136. Palladium (II) Complexes of α -Naphthoquinoline

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Recently Fischer *et al.*¹⁾ reported the preparation of α -naphthoquinoline chromium tricarbonyl in which α -naphthoquinoline coordinated to chromium as a π ligand. As is clear from the structure (Fig. 1), α -naphthoquinoline will be able to form an ortho-metallation compound with palladium (II) like azobenzene and 2-phenylpyridine.^{2),3)} Therefore we attempted to prepare such a compound by

Fig. 1. The structure of α -naphthoquinoline.

mixing α -naphthoquinoline and sodium tetrachloropalladate(II) or potassium tetrabromopalladate(II) in methanol. The reaction was carried out at room temperature, and after 5–6 hours under stirring a pale yellow compound was precipitated, which gave the chemical composition PdLX ($\text{L}=\alpha$ -naphthoquinoline, $\text{X}=\text{Cl}$, Br).

Found: C, 48.90; H, 2.55, N, 4.32%. Calcd. for $\text{PdClC}_{13}\text{H}_8\text{N}$: C, 48.78, H, 2.52, N, 4.38%. Decomposition pt. ca. 335°C.

Found: C, 42.81, H, 2.25, N, 3.82%. Calcd. for $\text{PdBrC}_{13}\text{H}_8\text{N}$: C, 42.84, H, 2.21, N, 3.84%. Decomposition pt. ca. 300°C.

The infrared spectra of these two complexes are similar to each other in the region above 400 cm^{-1} , whereas they are quite different in the region below 400 cm^{-1} . This is probably due to the difference of coordinated halogen atoms. In common organic solvents these two complexes are soluble only with difficulty, and the n.m.r. spectra are not obtained. These results indicate the dimeric structure of these two complexes as shown in Fig. 2.

Fig. 2. Proposed structure for $\text{Pd}(\alpha\text{-naph})\text{X}$ ($\text{X}=\text{Cl}$ or Br).

Fig. 3. ^1H n. m. r. spectra of α -naphthoquinoline and the complexes in CDCl_3 in δ unit at room temperature (60 Mc/sec). The signals arising from the protons of α -naphthoquinoline are labeled with relative area ratios in parentheses.

a): α -naphthoquinoline, b): $\text{Pd}(\alpha\text{-naph}) \text{P}(\text{n-Bu})_3 \text{Cl}$,
 c): $\text{Pd}(\alpha\text{-naph}) \text{AsPh}_3 \text{Cl}$.

With tri-*n*-butylphosphine and triphenylarsine reacted these two complexes to give the products, $\text{Pd}(\alpha\text{-naph})\{\text{P}(\text{n-Bu})_3\}\text{X}$ and $\text{Pd}(\alpha\text{-naph})\text{AsPh}_3\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$) respectively. As these products are soluble in CDCl_3 we measured their n.m.r. spectra to elucidate their structures. The n.m.r. spectra of α -naphthoquinoline and the complexes are shown in Fig. 3.

The spectral data of α -naphthoquinoline in acetone- d_6 reported by Fischer *et al.*¹⁾ was used to assign the spectrum of the ligand in CDCl_3 . From the comparison of the spectrum of α -naphthoquinoline with those of the complexes the peaks at $\delta=8.25$ are assigned to the 4-proton in the tributylphosphine and triphenylarsine complexes respectively. In the former complex the relative area ratios of the protons of α -naphthoquinoline were determined. Thus, in the free ligand there are nine protons, whereas in the complex the number is eight as shown in Fig. 3. This means that one proton is removed by complex formation, and the proton is believed to be the 10-proton, since the signal corresponding to it was not observed till $\delta=15$.

In the triphenylarsine complex, however, the relative area ratios of the ligand protons were not determined due to the presence of phenyl groups. The comparison of its spectrum with that of the tributylphosphine complex gave a very interesting result. The signal of the 2-proton is quartet in the former, whereas it is septet in the latter. This fact is probably due to the coupling of the 2-proton with ^{31}P and this may indicate the trans coordination of tributylphosphine group to nitrogen of naphthoquinoline.

The far infrared spectra of phosphine and arsine chloro-complexes show a strong band at 297 and 292 cm^{-1} respectively which are assigned to the Pd-Cl stretching vibration. Since the

Fig. 4. Proposed structure for $\text{Pd}(\alpha\text{-naph})\text{LX}$.

$\text{Pd-Cl}^{(4)}$ stretching vibration usually appears in the region 370–345 cm^{-1} , the lower position of these bands observed here may indicate the trans- effect of the carbon atom over the chlorine atom (Fig. 4), and consequently its trans coordination to palladium. From the above results it may be concluded that α -naphthoquinoline forms the ortho-metallation compounds in which the 10-carbon and 1-nitrogen

coordinate to palladium forming chelate rings (Fig. 4). The details of the results will be published later. The n.m.r. measurement is indebted to Dr. H. Takaya.

References

- 1) E. O. Fischer, H. A. Goodwin, C. G. Kreiter, H. D. Simmon, K. Sonogashira, and S. B. Wild: *J. Organometal. Chem.*, **14**, 359 (1968).
- 2) A. C. Cope and R. W. Siekman: *J. Am. Chem. Soc.*, **87**, 3272 (1967).
- 3) A. Kasahara: *Bull. Chem. Soc. Japan*, **41**, 1272 (1968).
- 4) K. Nakamoto and P. J. McCarthy: *Spectroscopy and Structure of Metal Chelate Compounds*. John Wiley, New York, p. 216 (1968).