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Photochemical Ligand Substitution in Hexakis(aryl isocyanide)-chromium(0)–Olefin Systems

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Synopsis. Isocyanide chromium(0) complexes coordinated by dimethyl fumarate, fumaronitrile and maleic anhydride were prepared photochemically by the irradiation of hexakis(aryl isocyanide)chromium(0) with the corresponding olefin. Tetracyanoethylene reacts with hexakis(aryl isocyanide)chromium(0) thermally without illumination, while acrylonitrile and dimethyl maleate do not react even with irradiation.

The chemistry of isocyanide metal complexes coordinated by olefins is a newly developing field. Otsuka *et al.* studied the thermal ligand substitution of *t*-butyl isocyanide metal complexes and prepared nickel and palladium isocyanide complexes coordinated by electron poor olefins.[1] They presumed that the reaction proceeds by S_N1 mechanism. Kawakami *et al.* concluded that tetrakis(aryl isocyanide)rhodium(I) perchlorates form TCNE adducts of square pyramidal structure, in which TCNE rotates freely.[2]

Although the photochemical ligand substitution of metal carbonyls has been extensively investigated,[3] the photochemical method has rarely been applied to the preparation of isocyanide metal complexes. We found that some aryl isocyanide chromium(0) complexes coordinated by electron poor olefins are formed under irradiation.[4]

Experimental

Materials. Aryl isocyanides were prepared by the carbylamine reaction according to Weber *et al.*[5] Phenyl isocyanide; bp 64 °C/20 mmHg. *p*-Tolyl isocyanide; bp 70 °C/8 mmHg. *p*-Anisyl isocyanide; bp 80 °C/20 mmHg. Hexakis(aryl isocyanide)chromium(0) (**1**) were synthesized by the reaction of aryl isocyanide and chromium(II) salt according to Malatesta *et al.*[6]

Commercial GR grade dimethyl fumarate, dimethyl maleate, fumalonitrile, maleic anhydride and EP grade TCNE were used.

Irradiation. **1** ($7—8\times10^{-5}$ mol) and olefin ($7—10\times10^{-5}$ mol) were irradiated in benzene (in the case of NMR measurement in benzene-d_6) or THF solutions (10 ml) in quartz vessels with a high pressure mercury lamp under a nitrogen atmosphere. The color of the solution changed from red to dark brown during the course of irradiation.

Product. Some of the photo-products were stable and isolated by means of alumina chromatography. They were identified as pentakis(aryl isocyanide)(olefin)chromium(0). Spectral data and the results used for identification are listed in Table 1. Some of the photo-products could not be isolated, but the IR and NMR spectra of the reaction mixtures showed characteristic absorption due to the complex coordinated by olefin. IR and NMR spectra assigned to the olefin-coordinated complexes are shown in Table 1.

Results and Discussion

Hexakis(aryl isocyanide)chromium(0) (**1**) undergoes ligand exchange with electron-poor olefins either thermally or photochemically. Fumaronitrile, dimethyl fumarate and maleic anhydride react with $[Cr(ArNC)_6]$ (Ar=phenyl, *p*-tolyl, and *p*-anisyl) photochemically, affording the corresponding $[Cr(ArNC)_5(olefin)]$. Among them three complexes are stable enough to be isolated by means of alumina chromatography in the air. Other complexes were identified spectroscopically in the irradiated reaction mixture.

$$[Cr(ArNC)_6] + \text{olefin} \xrightarrow{h\nu} [Cr(ArNC)_5(\text{olefin})] + ArNC$$

The reactivity of olefins for the ligand substitution depends principally on the electron affinities of the olefins and secondarily on the steric factor. Acrylonitrile, a weaker electron acceptor, does not undergo photochemical ligand substitution. TCNE, a stronger electron acceptor, reacts with **1** without illumination to give pentakis(aryl isocyanide) (TCNE)chromium(0).

The difference between the reactivities of dimethyl fumarate and dimethyl maleate can not be explained in terms of their electronic character. The electron affinity values are similar: E_a for dimethyl maleate, 0.60 eV; E_a for dimethyl fumarate, 0.59 eV.[7] Dimethyl fumarate reacts photochemically with **1**, whereas dimethyl maleate undergoes no ligand substitution, but isomerization to the *trans* isomer. In the photoreaction of hexakis(phenyl isocyanide)chromium(0)–dimethyl fumarate system, no *trans-cis* isomerization was observed.

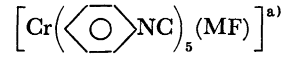
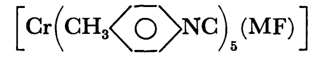
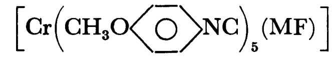
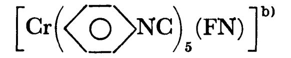
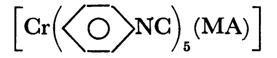
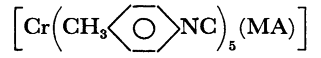
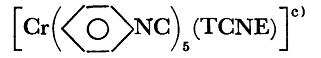
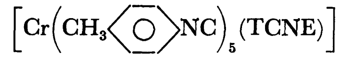
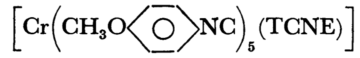
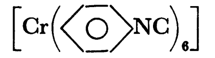
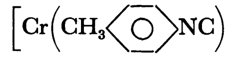
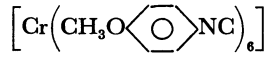
UV-irradiation of **1** with dimethyl acetylenedicarboxylate and phenylacetylene gave decomposition products, but no substitution products.

IR and NMR spectra of the isocyanide–chromium(0) complexes coordinated by olefins clearly show electron transfer from the central metal to the olefins. A similar phenomenon is observed in nickel and palladium complexes.[1] NC-stretching frequencies of the chromium complexes increase with the introduction of olefins. On the other hand, the CN-stretching frequencies of coordinated TCNE and fumaronitrile are lower than those of free TCNE and fumaronitrile. Analogous shift was observed for the CO-stretching vibration of dimethyl fumarate and maleic anhydride. NMR peaks due to olefinic protons of coordinated olefins are found in a lower δ region than those of free olefins.

The photochemical ligand substitution occurs also with solar light in a glass vessel.

For the ligand substitution of metal carbonyls, the

Table 1. Photo-products of hexakis(aryl isocyanide)chromium(0)-olefin systems
MF=dimethyl fumarate, FN=fumaronitrile, MA=maleic anhydride

Compound	Formation		Spectral properties			
	Irradiation time (h)	Yield (%)	IR (cm^{-1})[d]			NMR (δ) olefin H
			ν_{NC}	ν_{CN}	ν_{CO}	
 [a]	2	24	2030 1970		1680	4.85
		not isolated	2040 1990		1680	4.88
		not isolated	2040 1995		1675	
 [b]	2	25	2045 1980	2190		3.30
	0.5	38	2045 1995	2180		3.37
		not isolated	2050 1980	2180		
		not isolated	2040 1985			4.73
		not isolated	2040 1990			4.88
		not isolated	2040 1985			4.78
 [c]	thermal	48	2145 2045	2180 2170		
	thermal	80	2125 2050 2005	2190 2155		
	thermal	88	2125 2050 2000	2190 2170		
			2050 2000 1940			
			2040 1955 1920			
			2030 1955 1920			

Elemental analysis. a) 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%. b) 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%. c) Found: C, 69.58; H, 3.52; N, 16.08%. Calcd for $C_{41}H_{25}N_9Cr$: C, 70.78; H, 3.63; N, 18.12%. d) IR spectra of stable complexes were measured by means of KBr disk, those of unstable ones in benzene-d_6 solutions.

S_N1 mechanism has been established. S_N1 mechanism was kinetically confirmed for the exchange reaction between hexakis(phenyl isocyanide)chromium(0) and ^{14}C-labeled phenyl isocyanide.[8] However, the substitution of aryl isocyanide by TCNE is much faster (the reaction is completed immediately after the chromium complex and TCNE are mixed) than what would be expected for a S_N1 mechanism. The first order rate of the ligand exchange by ^{14}C-labeled phenyl isocyanide is very small; $\tau_{1/2}$, the half life of the reaction, is reported to be hundred hours at 20 °C. This indicates that the substitution of aryl isocyanide by TCNE can not proceed by a simple S_N1 mechanism. The fact that electron-poor olefins are reactive both in thermal and in photochemical substitution suggests that charge transfer interaction between olefins and **1**, in either the ground or the excited state, plays an important role in the ligand substitution reaction.

References

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