Preliminary communication

NMR evidence for free rotation of coordinated tetracyanoethylene in its square pyramidal adducts with tetrakis(arylisocyanide)rhodium(I) perchlorates

K. KAWAKAMI, T. KANESHIMA and T. TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka (Japan)

Many interesting data have been accumulated on the donor—acceptor interactions between transition metal basic complexes and various π-acids. In particular, tetracyanoethylene (TCNE) is known to be one of the strongest olefinic π-acids, forming rigid metallocyclopropane ring structures which more closely approximate to alkane complexes than alkene complexes[1]. It is anticipated that if the transition metal basicity[2] of a certain complex is only moderate or weak, then its interaction with the TCNE will be weaker than that of other complexes described so far.

We have found that tetrakis(arylisocyanide)rhodium(I) perchlorates[3,4] form TCNE adducts which are likely to have a square pyramidal structure with the TCNE rotating freely. We believe that these are the first examples of adducts of this kind that d^8 square planar complexes form with TCNE. Free rotation of coordinated ethylene was for the first time suggested and established by Cramer[5].

An equimolar mixture of the appropriate tetrakis(arylisocyanide)rhodium perchlorate and TCNE was stirred for 1 h in CH_2Cl_2 at room temperature. The solvent was removed under reduced pressure. The product was recrystallized from petroleum ether—CH_2Cl_2 to give $[(p\text{-R}-C_6H_4-NC)_4Rh(TCNE)]ClO_4$ (I) (Ia, R = CH_3, Ib, R = CH_3O, or Ic, R = Cl) and $[(o\text{-}CH_3-C_6H_4-NC)_4Rh(TCNE)]ClO_4$ (II). TCNE is the only activated olefin that was found to form adducts in the present work. Others tried were tetrafluoroethylene, fumaronitrile, maleic anhydride, dimethyl- and diethyl-maleate, pyromellitic dianhydride and diphenylacetylene.

The IR spectra of these adducts in $CHCl_3$ at room temperature show only one N≡C stretching band due to arylisocyanides at 2228 (Ia), 2221 (Ib), and 2208 (II) cm^{-1}. The amounts of the shifts of the ν(N≡C) toward the higher frequencies are about 70 cm^{-1}, indicating the occurrence of oxidative addition reactions. The ν(C≡N) band of the TCNE seems to be masked by this strong and broad isocyanide vibration. The PMR spectrum of (Ia) in $Cl_2CHCHCl_2$ at room temperature shows a sharp singlet due to the CH_3 protons and only one set of an approximate AB type quartet arising from the ring protons with the lower field component coalesced. These results can only be rationalized in terms of a square pyramidal configuration around the rhodium atom with the four isocyanides in a plane and the TCNE at the apical site. The rhodium atom may

deviate out of the plane slightly. In contrast to our results, Kaska and Kimball[6] reported that $[(CH_3NC)_4Co(CH_3O_2C-C\equiv C-CO_2CH_3)]^{2+}$ exhibited four $\nu(N\equiv C)$ bands and two kinds of CH_3 proton signals due to CH_3NC. They assigned an octahedral configuration to this ion, with the acetylene coordinated rigidly. Very recently, Haines[7] has shown that $\{[(CH_3O)_3P]_4Rh(R-C\equiv C-R)\}^+$ ($R = CF_3$ and CO_2CH_3) adopt similar configurations.

The PMR spectra of (Ia) at various temperatures shown in Fig. 1 are quite interesting. It is clear from that at 39° that there is only one set of an AB type quartet around this temperature.
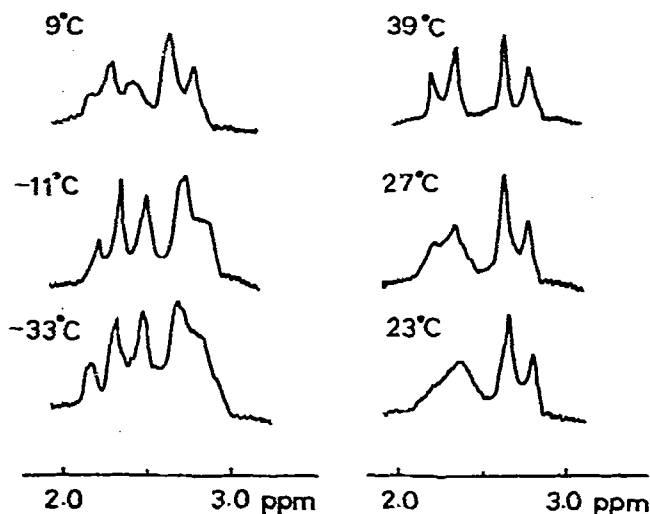

Fig. 1. PMR spectra of $[(p\text{-}CH_3-C_6H_4-NC)_4Rh(TCNE)]ClO_4$ in $Cl_2CHCHCl_2$ at various temperatures.

With the temperature descending, the lower field component of the quartet coalesces around 23° and finally at −33° there appear two sets of the lower component, thus making an apparent triplet, while the higher field component does not completely coalesce at −33°. The same behaviour is observed with (Ib). These results show that the coalescence temperature of the *ortho*-protons is different from that of the *meta*-protons*. This kind of the magnetic nonequivalence of the phenyl ring protons can only be due to some intramolecular phenomenon arising from the magnetic anisotropic effect of the TCNE; probably it is due to the partly restricted rotation of the TCNE or that of the phenyl ring around the C−N single bond.

The only model to explain the features of these PMR spectra with the TCNE fixed and with restricted rotation of the phenyl ring is one where the plane through the rhodium atom and the C=C portion of the TCNE intersects the ligand (denoted by L)

---

*The lower field component can be safely assigned to be due to the *ortho*-protons, since the electron transfer from the rhodium atom toward the TCNE moiety upon complex formation is thought to deshield them more strongly than *meta*-protons.

plane in the middle of the two adjacent ligands (structure A). This model, however, is not a suitable one for the most stable configuration if the TCNE were fixed, since the overlap of the π^* orbital of the TCNE with the d_{xz} or d_{yz} orbital of the rhodium atom is considered to be most effective when the TCNE stays above the rhodium atom and two ligands *trans* to each other (structure B). A structure B with restricted rotation of the phenyl

Structure A   Structure B
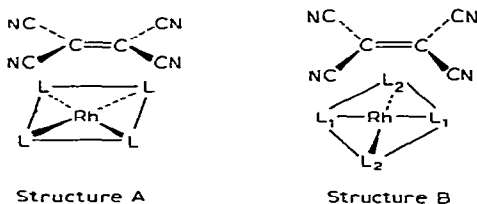
ring can be excluded since there would be two kinds of ligands to make the PMR spectral change much more complicated.

To further support our postulate that the TCNE is rotating, the PMR spectra of (II) in CH_2Cl_2 were observed at various temperatures. The CH_3 proton signal becomes broadened as the temperature is lowered and finally splits into a doublet at $-2°$. The chemical shift difference is 0.06 ppm at $-47°$. This spectral change can be explained by the restricted rotation of the TCNE at lower temperatures if it is assumed that the rotation of the phenyl ring is inhibited because of possible steric repulsion* between the *ortho*-CH_3 groups and the TCNE; that is, the ultimate structure of (II) at lower temperature is structure B, thus making two kinds of CH_3 groups.

All these experimental facts suggest strongly that the TCNE moiety of these adducts of the tetrakis(arylisocyanide)rhodium perchlorates is rotating freely at higher temperature in solution.

Thus, the novel bonding mode of the TCNE toward the rhodium atom in our case is quite different from many cases found in the TCNE adducts of other phosphine and/or carbonyl complexes of rhodium(I), iridium(I), and platinum(0). Here the ethylenic portion of the TCNE approximately makes a rigid plane $(ML_2(C_2))$ with two other ligands in octahedral or square planar configurations[8]. Recently, TCNE is suggested to rotate freely in Ni(TCNE) (t-BuNC)$_3$ in solution[9]. An X-ray crystallographic analysis has been reported for Ni(TCNE)(t-BuNC)$_2$ which shows the largest deviation from planarity of the $ML_2(C_2)$ portion yet reported[10].

Tetrakis(arylisocyanide)rhodium perchlorates reacted with halogens to give 1/1 adducts, *trans*-$[(p\text{-R}-C_6H_4-NC)_4RhX_2]ClO_4$ (R = CH_3 or CH_3O; X = Cl, Br, or I), thus confirming the tendency of those compounds to undergo oxidative addition reactions.

All compounds are crystalline solids and stable in air. Satisfactory analytical data have been obtained. The molecular weights in $CHCl_3$ by a vapor pressure osmometer are

---

*The existence of this kind of steric repulsion is strongly supported by the fact that $[(o,o'\text{-}(CH_3)_2-C_6H_3-NC)_4Rh]Cl$, which seems to have the phenyl rings nearly perpendicular to the ligand plane because of the mutual repulsion of the two CH_3 groups on the adjacent rings, does not form a TCNE adduct at all.