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Synthesis of a Few Derivatives of Cycloiridated 2-(2-Thienyl)pyridine

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Synopsis. A few derivatives of cycloiridated 2-(2-thienyl)pyridine were prepared and characterized by infrared and ^{1}H NMR spectra.

Numerous cyclometallation reactions of benzene derivatives with transition metal compounds have been reported,[1,2] but only a few cases are known of cyclopalladation and cycloplatination of thiophene derivatives.[3,4] Since various chemical properties of thiophene are similar to those of benzene, cyclometallation reactions found for benzene derivatives might occur also for thiophene derivatives. We have studied reactions of 2-(2-thienyl)pyridine with some platinum-metal halides and found the first example of cycloiridation of the thiophene ring. The results are reported in this paper.

2-(2-Thienyl)pyridine (abbreviated as H(2-thpy)) reacted with hydrated iridium(III) chloride in boiling 2-methoxyethanol to give an orange complex, [{IrCl(2-thpy)$_2$}$_2$]. The complex reacted easily with unidentate ligand (L) to give the adducts, [IrClL(2-thpy)$_2$] (L=pyridine (py), tributylphosphine (PBu$_3$), and dimethyl sulfoxide (dmso)). The new complexes are air-stable; spectral data are given in Table 1 and Fig. 1.

The infrared spectrum of free H(2-thpy) shows bands at 844, 856, and 894 cm^{-1} characteristic of 2-substituted thiophene in the region of C–H out-of-plane deformation vibrations.[5] These bands are replaced by a single band at 884 cm^{-1} in the spectrum of [{IrCl(2-thpy)$_2$}$_2$], indicating that the thiophene ring is 2,3-disubstituted.[3] The 60 MHz ^{1}H NMR spectrum of free H(2-thpy) is complicated. Only one signal of 6-H(py)[6] is distinctly separated from the main signals, lying at δ=8.61 ppm (as a doublet of triplets, J=5.0; 1.3 Hz). The ^{1}H NMR spectrum of [{IrCl(2-thpy)$_2$}$_2$] is shown in Fig. 1 and Table 1 together with assignments. A sharp doublet with a relative intensity 1 H at 5.94 ppm becomes a singlet upon irradiation of a sharp doublet with an intensity 1 H at 7.17 ppm (J=4.9 Hz) and *vice versa*. The two doublets are assigned to thiophene ring protons. Each of the signals assigned to 5-H(py) and 6-H(py) has an intensity 1 H and the relative intensity of the multiplet assigned to 3-H(py) and 4-H(py) amounts to 2 H. The results, together with the infrared spectra and the evidence for cyclopalladated cycloplatinated 2-thpy complexes[3] suggest that 3-H(th) of H(2-thpy) is lost and that the two 2-thpy ligands of [{IrCl(2-thpy)$_2$}$_2$] are equivalent. Significant shielding seems to be operative for 4-H(th). This can be explained in terms of Structure I,[7] where 4-H(th) is nearly above the pyridine ring of the other 2-thpy ligand, thus being

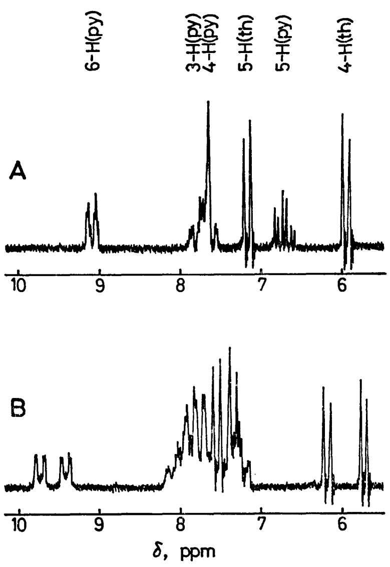
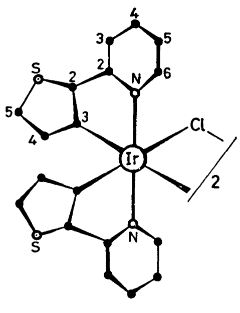


Fig. 1. 60 MHz ^{1}H NMR spectra of [IrCl(2-thpy)$_2$]$_2$ in CD$_2$Cl$_2$ (A) and [IrCl(dmso)(2-thpy)$_2$] in DMSO-d_6 (B).

Table 1. Infrared and ^{1}H NMR spectra of the complexes

Complex	ν(Ir–Cl)$^{a)}$	Solvent	δ/ppm$^{b)}$ 4-H(th)	δ/ppm$^{b)}$ 6-H(py)
[IrCl(2-thpy)$_2$]$_2$	245, 224	CD$_2$Cl$_2$	5.94d(4.9)	9.07d(5.8)
[IrCl(dmso)(2-thpy)$_2$]	255	dmso-*d*	5.77d(4.8)	9.45d(5.6)
			6.23d(4.8)	9.77d(5.6)
[IrCl(py)(2-thpy)$_2$]	243	CDCl$_3$	6.12d(4.6)	7.94d(5.6)
			6.24d(4.6)	9.72d(5.6)
[IrCl(PBu$_3$)(2-thpy)$_2$]	253	CDCl$_3$	5.92dd(4.8; 1.5)	8.78d(5.6)
			6.27d(4.8)	9.77d(5.6)
[IrBr(PBu$_3$)(2-thpy)$_2$]		CDCl$_3$	5.93dd(4.8; 1.5)	8.76d(5.6)
			6.22d(4.8)	9.91d(5.6)
[IrI(PBu$_3$)(2-thpy)$_2$]		CDCl$_3$	5.96dd(4.8; 1.5)	8.75d(5.6)
			6.14d(4.8)	10.11d(5.6)

a) Nujol mulls, cm^{-1}. b) Values in parentheses are coupling constants in Hz.



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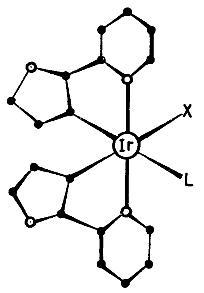

II

shielded by the aromatic ring current. Structure I is in line with low ν(Ir–Cl) frequency, since the chloride ligand is coordinated *trans* to a σ-carbon donor with strong *trans*-influence.

Table 2. Yields, melting points and analytical results

Complex	Yield %	Mp °C	Found (Calcd), % C	H	N
[IrCl(2-thpy)$_2$]$_2$	31	310 (dec)$^{a)}$	39.33(39.45)	2.23(2.21)	4.80(5.11)
[IrCl(py)(2-thpy)$_2$]	73	300 (dec)	44.07(44.05)	2.52(2.73)	6.60(6.70)
[IrCl(dmso)(2-thpy)$_2$]	75	240 (dec)	38.34(38.36)	2.91(2.90)	4.20(4.27)
[IrCl(PBu$_3$)(2-thpy)$_2$]	77	122—124	48.60(48.02)	5.30(5.24)	3.73(3.73)
[IrBr(PBu$_3$)(2-thpy)$_2$]	64	203—205	45.65(45.33)	4.88(4.95)	3.20(3.52)
[IrI(PBu$_3$)(2-thpy)$_2$]	83	230 (dec)	43.01(42.80)	4.62(4.67)	3.03(3.33)

Structure II is proposed for the complexes [IrClL(2-thpy)$_2$] on the basis of the following spectral data. In the ^{1}H NMR spectra of the complexes, the signal due to 4-H(th) splits into two doublets with a relative intensity 1 H (Fig. 1), that due to 6-H(py) also splitting into two apparent doublets with an intensity 1 H. The remaining protons give a complicated pattern with an intensity 8 H. Thus the two 2-thpy ligands are not equivalent in [IrClL(2-thpy)$_2$]. In the case of L=PBu$_3$, an additional small splitting (J(P–H)=1.5 Hz) is observed for one of the two doublets of 4-H(th) and the doublet, which shifts hardly upon exchange of halide donors, is assigned to 4-H of the thiophene ring coordinated *trans* to PBu$_3$. However, the other downfield doublet shifts to higher field in the order Cl<Br<I, and is assigned to 4-H of the thiophene ring coordinated *trans* to halide donors.

The separation of two doublets of 6-H(py) depends upon L. In the case of L=py, one of the two doublets is significantly shielded. This might be caused by anisotropic shielding by a pyridine (L) donor, since its least sterically hindered coordination brings the pyridine (L) ring nearly perpendicular to one of the chelated 2-thpy ligands. One 6-H(py) lies, therefore, nearly above the pyridine (L) ring. The other 6-H(py) is directed toward a Cl donor and the chemical shifts are almost independent of L.

The chemical shifts of 6-H(py) of [IrX(PBu$_3$)(2-thpy)$_2$](X=Cl, Br, I) are of interest. The positions of higher field doublets are nearly constant irrespective of the nature of halide donors, while the lower field doublets shift to a lower field in the order Cl<Br<I with increasing van der Waals radius of halide ions. The same trend was reported for square-planar palladium(II) complexes of pyridine derivatives,[8] the origin being interpreted as the result of spatial crowding between 6-H(py) and a halide ligand. The low ν(Ir–Cl) frequencies are in line with Structure II. The band at 1109 cm^{-1} of [IrCl(dmso)(2-thpy)$_2$] is assigned to ν(S=O), suggesting *S*-coordination of dmso.

The ligand H(2-thpy) behaves in a similar way to that of the corresponding benzene derivatives such as 2-phenylpyridine and benzo[*h*]quinoline.[7] H(2-thpy) has also been cyclorhodated to give [{RhCl(2-thpy)$_2$}$_2$] like 2-phenylpyridine and benzo[*h*]quinoline.[9] Structures I and II proposed above correspond to those of the complexes of these benzene derivatives.

Experimental

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

Synthesis of the Complexes. Yields, melting points and analytical results are given in Table 2.

[{IrCl(2-thpy)$_2$}$_2$]: A mixture of 3 mmol of hydrated iridium(III) chloride with 9 mmol of H(2-thpy) in 50 cm^3 of 2-methoxyethanol was refluxed for 6 h to give a brown powder. The product was washed with ethanol, dried in air, and dissolved in dichloromethane. Addition of hexane to the filtered, concentrated dichloromethane solution gave an orange powder.

[IrClL(2-thpy)$_2$](L=py or PBu$_3$): To a solution of [{IrCl-(2-thpy$_2$}$_2$] in dichloromethane was added a stoichiometric amount of PBu$_3$ or 3-fold excess of pyridine. The mixture was stirred on a hot plate for 1 h. Hexane was added to the concentrated dichloromethane solution to precipitate a yellow orange product.

[IrCl(dmso)(2-thpy)$_2$]: One-fifth mmol of [{IrCl(2-thpy)$_2$}$_2$] was dissolved in 1 cm^3 of dimethyl sulfoxide on a steam bath. To the solution was added 20 cm^3 of ethanol to precipitate an orange yellow product.

[IrX(PBu$_3$)(2-thpy)$_2$](X=Br or I): To a solution of one-fourth mmol of [IrCl(PBu$_3$)(2-thpy)$_2$] in a mixture of 20 cm^3 of dichloromethane and 10 cm^3 of ethanol was added 1 mmol of lithium bromide or lithium iodide. The mixture was warmed on a hot plate for 3 h and concentrated to a small volume to give bromide or iodide complex.

References

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5) J. J. Peron, P. Saumagne, and J. M. Lebas, *Spectrochim. Acta, Part A*, **26**, 1651 (1970).

6) 4-H of a thiophene ring and 6-H of a pyridine ring of 2-(2-thienyl)pyridine are, abbreviated to 4-H(th) and 6-H-(py), respectively. Similar abbreviations are used in this paper.

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9) Found: C, 46.87; H, 2.67; N, 6.40%. Calcd for RhClC$_{18}$H$_{12}$N$_2$S$_2$: C, 47.12; H, 2.64; N, 6.11%.

10) M. Nonoyama and C. Hayata, *Transition Met. Chem.*, **3**, 366 (1978).