

CYCLOPALLADATION AND CYCLORHODATION OF *N*-(3-THIENYL)PYRAZOLE

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Summary

N-(2-Thienyl)pyrazole (H(2-tpz)) gives the pyrazole-*N*-coordinated complex $[\text{PdCl}_2(\text{H}(2\text{-tpz}))_2]$ with palladium(II) chloride and *N*-(3-thienyl)pyrazole (H(3-tpz)) gives similarly $[\text{PdCl}_2(\text{H}(3\text{-tpz}))_2]$ and cyclopalladated $[\text{PdCl}(\text{3-tpz})]_2$. The cyclopalladation occurs mainly at position 2 of the thiophene ring with a significant amount of the reaction at position 4 (ratio 3 : 1), contrary to lithiation which is reported to occur exclusively at position 2. H(3-tpz) is also metallated similarly by hexachlorotetrakis(tri-*n*-butylphosphine)dirhodium(III) to give $[\text{RhCl}_2(\text{PBU}_3)(\text{3-tpz})]_2$. These dimeric palladium and rhodium complexes form adducts with pyridine and tri-*n*-butylphosphine.

Introduction

Thiophene is an aromatic compound having physical and chemical properties very similar to those of benzene [1]. A wealth of cyclo(*ortho*)metallation reactions of benzene derivatives are known [2] and thiophene derivatives are expected to be similarly cyclometallated, but only a little is known of cyclo-metallation reactions of thiophene derivatives so far. The thiophene derivatives for which cyclometallation is reported are 2-(2-thienyl)pyridine, which is cyclometallated by palladium(II) and platinum(II) [3], and thiophene-2 (or 3)-carbaldehyde anils, which are cyclometallated by iron carbonyls [4]. Thiophene-3-carbaldehyde *p*-methyl-anil was claimed to be cyclopalladated at position 4 of a thiophene ring but the evidence is not conclusive [5]. We are interested in cyclometallation reactions of thiophene derivatives and some results are already reported [6]. In this paper the reactions of *N*-(thienyl)pyrazoles are described.

Results and discussion

The reaction of *N*-(2-thienyl)pyrazole (abbreviated as H(2-tpz)) with palladium chloride in methanol gave $[\text{PdCl}_2(\text{H}(2\text{-tpz}))_2]$ irrespective of the molar

TABLE 1
MELTING POINTS, YIELDS, ANALYTICAL RESULTS, AND $\nu(\text{Pd-X})$ OF THE COMPLEXES

No.	Complex	M.p. ^a (°C)	Yield (%)	Analysis, found (calcd.) %			$\nu(\text{M-X})$ (cm^{-1})
				C	H	N	
1	$[\text{PdCl}_2(\text{H}(2\text{-tpz}))_2]$	175 (dec)	79	35.07 (35.20)	2.45 (2.53)	11.77 (11.73)	351
2	$[\text{PdCl}_2(\text{H}(3\text{-tpz}))_2]$	165 (dec)	60	35.12 (35.20)	2.22 (2.53)	11.68 (11.73)	339
3	$[\text{PdCl}(\text{3-tpz})_2]$	240 (dec)	84	29.10 (28.89)	1.58 (1.73)	9.72 (9.62)	223, 252
4	$[\text{PdBr}(\text{3-tpz})_2]$	210 (dec)	57	25.20 (25.06)	1.50 (1.50)	8.31 (8.35)	210
5	$[\text{PdCl}(\text{py})(\text{3-tpz})]$	160 (dec)	59	39.11 (38.91)	2.75 (2.72)	11.39 (11.35)	252
6	$[\text{PdI}(\text{py})(\text{3-tpz})]$	135 (dec)	60	31.45 (31.22)	2.18 (2.18)	9.12 (9.10)	
7	$[\text{PdCl}(\text{PBu}_3)(\text{3-tpz})]$	118–120	38	46.11 (46.26)	6.65 (6.54)	5.63 (5.67)	250
8	$[\text{PdI}(\text{PBu}_3)(\text{3-tpz})]$	87–89	52	39.01 (39.02)	5.13 (5.51)	5.14 (4.79)	
9	$[\text{RhCl}_2(\text{PBu}_3)(\text{3-tpz})_2]$	270 (dec)	60	43.46 (43.44)	6.54 (6.14)	5.36 (5.33)	231, 276 318
10	$[\text{RhCl}_2(\text{PBu}_3)_2(\text{3-tpz})]$	245 (dec)	50	51.15 (51.17)	8.28 (8.17)	3.71 (3.85)	246, 313
11	$[\text{RhICl}(\text{PBu}_3)_2(\text{3-tpz})]$	230 (dec)	30	45.46 (45.46)	6.95 (7.26)	3.39 (3.42)	312

^a dec = decomposition.

ratio $\text{PdCl}_2/\text{H}(2\text{-tpz})(1/1 \text{ or } 1/2)$ (Table 1). Upon addition of sodium acetate, the reaction mixture turned dark. *N*-(3-Thienyl)pyrazole ($\text{H}(3\text{-tpz})$) gave a similar complex $[\text{PdCl}_2(\text{H}(3\text{-tpz}))_2]$ when $\text{PdCl}_2/\text{H}(3\text{-tpz}) = 1/2$, but when the ratio was 1/1, $[\text{PdCl}(\text{3-tpz})_2]$ was obtained in the presence of sodium acetate. $\text{H}(3\text{-tpz})$ reacted with $[\text{RhCl}_3(\text{PBu}_3)_2]_2$ ($\text{PBu}_3 = \text{tri-}n\text{-butylphosphine}$) in refluxing xylene to give $[\text{RhCl}_2(\text{PBu}_3)(\text{3-tpz})_2]$, but $\text{H}(2\text{-tpz})$ did not afford the desired compound. The palladium and rhodium complexes of 3-tpz reacted readily with pyridine(py) and tri-*n*-butylphosphine to give adducts like other cyclometallated, halogen-bridged dimeric complexes [2].

The ^1H NMR spectral data are summarized in Table 2 and the numbering of ring protons is shown in Structures a and b. The relative intensities of ^1H NMR signals clearly suggest that in $[\text{PdCl}_2(\text{H}(2\text{-tpz}))_2]$ and $[\text{PdCl}_2(\text{H}(3\text{-tpz}))_2]$ all of the ring protons of $\text{H}(2\text{-tpz})$ or $\text{H}(3\text{-tpz})$ remain. The far infrared spectra of the two show $\nu(\text{Pd-Cl})$ at 351 and 339 cm^{-1} , respectively. The two complexes may have a *trans* structure with $\text{H}(2\text{-tpz})$ and $\text{H}(3\text{-tpz})$ coordinated through pyrazole N atoms.

The assignments of each peak in the ^1H NMR spectrum of $[\text{PdCl}(\text{3-tpz})_2]$ in $\text{DMSO-}d_6$ are given in Table 2. The spectrum can be explained by assuming the presence of a mixture of two isomers; a major component and a minor one. The relative ratio is estimated to be approximately 3 : 1 from the ^1H NMR spectrum.

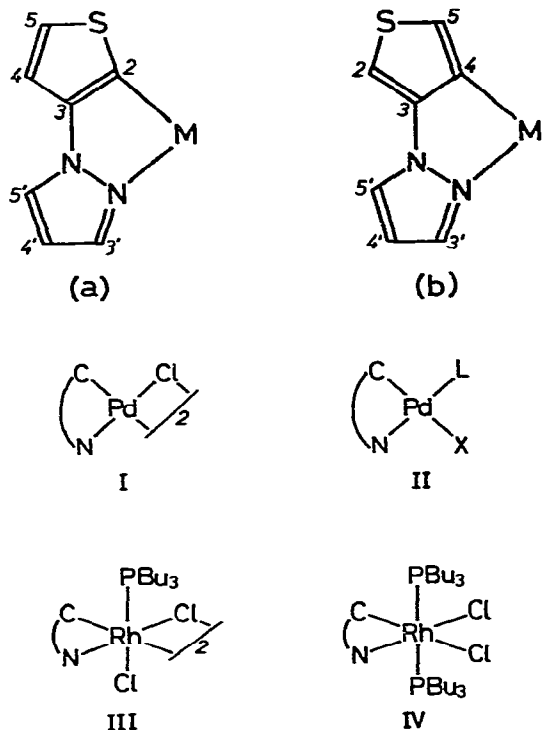
The two partially overlapped triplets at the highest field ($\delta = 6.6\text{--}6.9 \text{ ppm}$)

TABLE 2

¹H NMR SPECTRA OF THE LIGANDS AND COMPLEXES (AT 60 MHz)^a

Complex	Solvent	Major component			Minor component		
		4,5-H	3',5'-H	4'-H	2,5-H	3',5'-H	4'-H
H(2-tpz)	CDCl ₃	7.03 m ^b	7.83 d (2.4) 7.71 d (2.0)	6.46 t (2.2)			
[PdCl ₂ (H(2-tpz)) ₂]	CDCl ₃	7.08-7.69 m ^b	7.97 d (2.4) 7.73 d (2.0)	6.54 t (2.6)			
H(3-tpz)	CDCl ₃	7.43 s ^c	7.87 d (2.4) 7.74 d (2.0)	6.48 t (2.0)			
	DMSO-d ₆	7.77 m ^c	7.77 m	6.59 t (2.1)			
			8.47 d (2.4)				
[PdCl ₂ (H(3-tpz)) ₂]	CDCl ₃	7.48-7.82 m ^c	7.94 dd (2.4; 0.8) 8.13 dd (2.8; 1.6)	6.55 t (2.6)			
[PdCl(3-tpz)] ₂	DMSO-d ₆	7.52 s	8.65 d (2.4) 7.99 d (2.4)	6.67 t (2.6)	7.73 d (2.8) d	8.81 d (2.4) 8.05 d (2.4)	6.80 t (2.4)
[PdBr(3-tpz)] ₂	DMSO-d ₆	7.52 s	8.12 br	6.67 t (2.5)	d	8.80 d (2.6) d	6.78 t (2.5)
			8.65 d (2.3)				
[PdCl(py-d ₅)(3-tpz)]	CDCl ₃	7.17 s	7.48 d (2.8) 7.80 d (2.4)	6.42 t (2.4)	7.02 d (2.5) 6.12 d (2.5) d	7.85 d (2.4) 7.65 d (2.8) 8.47 d (2.4)	6.52 t (2.4)
[Pd(py-d ₅)(3-tpz)]	CDCl ₃	6.85-7.17 m	7.30 d (2.0) 7.79 d (2.4)	6.38 t (2.4)	5.95 d (2.5) 7.13 d (2.8)	7.97 d (2.4) 8.12 m	6.47 t (2.4)
			7.83 m				
[PdCl(PBu ₃)(3-tpz)]	CDCl ₃	7.17 d (5.6)	8.09 m	6.38 t (2.3)	6.73 dd (2.8; 1.6)	8.02 m	6.48 t (2.0)
		7.32 dd (5.6; 1.2)					
[Pd(PBu ₃)(3-tpz)]	CDCl ₃	7.13 d (5.6)	7.80 m	6.35 t (2.3)	7.03 d (2.8)	8.67 m	6.48 t (2.3)
		7.32 dd (5.6; 1.2)	8.57 m		7.83 dd (2.8; 1.6)	7.97 m	
[RhCl ₂ (PBu ₃)(3-tpz)] ₂	DMSO-d ₆	7.67 s	8.72 d (2.6) 8.01 d (2.4)	6.68 t (2.4)	7.14 d (2.8) 7.88 d (2.8) d	8.84 d (2.6) 8.07 d (2.4)	6.77 t (2.4)
			8.13 s, br				
[RhCl ₂ (PBu ₃) ₂ (3-tpz)]	CDCl ₃	7.38 d (5.2)	8.02 d (2.4)	6.51 t (2.4)	7.08 br d	8.20 br d	6.63 t (2.4)
		7.23 d (5.2)					
[RhCl(PBu ₃) ₂ (3-tpz)]	CDCl ₃	7.39 d (5.2)	8.50 s, br	6.45 t (2.4)	d	8.17 d (2.4)	6.53 t (2.4)
		7.22 d (5.2)	7.98 d (2.4)		d	8.62 br	

^a Figures in parentheses are coupling constants in Hz. s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. ^b The signal of 3-H overlaps with those of 4,5-H and the total intensity corresponds to three protons. ^c The signal of 2-H overlaps with those of 4,5-H and the total intensity amounts to three protons. ^d Obscured by the signals of major components.



are assigned to 4'-H of the pyrazole ring, and the intensity of the signals is taken as a standard. Doublets below 7.9 ppm are assigned to protons of the pyrazole ring, and the total intensity of the doublets amounts to two protons. The remaining signals are assigned to protons of the thiophene ring and the intensity sums to two protons. These facts suggest that one proton has been lost from the ligand, consistent with the analytical results (Table 1). The doublet at 7.73 ppm ($J = 2.8$ Hz) has an intensity of $1/4$ proton, and the coupling constant, $J = 2.8$ Hz, is a value typical of $J(2\text{-H}, 5\text{-H})$ of a 3,4-disubstituted thiophene [1,7], suggesting the structure b for the minor component. The major one is, therefore, assumed to have the structure a.

The strong band at 252 cm^{-1} of $[\text{PdCl}(\text{py})(3\text{-tpz})]$ and the one at 250 cm^{-1} of $[\text{PdCl}(\text{PBU}_3)(3\text{-tpz})]$ disappear in the infrared spectra of the corresponding iodo complexes, respectively. The strong bands are assigned to $\nu(\text{Pd}-\text{Cl})$ and the low frequencies suggest that the Cl ligand is situated *trans* to a σ -carbon donor with a large *trans* influence [8]. The structure II is thus suggested. The ^1H NMR spectra of the py and PBU_3 adducts show that they are also a mixture of two components and are similarly assigned as above (Table 2). The signals of 4,5-H (with a total intensity of $3/2$ protons) assigned to the thiophene ring of the major components of $[\text{PdX}(\text{PBU}_3)(3\text{-tpz})]$ show a coupling constant $J = 5.6$ Hz which is the value expected for $J(4\text{-H}, 5\text{-H})$ of a 2,3-disubstituted thiophene [1,7]. The minor components (the total signal intensity is $1/2$ proton) show $J = 2.8$ Hz which is the normal value for a 3,4-disubstituted thiophene. These facts support the above presumption that the major component has the structure a and the minor one the structure b.

It should be noted that in the ^1H NMR spectra of the minor component of $[\text{PdX}(\text{py-d}_5)(3\text{-tpz})]$ the signal due to one of thiophene ring protons appears at significantly higher field (6.12 ppm ($\text{X} = \text{Cl}$) and 5.95 ($\text{X} = \text{I}$)). The shielding is considered to arise from a ring current of the coordinated pyridine (L) in the following manner. The pyridine ring should be coordinated perpendicular to the plane of coordination because of the steric interactions between the pyridine ring 2(6)-H and thiophene ring 5-H, and the thiophene ring 5-H lies nearly above the pyridine ring, that is, in the shielding region. This is in accord with structure II (L = py) and with the structure b.

The rhodium complexes are also mixtures of two components like the palladium complexes, and the ^1H NMR spectra can be similarly interpreted (Table 2). For these rhodium complexes structures III and IV are inferred from analogy with other cyclorhodated benzene derivatives [2]. Only one Cl ligand is exchanged by an I^- upon metathesis reaction of $[\text{RhCl}_2(\text{PBU}_3)_2(3\text{-tpz})]$ with excess lithium iodide, and disappearance of only the lower $\nu(\text{Rh}-\text{Cl})$ band (Table 1) indicates the displacement of the Cl *trans* to a σ -carbon donor by I^- (structure IV).

Attempts to separate the isomers arising from these two coordination modes a and b have been unsuccessful so far. It should be noted that cyclopalladation and cyclorhodation of H(3-tpz) occur at positions 2 and 4 of a thiophene ring in a ratio 3 : 1, but lithiation with butyllithium [9] exclusively at position 2. The different courses of the two metallation reactions cannot be explained at the present and more detailed investigations will be undertaken.

Experimental

Measurements

Measurements were carried out by the methods reported previously [10].

Synthesis

Elemental analyses, melting points, and yields of the complexes are summarized in Table 1. *N*-(2-Thienyl)pyrazole and *N*-(3-thienyl)pyrazole were prepared by the known procedures [9].

$[\text{PdCl}_2(\text{HL})_2]$ (HL = H(2-tpz) and H(3-tpz)). To a solution of lithium tetrachloropalladate prepared in situ from 2 mmol of lithium chloride and 1 mmol of palladium chloride in 30 ml of methanol was added 2 mmol of H(2-tpz) or H(3-tpz), and the mixture was stirred for 1 day at room temperature. A yellow precipitate was collected, washed with methanol, and dried in air.

$[\text{PdCl}(3\text{-tpz})]_2$. To a suspension of 1 mmol of palladium chloride in 30 ml of methanol was added 1 mmol of H(3-tpz) and the mixture was stirred at room temperature for 1 day. To the resulting yellow solution was added 1 mmol of sodium acetate and stirring was continued for additional 2 days. The yellow product was collected, washed with methanol, and dried in air.

$[\text{RhCl}_2(\text{PBU}_3)(3\text{-tpz})]_2$. To a suspension of 0.5 mmol of $[\text{RhCl}_3(\text{PBU}_3)_2]_2$ in 50 ml of xylene was added 1 mmol of H(3-tpz), and the mixture was stirred at refluxing temperature for 6 h. After cooling a yellow precipitate was collected, washed with xylene, and dried in air.

*Pyridine and tri-*n*-butylphosphine adducts.* These were prepared by mixing

the above complexes with pyridine (excess) or tri-*n*-butylphosphine (stoichiometric amount) in dichloromethane and by precipitating the adducts with *n*-hexane (in the case of tri-*n*-butylphosphine complexes the dichloromethane solution was required to be concentrated to a small volume).

Bromo and iodo complexes. Metathesis reactions of the chloro complexes with excess of lithium bromide or iodide in hot acetone gave the bromo and iodo complexes, respectively.

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