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Molecular Complexes of Arenetricarbonylchromium

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Arenetricarbonylchromium forms a charge-transfer molecular complex with electron acceptors such as 1,3,5-trinitrobenzene and tetracyanoethylene but not with electron donors such as *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. The ionization potentials of arenetricarbonylchromium complexes were determined from the charge-transfer transition energies in the molecular complexes. The molecular complexes are formed by a charge-transfer interaction of electron acceptor toward the π-coordinating benzene ring of arenetricarbonylchromium in the case of 1,3,5-trinitrobenzene, and by a charge-transfer toward the central chromium in the case of tetracyanoethylene.

Effects of the tricarbonylchromium group on the chemical properties of the π-coordinating benzene ring in arenetricarbonylchromium are more likely those of an electron-withdrawing group such as a para-nitro substituent. In fact, pK_a of phenylacetic acid coordinating to tricarbonylchromium is as high as that of *p*-nitrophenylacetic acid. Benzoic acid-tricarbonylchromium is an acid stronger than benzoic acid and anilinetricarbonylchromium is a base weaker than aniline.[1,2] Furthermore arenetricarbonylchromium complexes show a higher susceptibility to nucleophilic substitutions such as[1,3]

$$C_6H_5ClCr(CO)_3 \xrightarrow{NaOCH_3} C_6H_5OCH_3Cr(CO)_3$$

whereas the complexes are less susceptible to electrophilic substitutions such as Friedel-Crafts acylation.[4] This indicates an electron-withdrawing effect of tricarbonylchromium group. Larger dipole moments of arenetricarbonylchromium complexes might indicate a large charge-migration toward tricarbonylchromium.[5–7]

In the present work, arenetricarbonylchromium complexes were found to behave as electron donor rather than electron acceptor in charge-transfer molecular complex formation. Arenetricarbonylchromium forms molecular complexes with 1,3,5-trinitrobenzene (1,3,5-TNB) and tetracyanoethylene (TCNE) but not with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD). Bis-π-benzenechromium, however, forms a 1 : 1 salt-like molecular complex with TCNE described as $[\pi\text{-}(C_6H_6)_2Cr]^+TCNE^-$.[8] Arenetricarbonylchromium is not so readily oxidized as bis-π-benzenechromium but a charge-transfer molecular complex formation of arenetricarbonylchromium with 1,3,5-TNB has been reported.[9–10] An X-ray crystallography study has revealed a geometry of "face to face" contact of the counterpart benzene rings in a molecular complex of anisoletricarbonylchromium and 1,3,5-TNB.[11] We have obtained the ionization potentials of arenetricarbonylchromium complexes from the charge-transfer transition energies in the molecular complexes of

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[2] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958).

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TABLE 1. ANALYSES OF ARENETRICARBONYLCHROMIUM COMPLEXES

Complexes	Found (%)				Calcd (%)			
	C	H	N	Cr	C	H	N	Cr
$C_6H_5COOHCr(CO)_3$	46.3	2.2		20.1	46.5	2.3		20.1
$C_6H_5COCH_3Cr(CO)_3$	51.2	3.0		20.4	51.5	3.1		20.3
$C_6H_5FCr(CO)_3$	—	—		22.0	46.6	2.2		22.4
$C_6H_5ClCr(CO)_3$	43.8	2.2		20.9	43.5	2.0		20.9
$C_6H_6Cr(CO)_3$	51.0	2.9		24.2	50.5	2.8		24.3
$C_6H_5CH_3Cr(CO)_3$	52.2	3.3		22.5	52.6	3.5		22.8
$C_6H_5OCH_3Cr(CO)_3$	49.0	3.3		21.2	49.2	3.3		21.3
o-$C_6H_4(CH_3)_2Cr(CO)_3$	55.3	4.6		21.2	54.5	4.2		21.5
m-$C_6H_4(CH_3)_2Cr(CO)_3$	55.5	4.3		21.5	54.5	4.2		21.5
p-$C_6H_4(CH_3)_2Cr(CO)_3$	54.8	4.2		21.5	54.5	4.2		21.5
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	55.9	4.7		20.4	56.2	4.7		20.3
$C_6H_5N(CH_3)_2Cr(CO)_3$	51.0	4.3	5.5	20.3	51.4	4.3	5.5	20.2

arenetricarbonylchromium with TCNE or 1,3,5-TNB.

Experimental

Materials. Arenetricarbonylchromium complexes were prepared according to the methods in the literature[1] by refluxing hexacarbonylchromium (High Pressure Chem. Co. Penn. U.S.A.) with the corresponding benzene derivatives under dry nitrogen atmosphere. For the arenes of low boiling point such as fluorobenzene, chlorobenzene, benzene, toluene, and acetophenone, diglyme was used as solvent. Solid benzoic acid was also dissolved in diglyme. The refluxed mixture was filtered, the filtrate being then condensed by vacuum distillation. The residue thus obtained was recrystallized from petroleum ether. The complexes were identified by elemental analysis (Table 1). Diglyme, petroleum ether and benzene derivatives used for the preparation of arenetricarbonylchromium complexes were dried and distilled by the usual methods.[12]

N,N,N',N'-Tetramethyl-*p*-phenylenediamine (TMPD) dihydrochloride (Tokyo Kasei Co.) was neutralized with NaOH and the free amine thus obtained was purified by vacuum distillation. 1,3,5-Trinitrobenzene (1,3,5-TNB, Tokyo Kasei Co.) was recrystallized from dil HNO_3 and then from ethanol. Tetracyanoethylene (TCNE, Tokyo Kasei Co.) was recrystallized from chlorobenzene.

Preparation of Molecular Complexes with 1,3,5-Trinitrobenzene. 150 mg of toluenetricarbonylchromium (toluene$Cr(CO)_3$) in 5 ml *n*-heptane and 70 mg of 1,3,5-TNB in 5 ml *n*-heptane were separately heated up to 80 °C and then mixed. When the solution was cooled, red crystals of a 1 : 1 molecular complex of toluene$Cr(CO)_3$ and 1,3,5-TNB were precipitated. The complex was repeatedly recrystallized from *n*-heptane. mp 85.5—86.0 °C (mp of toluene$Cr(CO)_3$: 80.0—81.0 °C; mp of 1,3,5-TNB: 123.0—123.5 °C).

Found: C, 43.0; H, 2.3; N, 10.1; Cr, 11.8%. Calcd for $C_{16}H_{11}N_3O_9Cr$: C, 43.5; H, 2.5; N, 9.5; Cr, 11.8%.

Chromium was determined by colorimetry after carbonate fusion.

The 1 : 1 1,3,5-TNB molecular complexes of *o*-xylene-$Cr(CO)_3$, *N,N*-dimethylaniline$Cr(CO)_3$ and anisole$Cr(CO)_3$ were prepared by similar methods: *o*-xylene$Cr(CO)_3$–1,3,5-TNB mp 86.0—87.0 °C (mp of *o*-xylene$Cr(CO)_3$: 90.0—90.5 °C).

Found: C, 44.9; H, 2.8; N, 9.3; Cr, 11.7%. Calcd for $C_{17}H_{13}N_3O_9Cr$: C, 44.9; H, 2.9; N, 9.2; Cr, 11.4%. *N,N*-dimethylaniline$Cr(CO)_3$·1,3,5-TNB mp 102.0—102.5 °C (mp of *N,N*-dimethylaniline$Cr(CO)_3$: 143.5—144.0 °C).

Found: C, 43.5; H, 2.8; N, 12.3; Cr, 11.2%. Calcd for $C_{17}H_{14}N_4O_9Cr$: C, 43.4; H, 3.0; N, 11.9; Cr, 11.1%. Anisole$Cr(CO)_3$·1,3,5-TNB mp 93.0—93.5 °C (mp of anisole-$Cr(CO)_3$: 84.5—85.0 °C).

Found: C, 42.1; H, 2.2; N, 9.4; Cr, 11.3%. Calcd for $C_{16}H_{11}N_3O_{10}Cr$: C, 42.0; H, 2.4; N, 9.2; Cr, 11.4%.

Measurements of Absorption Spectra and Determination of the Complex Formation Constants. Absorption spectra were recorded on a Shimadzu automatic recording spectrophotometer Model MPS-50. The cell compartment was thermostatted at a constant temperature (25 °C).

The solvent 1,2-dichloroethane (Wako Pure Chem. Co.) was dried and purified by the usual procedure.[12]

The equilibrium constant K of a 1 : 1 molecular complex formation between electron donor D and electron acceptor A is given by

$$K = \frac{[D\cdot A]}{([D]_0-[D\cdot A])([A]_0-[D\cdot A])},$$

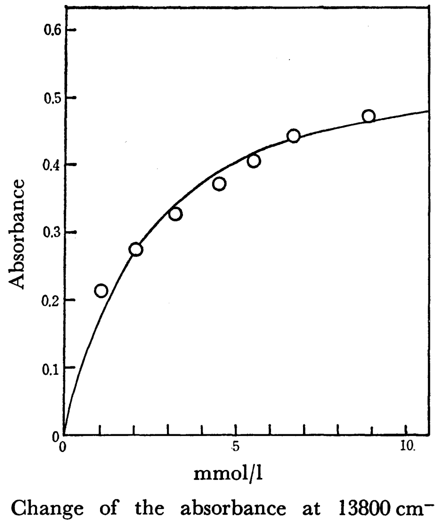

Fig. 1. Change of the absorbance at 13800 cm⁻¹ in the charge-transfer band of 1:1 molecular complex of toluene-$Cr(CO)_3$ and TCNE as a function of the initial concentration of toluene$Cr(CO)_3$ at 25°C.
$[TCNE]_0 = 1.06\times10^{-3}$ mol·l⁻¹,

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[12] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford (1966).

where [$]_0$ denotes the initial concentrations, and [D·A], the concentration of molecular complex D·A. Measurements were carried out at a wave number in the charge-transfer band of the molecular complex where molar absorption coefficients ε_D and ε_A are negligibly small. Assuming Beer's law, [D·A] is rewritten in terms of the observed absorbance $E=\varepsilon_C\cdot[D\cdot A]\cdot l$, where ε_C is the molar absorption coefficient of molecular complex formed in solution, and l, the optical path length. Thus it follows that

$$[D]_0[A]_0\, l/E = \{[D]_0+[A]_0-E/\varepsilon_C\cdot l\}\cdot 1/\varepsilon_C+1/K\varepsilon_C\,.$$

Measurements were carried out at 25 °C for various initial concentrations of D and A. K and ε_C were then evaluated according to the methods described by Rose and Drago,[13] and Lang.[14] In Fig. 1, the absorbance measured at 13800 cm^{-1} is shown as a function of the initial concentration o toluene$Cr(CO)_3$ in the presence of constant initial concentration of TCNE (1.06×10^{-3} mol·l^{-1}). Plots of $[D]_0[A]_0 l/E$ *versus* $\{[D]_0+[A]_0-E/\varepsilon_C\cdot l\}$ give a straight line (Fig. 2) for a self-consistent value of ε_C obtained by iterative calculations.

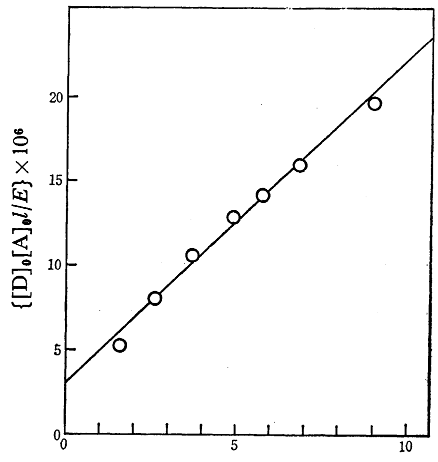

Fig. 2. Plots of $[D]_0[A]_0\cdot l/E$ *versus* $\{[D]_0+[A]_0-E/\varepsilon_C\cdot l\}$ for a self-consistent of ε_C at 25 °C. $[D]_0\equiv$[toluene-$Cr(CO)_3]_0$; $[A]_0\equiv[TCNE]_0=1.06\times10^{-3}$ mol·l^{-1}; $\varepsilon_C=520$.

Infrared Absorption Spectra. Infrared absorption spectra of arenetricarbonylchromium complexes and their molecular complexes with 1,3,5-TNB were taken on a Hitachi spectrophotometer Model EPI-G3.

NMR and ESR Spectra. NMR spectra in 1,2-dichloroethane were recorded on a 60 MHz Varian spectrometer Model T-60. Tetramethylsilane was used as an internal standard. ESR spectra in 1,2-dichloroethane were measured with a Japan Electron Optics Laboratory Co. spectrometer Model JES-3BX.

Results and Discussion

No molecular complex formation of arenetricarbonylchromium with electron-donating TMPD was detected in the absorption measurements. We have not succeeded so far in the isolation of a molecular complex of arenetricarbonylchromium with TMPD, but some 1 : 1 molecular complexes with 1,3,5-TNB could be isolated in a pure state. A charge-transfer band at 20200 cm^{-1} (Fig. 3) implies a molecular complex formation between toluene$Cr(CO)_3$ and 1,3,5-TNB in 1,2-dichloroethane. Molar absorption coefficient of the molecular complex and the equilibrium constant of complex formation were determined to be $\varepsilon_C=55$ l·mol^{-1}·cm^{-1} and $K=70$ l·mol^{-1} at 25 °C from the measurements for various initial concentrations of toluene$Cr(CO)_3$ and 1,3,5-TNB. Since TCNE is a stronger acceptor than 1,3,5-TNB and thus the charge-transfer band in the molecular complex with TCNE shows a remarkable shift toward lower wave number, a good resolution of the charge-transfer band is ob-

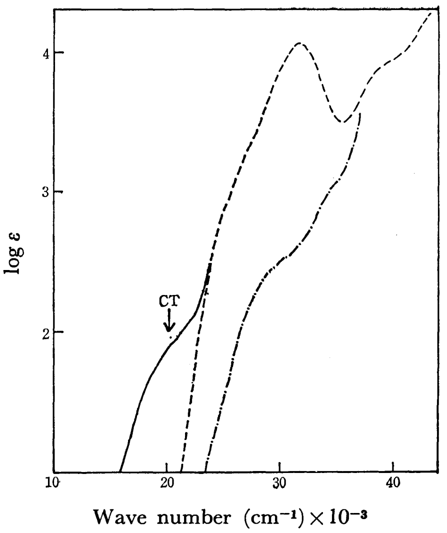

Fig. 3. The charge-transfer band (CT) of toluene$Cr(CO)_3$-1,3,5-TNB system in 1,2-dichloroethane at 25 °C.
[toluene$Cr(CO)_3]_0=0.442$ mol·l^{-1};
$[1,3,5\text{-TNB}]_0=0.462$ mol·l^{-1}
——: toluene$Cr(CO)_3$-1,3,5-TNB
----: toluene$Cr(CO)_3$
—·—: 1,3,5-TNB

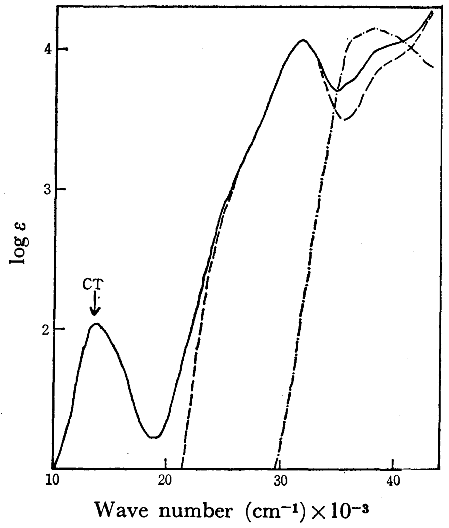

Fig. 4. The charge-transfer band (CT) of toluene$Cr(CO)_3$-TCNE system in 1,2-dichloroethane at 25 °C.
[toluene$Cr(CO)_3]_0=4.51\times10^{-3}$ mol·l^{-1};
$[TCNE]_0=1.06\times10^{-3}$ mol·l^{-1}.
——: toluene$Cr(CO)_3$-TCNE
----: toluene$Cr(CO)_3$
—·—: TCNE

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[13] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).

[14] R. P. Lang, *ibid.*, **84**, 1185 (1962).

TABLE 2. MOLAR ABSORPTION COEFFICIENTS AND COMPLEX FORMATION CONSTANTS OF 1 : 1 MOLECULAR COMPLEXES OF ARENETRICARBONYLCHROMIUM WITH 1,3,5-TNB AND TCNE

Donors	Acceptors	K at 25 °C (l·mol^{-1})	ε_c (max) (l·mol^{-1}·cm^{-1})
$C_6H_6Cr(CO)_3$	1,3,5-TNB	67	50
$C_6H_5CH_3Cr(CO)_3$	1,3,5-TNB	70	55
$C_6H_5OCH_3Cr(CO)_3$	1,3,5-TNB	76	56
o-$C_6H_4(CH_3)_2Cr(CO)_3$	1,3,5-TNB	56	44
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	1,3,5-TNB	60	47
$C_6H_5N(CH_3)_2Cr(CO)_3$	1,3,5-TNB	79	60
$C_6H_5COOHCr(CO)_3$	TCNE	4400	410
$C_6H_5COCH_3Cr(CO)_3$	TCNE	3960	444
$C_6H_5FCr(CO)_3$	TCNE	2000	528
$C_6H_5ClCr(CO)_3$	TCNE	1030	800
$C_6H_6Cr(CO)_3$	TCNE	1070	553
$C_6H_5CH_3Cr(CO)_3$	TCNE	661	520
$C_6H_5OCH_3Cr(CO)_3$	TCNE	265	538
o-$C_6H_4(CH_3)_2Cr(CO)_3$	TCNE	952	667
m-$C_6H_4(CH_3)_2Cr(CO)_3$	TCNE	504	482
p-$C_6H_4(CH_3)_2Cr(CO)_3$	TCNE	240	616
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	TCNE	686	703
$C_6H_5N(CH_3)_2Cr(CO)_3$	TCNE	139	2510

TABLE 3. IONIZATION POTENTIALS (I_p) OF ARENES AND ARENETRICARBONYLCHROMIUM COMPLEXES EVALUATED FROM THE CHARGE-TRANSFER EXCITATION ENERGIES ($h\nu_{CT}$) IN THE 1 : 1 MOLECULAR COMPLEXES WITH 1,3,5-TNB AND TCNE

Donors	Acceptors						Photoionization potentials[4] (eV)
	1,3,5-TNB			TCNE			
	$h\nu_{CT}$ (kK)	solvent	I_p (eV)	$h\nu_{CT}$ (kK)	solvent	I_p (eV)	
C_6H_6	35.2[1]	$CHCl_3$	9.20	25.9	1,2-$C_2H_4Cl_2$	9.13	9.245
$C_6H_6Cr(CO)_3$	20.5	1,2-$C_2H_4Cl_2$	7.23	13.4	1,2-$C_2H_4Cl_2$	7.33	
$C_6H_5CH_3$	33.0[2]	CCl_4	8.91	24.2[3]	$CHCl_3$	8.90	8.82
$C_6H_5CH_3Cr(CO)_3$	20.2	1,2-$C_2H_4Cl_2$	7.18	13.9	1,2-$C_2H_4Cl_2$	7.40	
$C_6H_5OCH_3$	29.1[1]	CH_2Cl_2	8.40	19.9	1,2-$C_2H_4Cl_2$	8.33	8.20
$C_6H_5OCH_3Cr(CO)_3$	20.1	1,2-$C_2H_4Cl_2$	7.17	14.2	1,2-$C_2H_4Cl_2$	7.47	
o-$C_6H_4(CH_3)_2$	31.4[1]	CH_2Cl_2	8.70	22.8[3]	$CHCl_3$	8.70	8.56
o-$C_6H_4(CH_3)_2Cr(CO)_3$	20.0	1,2-$C_2H_4Cl_2$	7.16	13.9	1,2-$C_2H_4Cl_2$	7.42	
1,3,5-$C_6H_3(CH_3)_3$	29.1[1]	CH_2Cl_2	8.40	21.3[3]	$CHCl_3$	8.52	8.39
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	19.8	1,2-$C_2H_4Cl_2$	7.14	14.0	1,2-$C_2H_4Cl_2$	7.43	
$C_6H_5N(CH_3)_2$	20.7	1,2-$C_2H_4Cl_2$	7.26	14.9[3]	$CHCl_3$	7.57	
$C_6H_5N(CH_3)_2Cr(CO)_3$	18.9	1,2-$C_2H_4Cl_2$	6.99	16.1	1,2-$C_2H_4Cl_2$	7.77	

1) R. Foster, "Organic Charge-transfer Complexes," Academic Press, London and New York, (1969) p. 40. 2) Ref. 17. 3) Ref. 18. 4) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

tained as shown in Fig. 4. Molar absorption coefficients and complex formation constants of 1 : 1 molecular complexes of arenetricarbonylchromium with 1,3,5-TNB or TCNE are given in Table 2.

Although an ESR signal has been reported for bis-π-benzenechromium with TCNE,[8] no signal was found for the molecular complexes of arenetricarbonylchromium with 1,3,5-TNB or TCNE formed in 1,2-dichloroethane. Thus their ground state should be a singlet. In fact, proton NMR spectra were observed in the usual region even when most part of the arenetricarbonylchromium complex present in solution forms a molecular complex with acceptor. Since no appreciable shift was observed in molecular complex formation, no further information has been obtained from the NMR spectra.

The charge-transfer transition energies of the molecular complexes with a common acceptor are given by a linear function of the ionization potential I_p of the donor

$$h\nu_{CT} = \{I_p - C_1\} + C_2/\{I_p - C_1\},$$

where C_1 and C_2 are constants determined only by the acceptor. The values given for 1,3,5-TNB are C_1=5.00 and C_2=0.70,[15] and for TCNE, C_1=6.10 and C_2=0.54.[16] The ionization potential of tolueneCr(CO)$_3$ was estimated to be 7.18 eV from the charge-transfer excitation energy in a molecular complex with 1,3,5-TNB, and 7.40 eV from the one with TCNE.

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[15] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

[16] G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem.*, *N. F.*, **30**, 333 (1961).

TABLE 4. IONIZATION POTENTIALS (I_p) OF ARENETRICARBONYLCHROMIUM COMPLEXES EVALUATED FROM THE CHARGE-TRANSFER EXCITATION ENERGIES ($h\nu_{CT}$) IN THE MOLECULAR COMPLEXES WITH TCNE

AreneCr(CO)$_3$	$h\nu_{CT}$ (kK)	I_p (eV)	$\tilde{\nu}_{CO}$ in areneCr(CO)$_3$ (cm^{-1}) in 1,2-$C_2H_4Cl_2$	in C_6H_{12}	I_p of corresponding arenes[3] (eV)
$C_6H_5COOHCr(CO)_3$	12.3	7.06	1983	—	9.59[4]
$C_6H_5COCH_3Cr(CO)_3$	12.1	7.00	1979	—	(9.42)[5]
$C_6H_5FCr(CO)_3$	12.9	7.22	1977	1996[1]	9.36[4]
$C_6H_5ClCr(CO)_3$	12.7	7.16	1975	1992[2]	9.14
$C_6H_6Cr(CO)_3$	13.4	7.33	1970	1987[1]	9.13[4]
$C_6H_5CH_3Cr(CO)_3$	13.9	7.40	1965	1982[1]	8.90
$C_6H_5OCH_3Cr(CO)_3$	14.2	7.47	1964	1982[1]	8.27, 8.33[4]
o-$C_6H_4(CH_3)_2Cr(CO)_3$	13.9	7.42	1962	—	8.70
m-$C_6H_4(CH_3)_2Cr(CO)_3$	14.0	7.43	1962	—	8.69
p-$C_6H_4(CH_3)_2Cr(CO)_3$	14.2	7.46	1960	1979[1]	8.52
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	14.0	7.43	1958	1975[1]	8.52
$C_6H_5N(CH_3)_2Cr(CO)_3$	16.1	7.77	1951	1969[1]	7.57

1) Ref. 19. 2) Ref. 20. 3) Ref. 18; evaluated from the charge-transfer excitation energies in the molecular complexes with TCNE. 4) determined in the present work. 5) Plots shown in Fig. 5 predict I_p=9.42 eV from the observed carbonyl stretching frequency in $C_6H_5COCH_3Cr(CO)_3$ 1979 cm^{-1}. The charge-transfer band in the molecular complex with TCNE is not well resolved from the (n, π^*) transition of $C_6H_5COCH_3$ and thus the ionization potential is not determined directly by method 3).

The ionization potential of toluene in the molecular complex with 1,3,5-TNB is 8.91 eV,[17] while that in the complex with TCNE is 8.90 eV.[18] The ionization potential of tolueneCr(CO)$_3$ is lower than that of free toluene by 1.73 eV in the complex with 1,3,5-TNB and 1.5 eV in that with TCNE. The ionization potentials of some arenes and their coresponding arenetricarbonylchromium complexes, evaluated from the charge-transfer excitation energies in the molecular complexes with 1,3,5-TNB and TCNE, are given in Table 3. The empirical linear functions used to estimate the ionization potentials of arenetricarbonylchromium complexes originally fitted naphthalene.[15,16] The functions, however, can well reproduce the ionization potentials of various aromatic hydrocarbons and show a difference of less than 0.1 eV of the ionization potentials obtained for molecular complexes with 1,3,5-TNB and TCNE. It should be noted that the ionization potentials of arenes evaluated from the charge-transfer excitation energies agree in the 1,3,5-TNB and TCNE systems, whereas those of arenetricarbonylchromium complexes differ in the two systems beyond experimental error. The ionization potentials of arenetricarbonylchromium complexes in the TCNE system obtained are given in Table 4, together with the carbonyl stretching frequencies of arenetricarbonylchromium in 1,2-dichloroethane measured in the present work and those in cyclohexane taken from literature.[19,20] A shift of the infrared peak toward higher frequency was observed in the order

$$C_6H_5COOH > C_6H_5COCH_3 > C_6H_5F > C_6H_5Cl > C_6H_6 > C_6H_5CH_3 > C_6H_5OCH_3 > o\text{-}C_6H_4(CH_3)_2 \geqq m\text{-}C_6H_4(CH_3)_2 > p\text{-}C_6H_4(CH_3)_2 > 1,3,5\text{-}C_6H_3(CH_3)_3 > C_6H_5N(CH_3)_2\,.$$

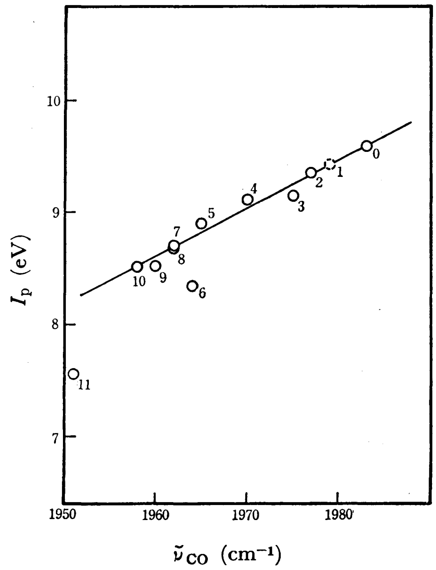

Fig. 5. Plots of the ionization potentials of arenes *versus* the carbonyl stretching frequencies in arenetricarbonylchromium complexes.
Arenes: 0, C_6H_5COOH; 1, $C_6H_5COCH_3$; 2, C_6H_5F; 3, C_6H_5Cl; 4, C_6H_6; 5, $C_6H_5CH_3$; 6, $C_6H_5OCH_3$; 7, o-$C_6H_4(CH_3)_2$; 8, m-$C_6H_4(CH_3)_2$; 9, p-$C_6H_4(CH_3)_2$; 10, 1,3,5-$C_6H_3(CH_3)_3$; 11, $C_6H_5N(CH_3)_2$.

When the antibonding orbital of carbonyl is given a certain charge by chromium-carbonyl back-donation, the carbonyl stretching frequency is shifted toward lower frequency. The above order was in good agreement with that observed in the ionization potentials of arenes (Fig. 5). The stronger donating arene gives rise to more back-donation from chromium to carbonyl groups in arenetricarbonylchromium complex. Plots of the ionization potentials of arenetricarbonylchromium in the molecular complexes with 1,3,5-TNB against the carbonyl frequencies give a straight line except the point of dimethylanilineCr(CO)$_3$, where the ionization potential is much reduced (Fig. 6).

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17) G. Briegleb and J. Czekalla, *ibid.*, **24**, 37 (1960).
18) P. G. Farrell and J. Newton, *J. Phys. Chem.*, **69**, 3506 (1965).
19) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).
20) D. A. Brown and H. Sloan, *J. Chem. Soc.*, **1962**, 3849.

TABLE 5. INFRARED FREQUENCIES OBSERVED IN ARENETRICARBONYLCHROMIUM AND THEIR TNB COMPLEXES

Complex	Medium[1)]	Absorption peak (cm^{-1})[2)]					
		I	II	III	IV	V[3)]	VI[3)]
$C_6H_5CH_3Cr(CO)_3$	KBr	1959 s		814 w			665 m
	$C_2H_4Cl_2$	1965 s		811 w			—
$C_6H_5CH_3Cr(CO)_3TNB$	KBr	1960 s	1343 s	820 w	729 m	713 m	667 m
	$C_2H_4Cl_2$	1965 s	1345 s	814 w	731 m	—	—
$C_6H_5OCH_3Cr(CO)_3$	KBr	1960 s		812 w			662 m
	$C_2H_4Cl_2$	1964 s		808 w			—
$C_6H_5OCH_3Cr(CO)_3TNB$	KBr	1960 s	1345 s	820 w	731 m	717 m	663 m
	$C_2H_4Cl_2$	1962 s	1344 s	811 w	730 m	—	—
$C_6H_5N(CH_3)_2Cr(CO)_3$	KBr	1935 s		800 w			673 m
	$C_2H_4Cl_2$	1951 s		797 w			—
$C_6H_5N(CH_3)_2Cr(CO)_3TNB$	KBr	1957 s	1343 s	813 w	731 m	717 m	681 m
	$C_2H_4Cl_2$	1951 s	1345 s	802 w	731 m	—	—

1) KBr: disk, $C_2H_4Cl_2$: 1,2-dichloroethane solution. 2) I: symmetrical CO valence stretching frequency, III: symmetrical carbon-hydrogen bending vibration of the π-coordinating benzene ring, VI: metal-CO bending vibration, II, IV and V: 1,3,5-trinitrobenzene peaks. 3) The peaks V and VI could not be well resolved in 1,2-dichloroethane from the bands of the solvent.

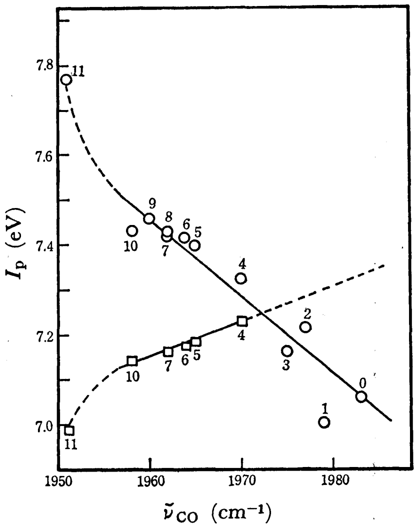

Fig. 6. Plots of the ionization potentials of arenetricarbonylchromium complexes in the molecular complex *versus* the carbonyl stretching frequencies in arenetricarbonylchromium complexes.

○: TCNE molecular complexes

□: 1,3,5-TNB molecular complexes

Arenes: 0, C_6H_5COOH; 1, $C_6H_5COCH_3$; 2, C_6H_5F; 3, C_6H_5Cl; 4, C_6H_6; 5, $C_6H_5CH_3$; 6, $C_6H_5OCH_3$; 7, *o*-$C_6H_4(CH_3)_2$; 8, *m*-$C_6H_4(CH_3)_2$; 9, *p*-$C_6H_4(CH_3)_2$; 10, 1,3,5-$C_6H_3(CH_3)_3$; 11, $C_6H_5N(CH_3)_2$.

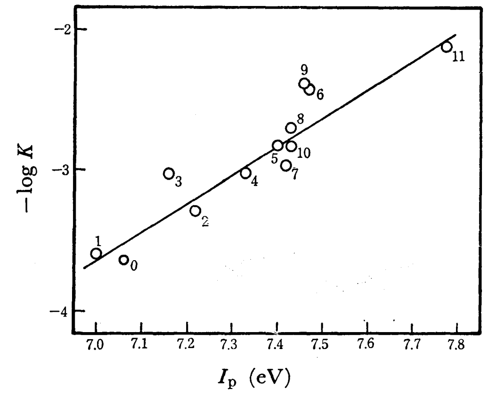

Fig. 7. Plots of the free energy changes of 1:1 molecular complex formation of arenetricarbonylchromium with TCNE against the ionization potentials of arenetricarbonylchromium in the molecular complex with TCNE. Arenes: 0, C_6H_5COOH; 1, $C_6H_5COCH_3$; 2, C_6H_5F; 3, C_6H_5Cl 4, C_6H_6; 5, $C_6H_5CH_3$; 6, $C_6H_5OCH_3$; 7, *o*-$C_6H_4(CH_3)_2$; 8, *m*-$C_6H_4(CH_3)_2$; 9, *p*-$C_6H_4(CH_3)_2$; 10, 1,3,5-$C_6H_3(CH_3)_3$; 11, $C_6H_5N(CH_3)_2$.

However, it is evident that the ionization potential of arenetricarbonylchromium in the 1,3,5-TNB molecular complex decreases with a decrease in the ionization potential of coordinating arene. Since the coordinating arene enhances the charge density on carbonyl groups, the acceptor 1,3,5-TNB might exert a charge-transfer interaction toward the carbonyl groups other than the coordinating arene. Apparently no shift was observed in the carbonyl stretching frequencies upon molecular complex formation in solution. The molecular complexes even in the solid state showed no appreciable shift of the IR peaks except dimethylanilineCr$(CO)_3$ (Table 5). DimethylanilineCr$(CO)_3$ shows an appreciable shift of the carbonyl frequency in KBr disk, arising from an intermolecular interaction between dimethylanilineCr$(CO)_3$ in the solid state. Thus the remarkable difference of carbonyl stretching frequencies in the KBr disk of dimethylanilineCr$(CO)_3$ and its 1,3,5-TNB complex does not necessarily imply a reduction in the bond order of the carbonyl groups by a direct charge-transfer interaction of 1,3,5-TNB toward the carbonyl groups. In fact, the carbonyl stretching frequency makes no sizable shift in 1,2-dichloroethane solution, even when the concentrations of dimethylanilineCr$(CO)_3$ and 1,3,5-TNB were so chosen as to obtain an almost complete complex formation. An X-ray crystallography study of a molecular complex anisoleCr$(CO)_3$·1,3,5-TNB has revealed that the acceptor 1,3,5-TNB makes a charge-transfer interaction with coordinating arene rather than carbonyl groups.[11)] The absorption spectra of the KBr disk of anisoleCr$(CO)_3$·1,3,5-TNB and dimethylanilineCr-

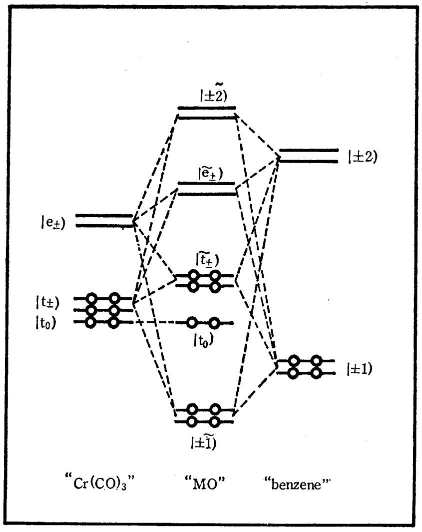

Fig. 8. Molecular orbital levels in arenetricarbonylchromium (schematic). "Cr(CO)$_3$" implies molecular orbitals mainly localized on zero-valent chromium d orbitals which are split by σ ligand field and π back-donation in tricarbonyl chromium, and "benzene" implies the highest occupied and the lowest vacant orbitals of benzene. Chromium d orbitals are given by

$$|e_+) = \sqrt{\frac{2}{3}}\,|+1) - \sqrt{\frac{1}{3}}\,|-2)$$

$$|e_-) = \sqrt{\frac{2}{3}}\,|-1) + \sqrt{\frac{1}{3}}\,|+2)$$

$$|t_+) = \sqrt{\frac{1}{3}}\,|+1) + \sqrt{\frac{2}{3}}\,|-2)$$

$$|t_-) = \sqrt{\frac{1}{3}}\,|-1) - \sqrt{\frac{2}{3}}\,|+2)$$

$$|t_0) = |0)$$

The MO's formed are denoted by $\sim$with the name of a component orbital in the highest contribution.

(CO)$_3$·1,3,5-TNB were measured. The solid state spectra thus obtained were in good agreement with the solution spectra. This implies that the molecular complex formed in solution should have a similar geometry to the structure formed in the solid state. In the case of the TCNE complexes, however, the ionization potential increases with a decrease in the ionization potential of coordinating arene (Fig. 6). As Fig. 7 shows, the stability of molecular complexes with TCNE increases with a decrease in the ionization potential of arenetricarbonylchromium in the TCNE molecular complex and also a decrease in the charge-density of the carbonyl groups. No shift was observed in the carbonyl stretching frequencies upon molecular complex formation with TCNE. Thus it should be concluded that the acceptor TCNE makes a direct interaction with the central chromium.

Schematic molecular orbital levels of the outer electrons in arenetricarbonylchromium are shown in Fig. 8. An interaction of the highest filled benzene orbitals $|\pm1)$ and vacant chromium dσ orbitals $|e_\pm)$ gives rise to a charge-migration from π-coordinating benzene to chromium. In the contrast, an interaction of the filled chromium orbitals $|t_\pm)$, participating in the back-donation in Cr–CO, and the lowest vacant benzene orbitals $|\pm2)$ gives a charge-migration from chromium dπ orbitals to coordinating benzene. A semi-empirical molecular orbital calculation predicted that the resulting charge-migration occurs from π-coordinating benzene to carbonyl groups.[21] Regardless of the charge-migration, the highest filled orbitals $|\pm1)$ are stabilized by interaction with the chromium dσ orbitals $|e_\pm)$, leading to increase of the ionization potentials of coordinating arene. The ionization potential of arenetricarbonylchromium is a work to be done for detachment of an electron in the molecular orbital $|\tilde{t}_\pm)$ or $|t_0)$. The orbital $|t_0)$ is delocalized over the chromium and the carbonyls but has no population on the π-coordinating arene, whereas the orbitals $|\tilde{t}_\pm)$ have populations not only on the carbonyls but also on the π-coordinating arene.

When a molecular complex is formed by a charge-transfer interaction involving the orbital $|t_0)$, the acceptor accepts electronic charge from the carbonyl groups in an outer-sphere mechanism or directly from the central chromium in an inner-sphere mechanism. In fact, a protonation of arenetricarbonylchromium results in the formation of a hydrido complex,[22,23] in which a proton forms a direct binding with the central chromium. However, a bulky acceptor such as 1,3,5-TNB can not make an appreciable interaction with the chromium-localized $|t_0)$ orbital for steric hindrance, the molecular complex being formed by a charge-transfer interaction involving the molecular orbital $|\tilde{t}_\pm)$ delocalized over the π-coordinating benzene and carbonyl groups. Direct interaction between 1,3,5-TNB and carbonyl groups could be eliminated because of the small overlapping between the acceptor and carbonyl orbitals despite the high population of chromium dπ electron on the carbonyl groups.

In the case of TCNE, an enhancement in the charge-populations in π-coordinating arene and carbonyl groups of the donor reduces the stability of the molecular complex. Thus the acceptor TCNE makes direct interaction with the orbital $|t_0)$ localized on the central chromium by an inner-sphere mechanism, although TCNE is not so small. The stability of the molecular complex increases with a decrease in the ionization potential of the orbital $|t_0)$. With the decrease of ionization potential of arene the back-donation in Cr–CO is enhanced. By a charge-migration from the top filled orbitals $|\pm1)$ of arene, orbital $|t_0)$ is stabilized by an enhancement of the back-donation in Cr–CO, whereas orbital $|\tilde{t}_\pm)$ is rather destabilized. As is shown in Fig. 6, the ionization potential of arenetricarbonylchromium in the molecular complex with TCNE is the ionization potential of $|t_0)$, which increases with a decrease in the ionization potential of arene, while the ionization potential of arenetricarbonylchromium in the molecular complex with 1,3,5-TNB is the ionization potential of $|\tilde{t}_\pm)$, which decreases with a decrease in the ionization potential of arene.

Since orbital $|\pm1)$ of the π-coordinating arene is stabilized by interaction with orbital $|t_\pm)$, which makes

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a charge-transfer from arene to chromium-carbonyl orbitals, the substitution reactions in the π-coordinating benzene ring are more likely those of the benzene ring with electron-withdrawing substituents. However, the chromium-localized orbitals $|t_0)$ and $|\tilde{t}_\pm)$ play important roles in the charge-transfer molecular complex formation, and thus arenetricarbonylchromium acts as an electron donor rather than an electron acceptor as shown in the nucleophilic substitutions in π-coordinating benzene ring of arenetricarbonylchromium. The acceptor TCNE can accept electronic charge by an inner-sphere interaction with orbital $|t_0)$ on the π-coordinating arene.

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