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PHOTOCHEMICAL LIGAND SUBSTITUTION IN HEXAKIS(PHENYL ISOCYANIDE)CHROMIUM(0)-OLEFIN SYSTEMS

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Dimethyl fumarate and fumaronitrile undergo photochemical ligand substitution toward hexakis(phenyl isocyanide)chromium(0). The coodinated dimethyl fumarate is eliminated in the dark without accompanying trans-cis isomerization. Dimethyl maleate, the cis-isomer, does not undergo this type of photoreaction.

The photochemical substitution of metal carbonyls has been extensively investigated.[1] However, a few studies have been made on the ligand exchange of metal isocyanide complexes, especially under illumination.[2] We found the formation of some phenyl isocyanide chromium(0) complexes coodinated by olefins under UV-irradiation.

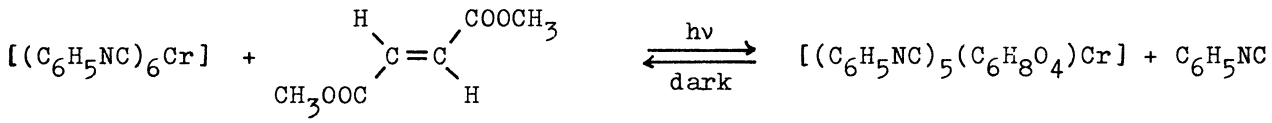
Hexakis(phenyl isocyanide)chromium(0) (7.5×10^{-5} mol) and dimethyl fumarate (8.3×10^{-5} mol) were irradiated in a benzene solution (10 ml) with a high pressure mercury lamp for 2 hours. The color of the solution changed from red to dark brown during irradiation. The product was quickly separated by means of alumina-chromatography and a brown solid substance was obtained in 21 % yield, which is stable in the solid state. The same product was also obtained in the irradiation in tetrahydrofuran. The compound was identified as pentakis(phenyl isocyanide)(dimethyl fumarate)chromium(0) from the following ground:
IR (KBr disk), 1680 cm^{-1} (ester C=O); 2030 and 1970 cm^{-1} (NC)
NMR (in C_6D_6), δ 4.83 (olefinic proton); 3.50(s) (CH_3)
Elemental analysis, Found: C, 68.89; H, 4.54; N, 9.87 %. Calcd. for $C_{41}H_{33}N_5O_4Cr$: C, 69.20; H, 4.64; N, 9.85 %.

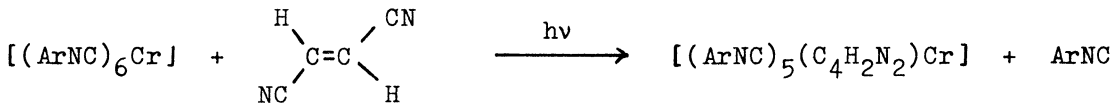
This type of photo-substitution was not observed in hexakis(p-tolyl isocyanide)chromium(0)-dimethyl fumarate system.

Pentakis(phenyl isocyanide)(fumaronitrile)chromium(0) (Found: C, 72.13; H, 4.14; N, 15.23 %. Calcd. for $C_{39}H_{27}N_7Cr$: C,72.56; H, 4.19; N, 15.19 %.) was obtained in a 24 % yield in 2 hours' irradiation of fumaronitrile and hexakis(phenyl isocyanide)chromium(0) in benzene. Contrary to dimethyl fumarate, fumaronitrile reacted photochemically with hexakis(p-tolyl isocyanide)chromium(0) to give pentakis(p-tolyl isocyanide)(fumaronitrile)chromium(0).

Dimethyl fumarate complex is not so stable in solutions and are reconverted to hexakis(phenyl isocyanide)chromium(0) and dimethyl fumarate on standing for 24 hours at room temperature. The reverse reaction was confirmed by means of IR and NMR spectra.

On the other hand, the fumaronitrile complexes are stable and undergo practically no reverse reaction in the dark.





Ar=Phenyl, p-Tolyl

In addition to the reversibility, the photochemical ligand substitution posesses the following characteristics: (1) The reverse reaction to give dimethyl fumarate accompanies no trans-cis isomerization. (2) Dimethyl maleate does not undergo the photo-substitution.[3] In this case, only cis-trans isomerization of the olefin was observed. (3) Acrylonitrile, a weaker electron acceptor, does not undergo the photo-ligand exchange. Tetracyanoethylene, a stronger electron acceptor, reacts with the complex without illumination.

References

1) V.Balzani and V.Carassiti, "Photochemistry of Coordination Compounds" Academic Press, London and New York, (1970) p. 323.
2) The ligand substitution reaction (without illumination) was recently reported in olefin-isocyanide nickel(0), palladium(0) and rhodium(I) complexes. S.Otsuka, T.Yoshida and Y.Tatsuno, J. Amer. Chem. Soc., 93 , 6462 (1971) K.Kawakami, T.Kaneshima and T.Tanaka, J. Organometal. Chem., 34 , C 21 (1972)
3) Electron affinities of diethyl fumarate and diethyl maleate are 0.59 and 0.60 eV, respectively. The difference in the reactivities between the isomers would be ascribed not to the electronic but to the steric factor. Electron affinity values; G.Briegleb, Angew. Chem., 76 , 326 (1964)

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