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# CYCLOMETALLATION OF A PYRROLE RING OF 2-(1-PYRROLYL)PYRIDINE WITH PALLADIUM(II) AND RHODIUM(III)

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## Summary

2-(1-Pyrrolyl)pyridine (Hplp) is cyclometallated with lithium tetrachloropalladate(II) and hexahalogenotetrakis(tri-n-butylphosphine)dirhodium(III) to give $[PdCl(plp)]_2$ and $[RhX_2(plp)(PBu_3)_2]$ ($X = Cl$, Br; $PBu_3$ = tri-n-butylphosphine), respectively, where deprotonated plp is coordinated via the pyridine-*N* and pyrrole-2*C* atoms forming a five-membered metallacycle. $[PdCl(plp)]_2$ reacts with pyridine (py) and with $PBu_3$ to form the adducts [PdCl(plp)L] ($L = py$, $PBu_3$) and with acetylacetone (Hacac) to afford the complex [Pd(plp)(acac)]. Metathesis of $[RhCl_2(plp)(PBu_3)_2]$ with excess lithium iodide gives a mixed halogeno complex $[RhClI(plp)(PBu_3)_2]$. These complexes are characterized spectroscopically.

## Introduction

Cyclo(*ortho*)metallation reactions of benzene derivatives suitably substituted by donor groups have been well studied but similar reactions of other aromatics to a lesser extent [1]. A few examples of such reactions of thiophene derivatives have been reported, while it is scarcely possible to find researches for similar reactions of pyrrole derivatives [2]. It is attractive to study cyclometallation reactions of pyrroles. Pyrrole derivatives substituted at the 2-position are familiar [3] but they are presumed to be unfavourable for such reactions, because cyclo(*ortho*)metallation with palladium(II) and rhodium(III) is an electrophilic substitution reaction and electrophilic substitution reaction of a pyrrole ring occurs preferentially at the 2-position [3]. We choose, therefore, a 1-substituted one, 2-(1-pyrrolyl)pyridine.

## Results and discussion

2-(1-Pyrrolyl)pyridine (abbreviated as Hplp) is obtained, by the reaction of 2-aminopyridine with 2,5-dimethoxytetrahydrofuran in acetic acid, as a colourless oil. In the $^1H$ NMR spectrum ($CDCl_3$ vs. TMS) pyrrole ring 2-H's are observed as a

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TABLE 1

MELTING POINTS, YIELDS, AND ANALYTICAL RESULTS FOR THE COMPLEXES [a]

| Complex | M.p. [b] (°C) | Yield (%) | Analysis (Found(calcd.)(%)) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| $[PdCl(plp)]_2$ | 235 (dec) | 89 | 38.17(37.93) | 2.69(2.48) | 9.90 (983) |
| [PdCl(plp)(py)] | 235 (dec) [c] | 30 | 46.09(46.18) | 3.26(3.32) | 11.72(11.54) |
| $[PdCl(plp)(PBu_3)]$ | 119–120 | 30 | 52.06(51.76) | 6.91(7.03) | 5.82 (5.75) |
| [Pd(plp)(acac)] | 215 (dec) | 25 | 48.23(48.23) | 4.00(4.05) | 7.99 (8.03) |
| $[RhCl_2(plp)(PBu_3)_2]$ | 240 (dec) | 36 | 54.61(54.93) | 8.97(8.52) | 3.61 (3.88) |
| $[RhBr_2(plp)(PBu_3)_2]$ | 245 (dec) | 27 | 48.98(48.90) | 7.43(7.59) | 3.48 (3.46) |
| $[RhClI(plp)(PBu_3)_2]$ | 235 (dec) | 70 | 48.77(48.75) | 7.58(7.65) | 3.41 (3.45) |

[a] Abbreviations: Hplp = 2-(1-pyrrolyl)pyridine, py = pyridine, $PBu_3$ = tri-n-butylphosphine, and Hacac = acetylacetone. [b] dec = decomposition. [c] Became opaque at 155°C.

triplet ($J$ 2.2 Hz) at $\delta$ 7.54 ppm and 3-H's as a triplet at 6.38 ppm [4]. The IR spectrum (neat) shows characteristic bands of a 1-substituted pyrrole ring [5] at 723, 928, 1022, 1068, 1336, 1397, and 1484 $cm^{-1}$. These assignments are confirmed by comparison of the spectra with those of 2-(1-pyrrolyl)-4-methylpyridine, which is prepared by the same method.

The substituted pyrrole, Hplp, reacted easily with lithium tetrachloropalladate in methanol at room temperature to give $[PdCl(plp)]_2$ and with hexahalogenotetrakis(tri-n-butylphosphine)dirhodium in xylene at refluxing temperature to give $[RhX_2(plp)(PBu_3)_2]$ (X = Cl, Br; $PBu_3$ = tri-n-butylphosphine). The palladium complex reacted with $PBu_3$ and with pyridine (py) to give [PdCl(plp)L] (L = $PBu_3$, py) and with acetylacetone (Hacac) to form [Pd(plp)(acac)] (Table 1). Upon metathesis of the chlororhodium complex with excess lithium iodide the mixed

TABLE 2

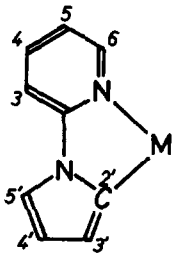
IR AND $^1H$ NMR SPECTRA OF THE COMPLEXES

| Complex | IR [a] ($cm^{-1}$) | | $^1H$ NMR [b] (ppm) | | |
|---|---|---|---|---|---|
| | $\pi$(C–H) | $\nu$(M–Cl) | 3'-H | 4'-H | 6-H |
| $[PdCl(plp)]_2$ | 772 | 226<br>265 | 6.47d(2.8) | 6.26t(3.1) | 8.93d(6.0) |
| [PdCl(plp)(py-$d_5$)] [c] | 771 | 249 | 5.43d(3.2) | 6.26t(3.2) | 9.22d(5.8) |
| $[PdCl(plp)(PBu_3)]$ | 774 | 257 | 6.00d(3.2) | 6.32t(3.2) | 9.25m [d] |
| [Pd(plp)(acac)] | 771 | 259 [e]<br>447 | 6.23d(3.2) | 6.36t(3.2) | 8.59d(5.6) |
| $[RhCl_2(plp)(PBu_3)_2]$ | 785 | 241<br>279 | 6.25br | 6.48t(3.2) | 9.47d(5.6) |
| $[RhBr_2(plp)(PBu_3)_2]$ | 787 | | 6.38br | 6.47t(3.2) | 9.61d(5.6) |
| $[RhClI(plp)(PBu_3)_2]$ | 779 | 279 | 6.32br | 6.52t(3.2) | 9.78d(5.6) |

[a] Nujol mulls. [b] Solvents used for NMR measurements were $CDCl_3$ (vs. tetramethylsilane, TMS), except for $[PdCl(plp)]_2$, for which dmso-$d_6$ was used (vs. sodium 2,2-dimethyl-2-silapentanesulphonate, DSS). Only primary splitting patterns are given and the coupling constants in Hz are shown in parentheses. (d = doublet, t = triplet, m = multiplet, and br = broad). [c] py-$d_5$ = deuterated pyridine. [d] See Fig. 1. [e] $\nu$(Pd–O).

halogeno complex [RhClI(plp)$(PBu_3)_2$] was obtained. These reactions are very similar to those of the cyclo(*ortho*)metallated complexes reported in the literature [1,6]. The spectral data of these new complexes are given in Table 2.

In the IR spectra of the complexes, most remarkable are the changes in frequencies of the out-of-plane deformation vibration modes of aromatic ring C–H groups. The four adjacent pyrrole ring C–H groups of free Hplp [5] give a strong band at 723 $cm^{-1}$ and in the complexes the band is replaced by a strong band at ca. 775 $cm^{-1}$. It is well known that upon reduction in the number of adjacent hydrogen atoms on aromatic rings from four to three, the absorption frequency of the out-of-plane C–H vibration shows a shift to higher frequency [7]. The shift to higher frequency by ca. 50 $cm^{-1}$ upon complexation should indicate the presence of three adjacent pyrrole ring C–H groups instead of the four of free Hplp.




I

In the $^1H$ NMR spectra of the complexes, integration of the signal intensities reveals that one proton has been lost from Hplp. The spectra are assigned as shown in Table 2 and explained in terms of Structure I, which shows the numbering of aromatic ring positions.

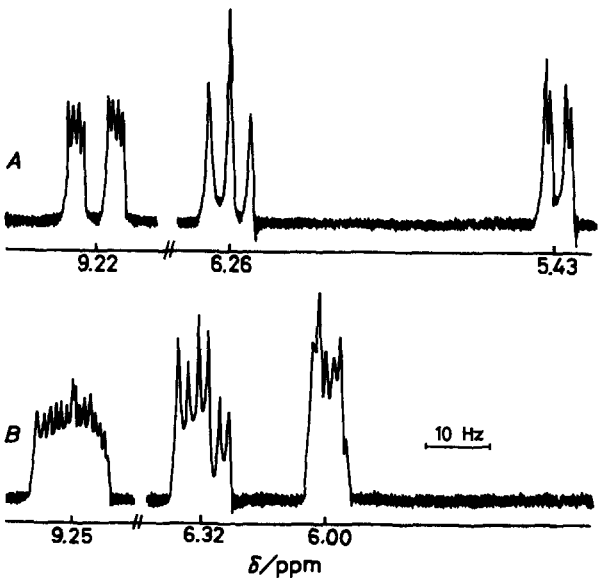
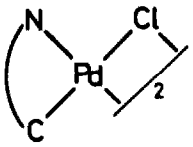
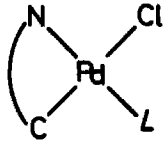



Fig. 1. $^1H$ NMR spectra of [PdCl(plp)L] in the region of the pyridine ring 6-H and the pyrrole ring 3'-H and 4'-H. (A) L = py and (B) L = $PBu_3$.

The large difference in the chemical shifts of the pyrrole ring 3′-H between [PdCl(plp)(py)] and [PdCl(plp)($PBu_3$)] (Table 2 and Fig. 1) is conspicuous. The shielding of the 3′-H of the former complex could be caused by the ring current of the py ligand, which is coordinated *trans* to the *N* atom of plp (Structure III) and is




II



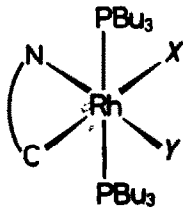

III

forced to be nearly perpendicular to the plane of coordination because of steric hindrance between 3′-H of plp and 2- or 6-H of the py ligand. The chemical shifts of the other protons are similar but the signal patterns of the $PBu_3$ complex are more complicated (Fig. 1) and additional small couplings are observed for 6-H, 3′-H, and 4′-H but are not clear for 5′-H, due to a partial overlapping with other signals. The additional couplings are due to $J$(P–H) but the spectrum is not analyzed further. The coordination of Cl *trans* to a carbon donor with a strong *trans* influence [8] is supported by low frequency $\nu$(Pd–Cl) bands (Table 2).

The methyl signals of acac of [Pd(plp)(acac)] appear as a singlet at 2.08 ppm (with an intensity of 6 H) and the methine one at 5.45 ppm (1 H). These values are normal for an *O,O*-chelated acac ligand. That the two methyl groups give one singlet could be due to an accidental coincidence of the chemical shifts of the two methyl groups. The IR spectrum also supports the result as two strong bands at 1514 and 1570 $cm^{-1}$ are observed. The bands $\nu$(Pd–O) (at 447 and 259 $cm^{-1}$) are at lower frequencies than those of [$Pd(acac)_2$] (463 and 294 $cm^{-1}$). This reflects the high *trans* influence of a carbon donor of a pyrrole ring.

In the far IR spectra between 350–200 $cm^{-1}$, [$RhCl_2$(plp)($PBu_3$)$_2$] shows four bands at 241, 279, 316, and 349 $cm^{-1}$ and [RhClI(plp)($PBu_3$)$_2$] three at 279, 316, and 342 $cm^{-1}$. The missing band at 241 $cm^{-1}$ is assigned to $\nu$(Rh–Cl) and the low frequency indicates that the Cl donor is situated *trans* to a carbon donor with high *trans* influence [8] (see structure IV; X = Cl, Br, I). In the spectrum of [$RhBr_2$(plp)($PBu_3$)$_2$], two bands appear at 305 and 339 $cm^{-1}$. The results show that the band at 279 $cm^{-1}$ of [$RhCl_2$(plp)($PBu_3$)$_2$] is primarily due to $\nu$(Rh–Cl) but the bands at 316 and 349 $cm^{-1}$ may get a share of some $\nu$(Rh–Cl) character since the two shift to lower frequencies in the bromo analogue.

The chemical shift of the 6-H of [RhClI(plp)($PBu_3$)$_2$] is significantly different from that of [$RhCl_2$(plp)($PBu_3$)$_2$] and the former proton is deshielded by ca. 0.3 ppm. The chemical shift in [$RhBr_2$(plp)($PBu_3$)$_2$] is intermediate. A similar trend in




IV

deshielding has been observed for a coordinated pyridine ring 6-H situated in close proximity to halogen donors [9]. It is assumed that the Cl, Br, and I are coordinated at the position X of structure IV, this being consistent with the above IR spectral results. The 3'-H of $[RhCl_2(plp)(PBu_3)_2]$ is similarly deshielded when the Cl donors are replaced with Br and the 3'-H is also assumed to be situated in close proximity to halogen donors (structure IV; Y = Cl, Br).

To confirm the proposed structure IV, $^{13}C$ $\{^1H\}$ NMR spectrum of $[RhCl_2(plp)(PBu_3)_2]$ was measured (in $CDCl_3$ vs. TMS). The chemical shifts of aromatic ring carbons range from 123 to 171 ppm and the signals are all singlets except that of 2'-C. The rhodium bonded 2'-C gives a doublet ($J$(Rh–C) 35.2 Hz) of triplets ($J$(P–C) 11.7) at 158.8 ppm indicating that the two $PBu_3$ groups are equivalent. The signal of the $\alpha$-carbon of $PBu_3$ is a triplet at 36.5 ppm ($J$ 12.7 Hz) and that of $\beta$-carbon also a triplet at 40.0 ($J$ 5.7 Hz) revealing that the two $PBu_3$ ligands are mutually *trans*. These results are consistent with structure IV.

## Experimental

### *Measurements*

Measurements were carried out by the methods reported previously [6]. $^{13}C$ NMR spectra were recorded with a JEOL FX-60 spectrometer.

### *Synthesis*

#### *2-(1-Pyrrolyl)pyridine*

A mixture of 2-aminopyridine (25.0 g) and 2,5-dimethoxytetrahydrofuran (35.1 g) in acetic acid (120 ml) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was neutralized with sodium hydroxide. The resulting mixture was extracted with diethyl ether and the extract was dried, evaporated to dryness under reduced pressure, and distilled, to give a colourless oil, 11.2 g (29% yield), b.p. 140–141°C/21 mmHg. (Found: C, 75.04; H, 5.57; N, 19.13. $C_9H_8N_2$ calcd.: C, 74.98; H, 5.59; N, 19.43%).

#### *2-(1-Pyrrolyl)-4-methylpyridine*

B.p. 157–159°C/22 mmHg, 12.1 g (33% yield). (Found: C, 76.06; H, 6.37; N, 17.73. $C_{10}H_{10}N_2$ calcd.: C, 75.92; H, 6.37; N, 17.71%).

### *Preparation of the complexes*

*$[PdCl(plp)]_2$.* To a methanol solution of lithium tetrachloropalladate (1 mmol), prepared in situ from palladium(II) chloride (1 mmol) and of lithium chloride (2 mmol) in methanol (30 ml), was added Hplp (2 mmol) and the mixture was stirred at room temperature for 30 min. A yellow-brown precipitate was collected, washed with methanol, and dried in air. The complex slowly changed to brown upon exposure to light.

*$[PdCl(plp)L]$ ($L = PBu_3$, py).* To a suspension of $[PdCl(plp)]_2$ in dichloromethane was added an equivalent amount of $PBu_3$ or an excess of py and the mixture was stirred until the complex had dissolved. The solution was treated with Florisil and filtered. To the filtrate was added n-hexane and the solution was concentrated to a small volume to precipitate light-yellow crystals.

*[Pd(plp)(acac)].* To a mixture of $[PdCl(plp)]_2$ (0.5 mmol) and of Hacac (1 mmol) in a (1 : 1) mixture of ethanol and dichloromethane (40 ml) was added 1,8-diazabicyclo(5.4.0)-7-undecene (DBU) (1 mmol) and the mixture was stirred on a hot plate for 30 min. The solution was treated with Florisil and filtered. The filtrate was concentrated to a small volume to precipitate light-yellow crystals.

*$[RhX_2(plp)(PBu_3)_2]$ (X = Cl, Br).* A mixture of $[Rh_2Cl_6(PBu_3)_4]$ (0.25 mmol) and Hplp (1 mmol) in xylene (15 ml) was heated with stirring for 3 h. After cooling, the precipitate was collected, washed with xylene and n-hexane, and dried in air. The product was dissolved in dichloromethane and treated with Florisil. To the filtrate was added n-hexane and the solution was concentrated to a small volume to give yellow crystals of $[RhCl_2(plp)(PBu_3)_2]$. The bromo-analogue was similarly prepared from $[Rh_2Br_6(PBu_3)_4]$.

*$[RhClI(plp)(PBu_3)_2]$.* This was obtained by metathesis of $[RhCl_2(plp)(PBu_3)_2]$ with an excess of lithium iodide in a mixture of acetone-dichloromethane (1 : 1).

## Acknowledgement

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## References

1 I. Omae, Chem. Rev., 79 (1979) 287.
2 During the course of this investigation, cyclopalladation of 1-benzenesulphonyl-2-dimethylaminomethylpyrrole was reported: M.E.K. Cartoon and G.W.H. Cheeseman, J. Organomet. Chem., 234 (1982) 123.
3 A.H. Jackson, in P.G. Sammes (Ed.), Comprehensive Organic Chemistry, Vol. 4, Pergamon Press, Oxford. 1979, p. 275.
4 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, Oxford, 2nd edn., 1969, p. 207.
5 R.A. Jones, Aust. J. Chem., 19 (1966) 289.
6 M. Nonoyama, J. Organomet. Chem., 229 (1982) 287.
7 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 2nd edn., 1966, p. 75.
8 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
9 M. Mikami, I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, Part A, 23A (1967) 1037.