (L) with [Pd(PhCN)₂ · Cl₂] in dry benzene affords a rather intractable yellow material, the elemental analysis of which suggests metallation to have occurred in one of the two thiophen rings present, hence the compound may be formulated [Pd(L - H)L · Cl · $\frac{1}{2}$ C₆H₆]. The insolubility of the material virtually leaves solid state infra-red spectroscopy as the major investigative tool. The spectrum between 900 and

700 cm^{-1} is extremely complex and simple comparison with a range of 2,3- and 3,4-dichloro- and dibromothiophens [25] implies that metallation has probably occurred at the 4-position.

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