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The Syntheses and Properties of Chloro(acrylonitrile) Complexes of Platinum(0)

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In the reaction of $Pt(PPh_3)_4$ with haloolefins, the formation of two kinds of complexes, *i.e.*, the olefin complex and the vinyl complex, has been reported.[1)]

Olefin complex Vinyl complex

This paper will deal with the reaction of $Pt(PPh_3)_4$ and $Pt(AsPh_3)_4$ with chloroacrylonitrile, CH_2=CClCN, and with the structures of the complexes formed; the discussion will be based on the spectroscopic data.

The treatment of the benzene solution of $Pt(PPh_3)_4$ with chloroacrylonitrile resulted in a pale yellow solution, from which $Pt(PPh_3)_2(CH_2CClCN)$ (I) was subsequently isolated. A similar treatment of $Pt(AsPh_3)_4$ with the same ligand gave a pale yellow substance formulated as $Pt(AsPh_3)_2(CH_2CClCN)$ (II). Both complexes, (I) and (II), are stable in air; they decompose at 160—170 and 160—165°C respectively. The infrared and proton magnetic resonance spectra data of the two complexes are summarized in Table 1. As is clear from the table, the stretching frequency, $\nu_{C=C}$ disappeared upon the complex formation, while ν_{C-Cl} was still present. Since Bland and Kemmitt[1)] proposed the coordination of the double bond, *i.e.* the formation of the olefin complex on the basis of the disappearance of $\nu_{C=C}$, it may be reasonable to assume the formation of olefin complexes for both the complexes studied here. The far-infrared spectral data also indirectly support the above assumption, because the stretching frequency, ν_{Pt-Cl}, expected for the product of the oxidative addition was not observed. For the complex II this was not clear due to the strong ligand absorption in the region 320—350 cm^{-1}.

The proton magnetic resonance spectra of methylene protons in the complexes I and II are shown in Fig. 1. For these complexes, it was difficult to obtain well-resolved spectra because of their low solubility in common organic solvents.

Furthermore, the non-equivalence of the methylene protons caused another difficulty in interpreting the spectra. The CH_2 protons of the coordinated ligand showed a high-field shift in both complexes, indicating the formation of olefin complexes, and the satellite due to the coupling with ^{195}Pt was also observed. In the complex I, the central peak of the CH_2 proton appeared as a complicated multiplet centered at around $\tau = \sim 7.6$ ppm. This complex signal may be

1) W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc., A*, **1969**, 2062.

TABLE 1. INFRARED AND PROTON MAGNETIC RESONANCE DATA OF THE COMPLEXES I AND II

Compound	Infrared		Proton magnetic resonance	
	$\nu_{C=C}$	ν_{C-Cl}	τ	J(Pt-H)
CH_2=CClCN	1608[2]	660[2] cm^{-1}	H_a=3.78 ppm H_b=3.86	3.0[b] Hz
(I)	—	667, 652[a]	~7.7	~50
(II)	—	672, 658[a]	~7.5	~55 (~7[b])

a) Tow strong absorptions were observed. One of them may probably be due to ν_{C-Cl}.
b) $J(H_a-H_b)$.

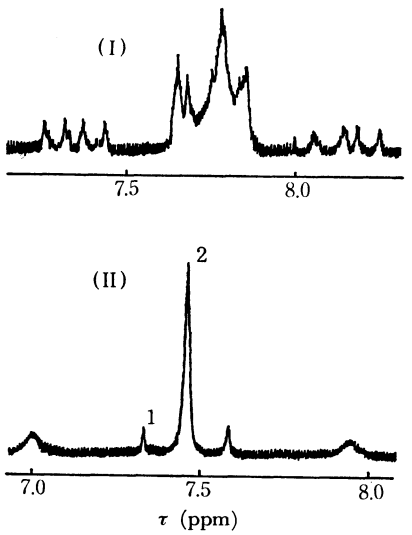

Fig. 1. PMR spectra of the CH_2 protons of the complexes I and II.
I: $Pt(PPh_3)_2(CH_2$=$CClCN)$
II: $Pt(AsPh_3)_2(CH_2$=$CClCN)$

due to the existence of an AB pattern, which is, in turn, able to couple with two non-equivalent phosphorus atoms. Since the CH_2 protons do not couple with an arsenic atom, the signal of the complex II can be expected to be much simpler than that of the complex I. However, as is shown in Fig. 1, the central peak of the CH_2 signal appeared as a triplet with the intensity ratio of 1 : 28 : 1. We interpret this triplet as being the case when the inside peakes of an AB quartet come very close to one another and as being a quartet changed into a triplet. To obtain accurate values of the coupling constant and chemical shift, the use of an AB quartet pattern is required, but the signal obtained could not be further resolved. Consequently, the $J(H_a-H_b)$ value was approximated to the difference in the values of the two signals, 1 and 2, and τ, to the value of the signal 2 in Fig. 1.

The electronic spectra of the complexes were measured in the 220—360 nm, region. They are quite similar to each other; there are three absorption maxima at 36.5, 39.7, and 43.2×10^3 cm^{-1} ($\varepsilon=1.8\times10^4$ sh, 2.6×10^4, and 3.8×10^4) far the complex I and at 35.8, 39.7, and 44.4×10^3 cm^{-1} ($\varepsilon=1.1\times10^4$ sh, 2.6×10^4, and 4.7×10^4) for the complex II. From these results, the formation of the olefin complexes is concluded for both cases. We further tried to prepare a vinyl complex by refluxing the complex I in ethanol but without success.

2) S. B. Lie and P. Klaboe, *Spectrochem. Acta*, **26A**, 1191 (1970).

Experimental

Materials. The $Pt(PPh_3)_4$ and $Pt(AsPh_3)_4$ were prepared by a method previously reported by other authors.[3,4]

Chloroacrylonitrilebis(triphenylphosphine)platinum(O)=(I). 2-Chloroacrylonitrile (0.2 m*l*, 2 mmol) was added to a solution of tetrakis(triphenylphosphine)platinum (12. g, 1 mmol) in benzene (100 m*l*) under nitrogen. The reddish-brown color of the original solution turned to a pale yellow, and a white substance was obtained on concentrating the solution. It was reprecipitated from a mixture of chloroform and ethyl ether as a white powder; mp 160—170°C (decomp.). Found: C, 57.86; H, 3.61: N, 1.35%. Calcd for $C_{39}H_{32}NClP_2Pt$≡$Pt(PPh_3)_2(CH_2CClCN)$: C, 58.03; H, 4.00; N, 1.74%.

Chloroacrylonitrilebis(triphenylarsine)platinum(O)=(II). To a suspension of tetrakis(triphenylarsine)platinum (1.4 g, 1 mmol) we added 0.2 m*l* (2 mmol) of 2-chloroacrylintirile. The suspension changed to a pale yellow solution in about 30 min. After the solution had then been stirred for 2 hr, it was filtered and the filtrate was concentrated under reduced pressure to give a pale yellow compound. It was precipitated from a mixture of dichloromethane and ethyl ether as a pale yellow powder; mp 160—165°C (decomp.). Found: C, 51.49; H, 3.48; N, 1.37%. Calcd for $C_{39}H_{32}NClAs_2Pt$≡$Pt(PPh_3)_2(CH_2CClCN)$: C, 52.33; H, 3.60; N, 1.57%.

Measurements. The infrared spectra were recorded with JASCO-DS-402G and HITACHI EPI-L2 spectrophotometers. The electronic spectra in the CH_3CN solution were obtained with a HITACHI 323 spectrometer. The proton magnetic resonance spectra were obtained with a JEOL C-60H spectrometer, using $CDCl_3$ as the solvent and TMS as the internal standard.

3) W. L. Jolly, "Inorganic Syntheses," Vol. 11, McGraw-Hill, New York (1968), p. 105.
4) L. Malatesta and C. Cariello, *J. Chem. Soc.*, **1958**, 2323.