Inorganica Chimica Acta, 28 (1978) L163–L164
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

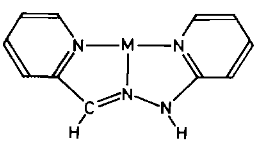
Cyclopalladation of 2-Acetylpyridine *p*-Tolylhydrazone

MATSUO NONOYAMA

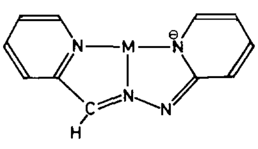
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464 Japan

Received April 4, 1978

Transition metal complexes of hydrazones and Schiff bases derived from 2-acetylpyridine and pyridine-2-aldehyde have extensively been studied [1, 2] and it has been shown that pyridine-2-aldehyde 2′-pyridylhydrazone is coordinated either as a neutral (*I*) or as an anionic N-N-N terdentate ligand (*II*) [1].

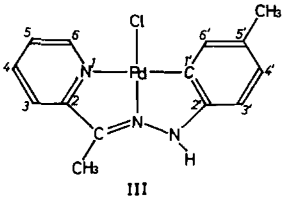


I



II

So far, no evidence has, however, been found for cyclometallation of these Schiff bases and hydrazones. Now, we have found that the related hydrazone (HL) derived from 2-acetylpyridine and *p*-tolylhydrazine acts also as an anionic terdentate ligand involving a Pd–C bond in the palladium(II) complex (*III*).



III

The palladium complex [PdClL] was prepared by the reaction of lithium tetrachloropalladate (1 mmol), the hydrazone (1 mmol), and sodium acetate (1 mmol) in methanol (40 ml) at room temperature for 5 days. The orange brown complex was obtained with a yield of 83%. Found C, 45.84: H, 3.78; N, 11.21%: Calcd. for $PdClC_{14}H_{14}N_3$: C, 45.93; H, 3.85; N, 11.48%. Lithium tetrabromopalladate gave [PdBrL] under similar conditions and metathesis of [PdClL] with lithium iodide gave [PdIL].

The pmr spectrum of the free hydrazone (HL) in dmso-d_6 *vs.* DSS [3] is shown in Fig. 1. The lowest peak at δ = 9.45 ppm disappears upon addition of D_2O and is attributed to N–H of a hydrazone group. In the spectrum of [PdClL] in dmso-d_6 the signal of N–H remains and is at 10.70 ppm. Ionization of the hydrazone group is denied. The presence of ν(N–H) at 3185 cm^{-1} in the ir spectrum also supports the fact. The characteristic band of a *p*-disubstituted benzene ring is observed at 818 cm^{-1} for HL and the new band at 882 cm^{-1} in the spectrum of [PdClL] suggests the presence of a 1,2,4-trisubstituted benzene ring [4]. The complicated signal at *ca.* 7.2 ppm due to the *p*-tolyl group of HL is transformed into a singlet at 7.03 ppm and an AB quartet between 6.4 and 6.9 ppm in the complex (Fig.) [5] accompanied with reduction of the total intensity by 1 H. These facts support structure *III*. The band at 311 cm^{-1} in the far infrared spectrum is assigned to ν(Pd–Cl).

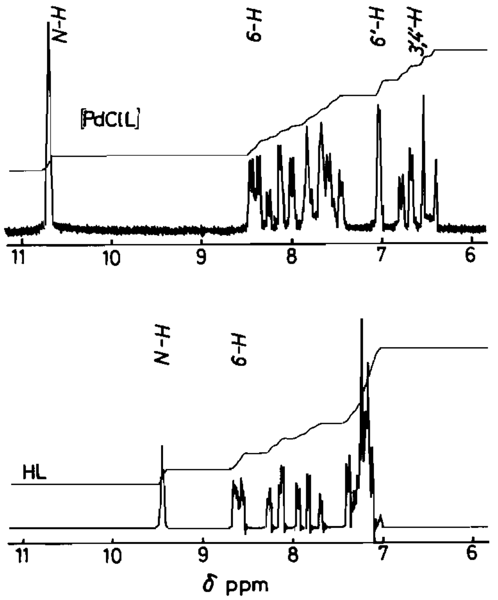


Figure 1. 60 MHz pmr spectra of HL and [PdClL] in dmso-d_6 *vs.* DSS.

The complexes [PdBrL] and [PdIL] have similar spectroscopic properties. The singlet [5] at 7.03 and the doublet at 8.42 ppm of [PdClL] shift downfield upon replacement of Cl with Br and I. These signals are at 7.23 and 8.53 (for Br) and at 7.65 and 8.77 (for I) ppm, respectively. The singlets are assigned to 6′-H (H *ortho* to a Pd–C bond) and the doublets to 6-H (or pyridine ring). These halogen-dependent chemical shifts are consistent with Structure *III*, where the two hydrogen atoms, 6-H and 6′-H, are in the proximity of the coordinated halogen atoms [6] and should be affected strongly by them.

Acknowledgement

This work was supported partially by the Matsunaga Research Grant.

References

1 For instance, J. G. Dunn and D. A. Edwards, *J. Chem. Soc. A*, 988 (1971) and references therein.

2 For instance, P. Krumholz, *Inorg. Chem., 4*, 757 (1965) and M. R. Litzow, L. F. Power, and A. M. Tait, *J. Chem. Soc. A*, 2907 (1970).

3 Sodium 2,2-dimethyl-2-silapentanesulfonate.

4 L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London (1966) p. 75.

5 Small couplings (less than 2 Hz) are ignored in discussion.

6 M. Nonoyama, *Inorg. Nucl. Chem. Lett., 13*, 439 (1977).