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cis- AND trans-DICHLOROBIS(BENZONITRILE)PLATINUM(II): PREPARATION AND ISOMERIZATION STUDIES BY ^{13}C NMR SPECTROSCOPY

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Although dichlorobis(benzonitrile)platinum(II) has been thought so far to exist solely as a cis isomer, the reaction of platinum(II) chloride with neat benzonitrile affords a mixture of cis and trans complexes in variable proportions depending on the temperature. The ^{13}C NMR spectra of the trans isomer and ^{13}CN-enriched cis isomer are reported together with the rate and equilibrium data for the cis $\rightleftarrows$ trans isomerization in $CDCl_3$.

Dichlorobis(benzonitrile)-palladium(II) and -platinum(II) are frequently used as the starting materials for preparation of organometallic complexes of these metals.[1)] While $PdCl_2(PhCN)_2$ has the trans structure,[2)] $PtCl_2(PhCN)_2$ has been thought to be cis[1)] since Jensen's measurement of the dipole moment in benzene.[3)] Lauher and Ibers[4)] determined the crystal structure of an adduct $[Pt(DISN)_2]$-$[PtCl_2(PhCN)_2]$ which was prepared by mixing stoichiometric quantities of bis(diiminosuccinonitrilo)platinum(II) and $PtCl_2(PhCN)_2$ in chloroform solution at ambient temperature, and found that the latter component has the trans geometry in crystals. Recently Braunstein, et al.[5)] obtained trans-$\overline{\mathrm{Pt[P(Ph)_2C(Y)=C(Ph)N}}\mathrm{H]_2}$ (Y = CO_2Et and CN) by the reactions of $PtCl_2(PhCN)_2$ with the carbanions $Ph_2P\bar{C}HY$ in THF at 0°C. We also found the nucleophilic attack of the acetylacetonate carbanions $(CH_3CO)_2CH^-$ on the cyanide carbons in $PtCl_2(PhCN)_2$ in dichloromethane at room temperature to yield trans-$\overline{\mathrm{Pt[N(COCH_3)=C(Ph)CH=CO}}\mathrm{CH_3]_2}$.[6)] In each of these three cases, it is not convincing to argue that cis-$PtCl_2(PhCN)_2$ isomerized to the trans form during the prompt reaction which occurred under quite mild conditions. Thus we suspected that these products must have originated from trans-$PtCl_2(PhCN)_2$, and have carried out detailed examination of the product from the reaction of $PtCl_2$ with benzonitrile.

When a suspension of $PtCl_2$ (0.255 g) in PhCN (20 cm^3) was stirred at room temperature, a clean solution was resulted after 7 h. After filtration a yellow precipitate (0.417 g) was obtained in a 92 % yield on addition of petroleum ether to the filtrate. Chromatographic separation of the crude product through a column (20 × ϕ2 cm) of silica gel (Merck 60 F_{254}, 70 – 230 mesh) with dichloromethane as an eluent gave trans- and cis-$PtCl_2(PhCN)_2$ in 26 and 58 % yields in this sequence, both isomers giving satisfactory analyses and molecular-weight data. The isomeric composition of the product depends on the reaction temperature, the trans/cis ratio being 0.46, 0.71, 4.2, and 5.3 at 26, 60, 100, and 180°C, respectively. Thus the approximate ΔH of isomerization cis $\rightleftarrows$ trans in PhCN is 18 kJ/mol, if these values are presumed to give the equilibrium quotients at given temperatures.

The trans isomer exhibits a single $\nu(C\equiv N)$ band at 2285 cm^{-1}, while the corresponding band at 2282 cm^{-1} for cis is accompanied by a minor peak at 2290 cm^{-1}. The most remarkable difference in IR spectra in Nujol is observed in the 800 – 650 cm^{-1} region. The trans isomer shows two very strong bands at 766 and 688 cm^{-1}, associated with the out-of-plane CH deformation vibrations of the phenyl groups. Each of these two bands is split into two well defined peaks in the spectrum of cis complex, giving rise to four strong bands at 779, 758, 695, and 684 cm^{-1}.

Since the cis isomer is much less soluble in chloroform than trans and the signal of its nitrile carbon is indiscernible, the cis complex containing ^{13}CN-enriched benzonitrile[7] as the ligand was used for ^{13}C NMR measurements. ^{13}C NMR shieldings of corresponding carbons in both isomers are not so different, δ (in ppm from internal Me_4Si) being 109.0 and 109.1 for the quarternary C, 133.7 and 133.7 for the ortho C, 129.5 and 129.6 for the meta C, 135.4 and 135.2 for the para C, and 116.8 and 115.3 for the nitrile C of the trans and cis isomers, respectively. The most remarkable difference is noticed in the $^2J(Pt\text{-}C)$ values for the nitrile carbon, the value for trans (289 Hz) being appreciably larger than that for cis (234 Hz). They are much larger than 82 Hz which was found for trans-$[PtMe(p\text{-}MeO\text{-}C_6H_4CN)L_2]PF_6$ (L = $AsMe_3$ and PMe_2Ph),[8] indicating that the sequence of trans influence is $CH_3^- \gg Cl^- > C_6H_5CN$.

The cis $\rightleftarrows$ trans isomerization reaction was followed by the ^{13}C NMR spectroscopy in chloroform at about 25°C, and $K = k_c/k_t = 13$, $k_c = 3.8 \times 10^{-6}\ s^{-1}$ and $k_t = 2.9 \times 10^{-7}\ s^{-1}$ were obtained. The isomerization is very slow as was expected and the equilibrium is more favourable to trans in chloroform than in benzonitrile.

References and Note

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