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Reaction of $PdCl(CH_2CN)(PPh_3)_2$ with 8-Hydroxyquinoline and 8-Mercaptoquinoline

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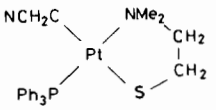
Our recent interest in organotransition metal chemistry is to obtain Pd(II) and Pt(II) complexes containing four different coordinating atoms and isolate all possible isomers. In a previous paper [1] we reported the synthesis of $Pt(CH_2CN)(PPh_3)(Me_2NCH_2CH_2S)$. For the complex, two kinds of geometrical isomers are possible, but the ^1H NMR spectrum indicated the presence of only one isomer. To the complex we assigned the structure shown below:



We have now examined the reaction of $MCl(CH_2CN)(PPh_3)_2$ (M = Pd, Pt) with 8-hydroxyquinoline (oxH) and 8-mercaptoquinoline (oxsH) hoping to isolate two isomers (A) and (B). $Pd(CH_2CN)(oxs)(PPh_3)$ (I) was prepared by the reaction of oxsH·HCl

(A) (B)

with $PdCl(CH_2CN)(PPh_3)_2$ in methanol. After stirring the mixture for 1 hr at room temperature a yellow precipitate was filtered off, washed with methanol and ether and then dried *in vacuo* for 5 hr at 100 °C. *Anal.* Found: C, 61.41; H, 3.99; N, 4.77. Required for (I): C, 61.22; H, 4.07; N, 4.92%. $Pt(CH_2CN)(oxs)(PPh_3)$ (II) was obtained in a similar fashion. *Anal.* Found: C, 53.06; H, 3.41; N, 4.07. Required for (II): C, 52.94; H, 3.53; N, 4.26%. Similarly $Pd(CH_2CN)(ox)(PPh_3)$ (III) was prepared by treatment of $PdCl(CH_2CN)(PPh_3)_2$ with oxH in methanol. *Anal.* Found: C, 62.59; H, 4.07; N, 5.12. Required for (III): C, 63.00; H, 4.19; N, 5.07%.

^1H nmr spectra of (I), (II) and (III) are shown in the Figure. Both (I) and (II) exhibit only one resonance assignable to the cyanomethyl protons. In addition, comparison of the spectra (I) and (II) suggests that the configuration of (I) is similar to that of (II). Although we do not have any experimental evidence to prefer one of two structures (A) and (B), a simple molecular model shows that a steric interaction between the triphenylphosphine and the 8-mercaptoquinolinato ion in (A) is larger than that in (B). Electronic considerations also support the structure (B) if we assume a π-bonding contribution to the metal–phosphorus and the metal–sulphur bonds (metal to donor atom) [2]: when the π-bonding is possible the phosphorus atom in (A) must compete with the sulphur atom for the same *d* orbital of the central metal because these two atoms are *trans* to each other, but in (B) they can combine with different *d* orbitals of the metal to achieve a stronger π-bonding. From these considerations the structure (B) was assigned to the complexes (I) and (II).

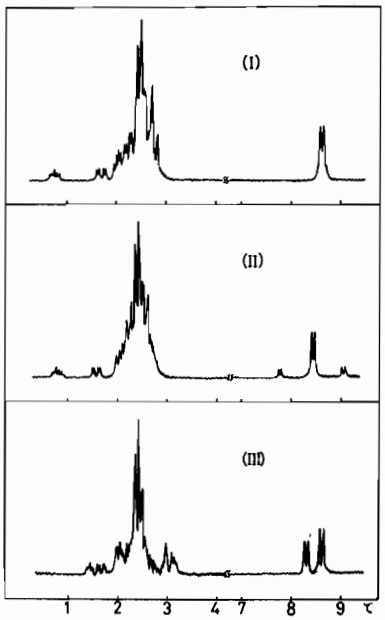


Figure. ^1H nmr spectra of $M(CH_2CN)(PPh_3)L$. (I) M = Pd, L = oxs^-, (II) M = Pt, L = oxs^-, (III) M = Pd, L = ox^-.

On the other hand the oxinato complex of palladium (III) shows two doublets ascribable to the cyanomethyl protons at τ 8.35 and 8.65 in intensity ratio 1:1.6. Clearly (III) is a mixture of two isomers (A) and (B) although the structural assignment to each signal was difficult. So far, any attempts to separate them have been unsuccessful. We also examined the reaction of 2-methyl-8-hydroxy-quinoline (MeoxH) with $PdCl(CH_2CN)(PPh_3)_2$ hoping that only isomer (B) would be isolated. However the result was to recover the starting material although PF_4(Meox) [3] has been reported. The reason for the

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occurrence of an isomer (A) in (III) but not in (I) and (II) is an increase in the bond angle ∠PdXC (X = O, S) on replacing sulphur with oxygen [4]. This might reduce the repulsion between the phenyl groups on the phosphorus atom and the *ortho*-proton (to the nitrogen) of the oxinato ligand in (A). Another is that π-bonding contribution (metal to donor atom) seems unlikely for oxygen. Thus it is expected that the difference in stability of (A) and (B) in (III) is probably very small compared to that in (I) and (II) and this might explain the formation of both isomers in the oxinato complex.

References

1 K. Suzuki and M. Sakurai, *Inorg. Chim. Acta, 20,* L13 (1976).
2 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience, New York, pp. 409, 745 (1966).
3 Klaus-Peter John, R. Schmutzer and W. S. Shedrick, *J. Chem. Soc. Dalton Trans.,* 1841 (1974).
4 A. F. Wells, 'Structural Inorganic Chemistry', Clarendon, Oxford, pp. 420, 575 (1975).