Molecular Complexes of Arenetricarbonylchromium, -molybdenum and -wolfram

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Arenetricarbonylchromium forms a charge-transfer complex with 1,3,5-trinitrobenzene (1,3,5-TNB), while arenetricarbonylmolybdenum and -wolfram do not form a charge-transfer complex with 1,3,5-TNB. On the other hand, arenetricarbonylchromium, -molybdenum and -wolfram form a charge-transfer complex with tetracyanoethylene (TCNE). Since the intramolecular charge transfer from coordinated arene to carbonyls increases in the molybdenum and wolfram derivatives, 1,3,5-trinitrobenzene cannot form a molecular complex accepting an electronic charge of the coordinated arene. In the case of TCNE, however, a molecular complex is formed by an inner-sphere charge-transfer interaction between the acceptor and the central metal atom. Thus the stability of the TCNE molecular complexes is dependent upon the charge density of the central metal atom and also the steric effects due to the functional groups in coordinated arenes. The ionization potentials of the molybdenum and wolfram derivatives observed for their TCNE molecular complexes are almost equal but higher than those of the corresponding chromium derivatives, whereas the highest stability is obtained for the molybdenum derivatives.

Arenetricarbonylchromium forms charge-transfer complexes with electron acceptors such as 1,3,5-trinitrobenzene (1,3,5-TNB) and tetracyanoethylene (TCNE) rather than with electron donors.1) Nevertheless, the effects of tricarbonylchromium group to the chemical properties of π-coordinated benzene ring are more likely those of an electron-withdrawing group. In fact, benzoic acid tricarbonylchromium is a stronger acid than benzoic acid and anilinetricarbonylchromium is a weaker base than aniline.2,3) Furthermore arenetricarbonylchromium exhibits a higher susceptibility to nucleophilic substitutions while it is less susceptible to electrophilic substitutions.2,4,5)

The ionization potential of arenetricarbonylchromium was determined from the charge-transfer transition energies in the molecular complexes with 1,3,5-TNB1,6) and with TCNE.1)

1,3,5-TNB forms a molecular complex with arenetricarbonylchromium by a charge-transfer interaction toward the π-coordinated benzene ring in "face-to-face" stack of the counter benzene rings as revealed by an X-ray study on the molecular complex of anisoletricarbonylchromium and 1,3,5-TNB.7) The ionization potentials of arenetricarbonylchromium obtained from the charge-transfer transition energies in the 1,3,5-TNB molecular complexes can well reproduce the ionization potentials measured directly by electron impact technique.8) The ionization potentials of arenetricarbonylchromium obtained from the charge-transfer transition energies in the TCNE molecular complexes increase with a decrease in the ionization potential of coordinated arene. This is opposite to the corresponding shift of the ionization potentials observed for the 1,3,5-TNB molecular complexes. The stability of the TCNE complexes increases with a decrease in the ionization potential of arenetricarbonylchromium obtained for the TCNE complexes. This indicates that TCNE forms a charge-transfer molecular complex with arenetricarbonylchromium in a structure different from the 1,3,5-TNB molecular complex. In a previous paper,1) an inner-sphere charge-transfer interaction of TCNE with the central chromium atom of arenetricarbonylchromium was proposed. In this paper, we present further evidences of the inner-sphere charge-transfer interaction of TCNE with arenetricarbonylchromium, -molybdenum and -wolfram.

Experimental

Materials. Arenetricarbonylchromium,2) -molybdenum,9,10) and -wolfram9,11) were prepared according to the methods described in the literature by refluxing hexacarbonylchromium (High Pressure Chem. Co., Pennsylvania, U.S.A.), hexacarbonylmolybdenum (High Pressure Chem. Co., Pennsylvania, U.S.A.), or hexacarbonylwolfram (Research Organic/Inorganic Chem. Corp., California, U.S.A.) with the corresponding benzene derivatives under dry nitrogen atmosphere. For the preparation of arenetricarbonylwolfram, diglyme was used as solvent. For the preparation of arenetricarbonylmolybdenum, however, the use of diglyme usually results in poor yield and thus hexacarbonylmolybdenum was refluxed directly in the corresponding arenes. The refluxed mixtures were filtered, and then the filtrate was condensed by vacuum distillation. In the case of arenetricarbonylmolybdenum, the condensed solution was filtered and the complex was precipitated by adding *n*-pentane, the precipitate being then washed with isopentane. Arenetricarbonylchromium and -wolfram were obtained as residue by condensation of the filtrates of the refluxed mixtures. Arenetricarbonylchromium was purified by recrystallization of the residue from petroleum ether. Raw arenetricarbonylwolfram was dissolved in a small amount of benzene and then filtered. By adding *n*-pentane to the filtrate, arenetricarbonylwolfram was precipitated, and then the precipitate was washed with isopentane. The complexes were identified by elemental analysis (Table 1).

Diglyme, petroleum ether, *n*-pentane, isopentane and benzene derivatives used for the preparations 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-TNB (Tokyo Kasei Co.) was recrystallized from dil HNO_3 and then from ethanol. TCNE (Tokyo Kasei Co.) was recrystallized from chlorobenzene.

Measurements of Absorption Spectra and Determinations 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).

TABLE 1. ANALYSES OF THE ARENETRICARBONYLCHROMIUM, -MOLYBDENUM, AND -WOLFRAM

Arene metal tricarbonyls	Found (%)			Calcd (%)		
	C	H	Cr	C	H	Cr
$C_6H_5CH_3Cr(CO)_3$	52.2	3.3	22.5	52.6	3.5	22.8
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
$C_6H_5CH_3Mo(CO)_3$	44.5	3.1		44.1	3.0	
o-$C_6H_4(CH_3)_2Mo(CO)_3$	46.4	3.4		46.2	3.5	
m-$C_6H_4(CH_3)_2Mo(CO)_3$	45.7	3.7		46.2	3.5	
p-$C_6H_4(CH_3)_2Mo(CO)_3$	46.3	3.4		46.2	3.5	
1,3,5-$C_6H_3(CH_3)_3Mo(CO)_3$	48.5	4.0		48.0	4.0	
$C_6H_5CH_3W(CO)_3$	33.4	2.3		33.4	2.2	
p-$C_6H_4(CH_3)_2W(CO)_3$	35.3	2.6		35.3	2.7	
1,3,5-$C_6H_3(CH_3)_3W(CO)_3$	36.8	3.2		37.1	3.1	

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

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

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

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

Measurements were carried out at 25 °C for various sets of the initial concentrations of D and A. K and ε_C were then evaluated according to the method described by Rose and Drago,[13] and Lang.[14] Plots of $[\mathrm{D}]_0[\mathrm{A}]_0l/E$ against $\{[\mathrm{D}]_0+[\mathrm{A}]_0-E/\varepsilon_C\cdot l\}$ give a straight line for a self-consistent value of ε_C obtained by iterative calculations.

Infrared Absorption Spectra. Infrared absorption spectra of arenetricarbonylchromium, -molybdenum, and -wolfram in 1,2-dichloroethane were taken on a Hitachi spectrophotometer Model EPI-G3.

NMR spectra. NMR spectra of arene metal tricarbonyls in 1,2-dichloroethane were recorded on a 100 MHz Japan Electron Optics Laboratory spectrometer Model JNM 4H-100. Tetramethylsilane was used as an internal standard.

He Photoelectron Spectra. He (584 Å) photoelectron spectra were measured on a JASCO PE-1 photoelectron spectrometer.

Results and Discussion

Arenetricarbonylchromium, -molybdenum and -wolfram do not form a molecular complex with electron donors such as TMPD. On the other hand arenetricarbonylchromium forms molecular complexes with electron acceptors such as TCNE and 1,3,5-TNB. In fact the molecular complexes of 1,3,5-TNB have been isolated.[1,15,16] Although we have not succeeded so far in the isolation of the molecular complexes of TCNE, the charge-transfer absorption band indicates the molecular-complex formation between TCNE and arenetricarbonylchromium.

Arenetricarbonylmolybdenum and -wolfram do not form a molecular complex with 1,3,5-TNB. Neither a complex could be isolated nor a significant spectroscopic evidence of molecular-complex formation was detected. However, arenetricarbonylmolybdenum and -wolfram evidently form a charge-transfer molecular complex with TCNE. Figures 1, 2 and 3 present the charge-transfer absorption bands of toluenetricarbonylchromium (toluene $Cr(CO)_3$)–TCNE, toluene $Mo(CO)_3$–TCNE and toluene $W(CO)_3$–TCNE systems in 1,2-dichloroethane.

The absorption measurements were carried out at 25 °C in the charge-transfer band for various sets of the initial concentrations of TCNE and arenetricarbonylchromium, -molybdenum or -wolfram. From the values thus obtained, K and ε_C were evaluated. Table 2 shows K and ε_C obtained in the present work for various 1 : 1 molecular complexes of arenetricarbonylchromium, -molybdenum, and -wolfram with TCNE.

The ionization potentials of arenetricarbonylchromium, -molybdenum and -wolfram were evaluated from the charge-transfer transition energies in the molecular complexes with TCNE using an empirical relationship[17]

$$h\nu_{CT} = (I_p-6.10) + 0.54/(I_p-6.10)\,,$$

where $h\nu_{CT}$ is the charge-transfer transition energy in eV and I_p is the ionization potential in eV of arenetricarbonylchromium, -molybdenum or -wolfram. The results are summarized in Table 3.

The ionization potentials determined by using the empirical relationship are in good agreement with the values directly observed for some chromium derivatives by photoelectron spectroscopy as shown in Fig. 5. The spectra are discussed later. The ionization potential of toluene is 8.90 eV[18] while the ionization potentials of toluene $Cr(CO)_3$, toluene $Mo(CO)_3$ and toluene $W(CO)_3$ are 7.40 eV, 8.13 eV and 8.14 eV,

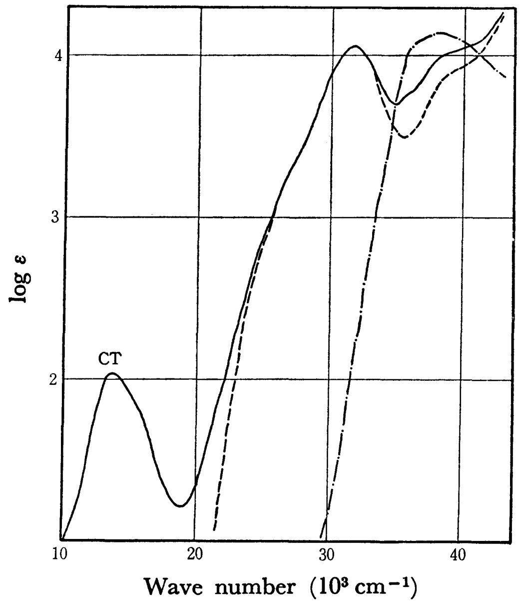

Fig. 1. The charge-transfer band (CT) of toluene Cr-$(CO)_3$-TCNE system in 1,2-dichloroethane at 25 °C. [toluene $Cr(CO)_3]_0 = 4.51 \times 10^{-3}$ mol l^{-1}; [TCNE]$_0 = 1.06 \times 10^{-3}$ mol l^{-1}.
——: toluene $Cr(CO)_3$-TCNE
----: toluene $Cr(CO)_3$
—·—: TCNE

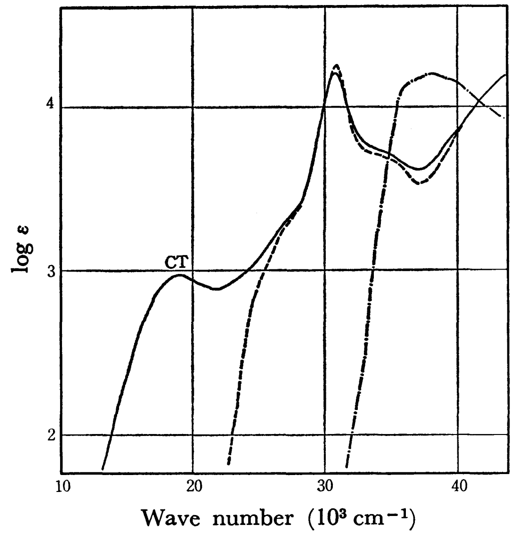

Fig. 2. The charge-transfer band (CT) of toluene $Mo(CO)_3$-TCNE system in 1,2-dichloroethane at 25 °C.
[toluene $Mo(CO)_3]_0 = 4.92 \times 10^{-4}$ mol l^{-1}; [TCNE]$_0 = 9.22 \times 10^{-5}$ mol l^{-1}.
——: toluene $Mo(CO)_3$-TCNE
----: toluene $Mo(CO)_3$
—·—: TCNE

respectively. The ionization potential of arenes varies with their substituents, while the ionization potential of arene metal tricarbonyls is rather independent of the substituents. The ionization potentials of the molybdenum and wolfram derivatives are almost equal but higher than those of the corresponding chromium derivatives.

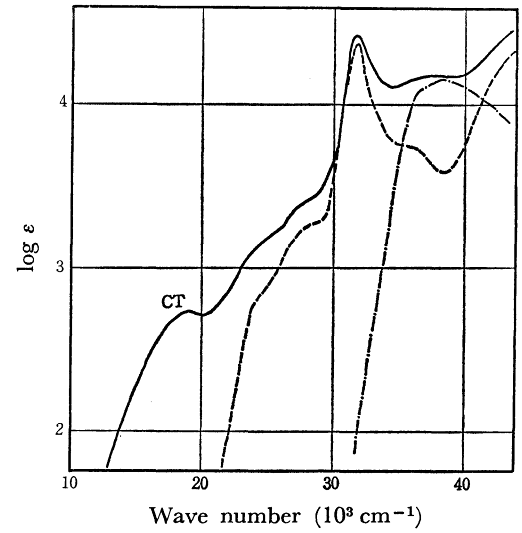

Fig. 3. The charge-transfer band (CT) of toluene $W(CO)_3$-TCNE system in 1,2-dichloroethane at 25 °C.
[toluene $W(CO)_3]_0 = 1.70 \times 10^{-3}$ mol l^{-1}; [TCNE]$_0 = 4.68 \times 10^{-4}$ mol l^{-1}.
——: toluene $W(CO)_3$-TCNE
----: toluene $W(CO)_3$
—·—: TCNE

Table 2. Molar absorption coefficients and complex formation constants of the 1 : 1 molecular complexes of arenetricarbonylchromium, -molybdenum, and -wolfram with TCNE[a)]

Donors	K at 25 °C (l·mol^{-1})	ε_c(max) (l·mol^{-1}·cm^{-1})
$C_6H_5CH_3Cr(CO)_3$	661	520
o-$C_6H_4(CH_3)_2Cr(CO)_3$	952	667
m-$C_6H_4(CH_3)_2Cr(CO)_3$	504	482
p-$C_6H_4(CH_3)_2Cr(CO)_3$	240	616
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	686	703
$C_6H_5CH_3Mo(CO)_3$	20400	5220
o-$C_6H_4(CH_3)_2Mo(CO)_3$	20100	5070
m-$C_6H_4(CH_3)_2Mo(CO)_3$	6810	5250
p-$C_6H_4(CH_3)_2Mo(CO)_3$	11200	5120
1,3,5-$C_6H_3(CH_3)_3Mo(CO)_3$	1110	4740
$C_6H_5CH_3W(CO)_3$	657	3960
p-$C_6H_4(CH_3)_2W(CO)_3$	468	3510

a) Quantitative values were not obtained for 1,3,5-$C_6H_3(CH_3)_3W(CO)_3$.

The stretching frequencies of coordinated carbonyl ($\tilde{\nu}_{CO}$) of arenetricarbonylchromium, -molybdenum and -wolfram in 1,2-$C_2H_4Cl_2$ are also presented in Table 3. An increase in the number of methyl groups in the coordinated arene gives rise to a decrease in the CO-stretching frequency, which indicates an enhancement of the back-donation of metal dπ electron toward coordinated carbonyl groups. For the same arene, the CO-stretching frequency shows a shift toward lower frequency in the order W>Mo>Cr. The NMR signals of methyl-proton presented in Table 4 also support an enhanced charge-transfer from coordinated arene to carbonyl groups in the order W>Mo>Cr.

TABLE 3. THE CHARGE-TRANSFER EXCITATION ENERGIES ($h\nu_{CT}$) IN THE TCNE MOLECULAR COMPLEXES, AND THE IONIZATION POTENTIALS (I_p) AND CO-STRETCHING FREQUENCIES ($\tilde{\nu}_{CO}$) OF THE ARENETRICARBONYLCHROMIUM, -MOLYBDENUM AND -WOLFRAM

Arene metal tricarbonyls	$h\nu_{CT}$ (kK)	I_p (eV)	$\tilde{\nu}_{CO}$ in 1,2-$C_2H_4Cl_2$ (cm^{-1})
$C_6H_5CH_3Cr(CO)_3$	13.9	7.40	1965
o-$C_6H_4(CH_3)_2Cr(CO)_3$	13.9	7.42	1962
m-$C_6H_4(CH_3)_2Cr(CO)_3$	14.0	7.43	1962
p-$C_6H_4(CH_3)_2Cr(CO)_3$	14.2	7.46	1960
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	14.0	7.43	1958
$C_6H_5CH_3Mo(CO)_3$	18.5	8.13	1964
o-$C_6H_4(CH_3)_2Mo(CO)_3$	18.6	8.14	1960
m-$C_6H_4(CH_3)_2Mo(CO)_3$	18.6	8.14	1961
p-$C_6H_4(CH_3)_2Mo(CO)_3$	18.7	8.15	1959
1,3,5-$C_6H_3(CH_3)_3Mo(CO)_3$	18.7	8.15	1957
$C_6H_5CH_3W(CO)_3$	18.6	8.14	1962
p-$C_6H_4(CH_3)_2W(CO)_3$	18.5	8.13	1959
1,3,5-$C_6H_3(CH_3)_3W(CO)_3$	18.6	8.14	1955
Arenes		I_p[a] (eV)	
$C_6H_5CH_3$		8.90	
o-$C_6H_4(CH_3)_2$		8.70	
m-$C_6H_4(CH_3)_2$		8.69	
p-$C_6H_4(CH_3)_2$		8.52	
1,3,5-$C_6H_3(CH_3)_3$		8.52	

a) Ref. 18.

TABLE 4. THE ^{1}H-CHEMICAL SHIFTS OF ARENETRICARBONYLCHROMIUM, -MOLYBDENUM, AND -WOLFRAM IN 1,2-DICHLOROETHANE

	Phenyl-H (ppm)	Methyl-H (ppm)	Ref.
$C_6H_5CH_3$	7.18	2.33	b)
$C_6H_5CH_3Cr(CO)_3$	5.21[a]	2.18	b)
$C_6H_5CH_3Mo(CO)_3$	5.48[a]	2.24	c)
$C_6H_5CH_3W(CO)_3$	5.31[a]	2.42	c)
p-$C_6H_4(CH_3)_2$	7.07	2.28	b)
p-$C_6H_4(CH_3)_2Cr(CO)_3$	5.23	2.12	b)
p-$C_6H_4(CH_3)_2Mo(CO)_3$	5.58	2.17	c)
p-$C_6H_4(CH_3)_2W(CO)_3$	5.42	2.32	c)
1,3,5-$C_6H_3(CH_3)_3$	6.77	2.25	b)
1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$	4.90	2.20	b)
1,3,5-$C_6H_3(CH_3)_3Mo(CO)_3$	5.23	2.25	c)
1,3,5-$C_6H_3(CH_3)_3W(CO)_3$	5.10	2.45	c)

a) Center of gravity of the multiplet. b) Ref. 19. In Ref. 19, the NMR peaks in deuterochloroform were given. c) Ref. 20. In Ref. 20, no details of the observation were presented. However the plots given in a graph of the chemical shifts of protons in the complexes are in good agreement with those observed in the present work.

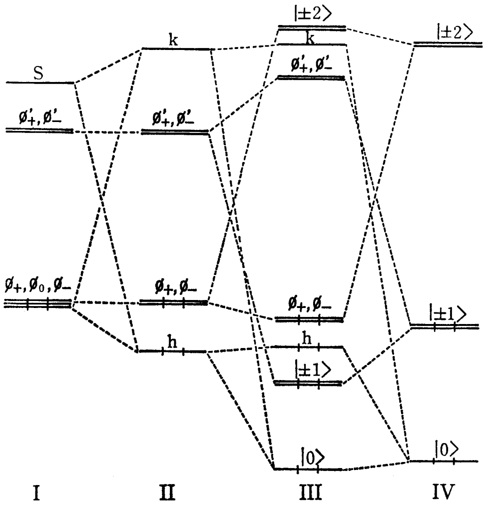

Fig. 4. The energy levels of the arene metal tricarbonyls (schematic).

I: The outer orbitals of the central metal.
II: The ϕ_0 and s orbitals are hybridized.
III: The molecular orbitals formed (Each molecular orbital is characterized by its predominant component).
IV: The π-orbitals of arene.

An upfield shift of phenyl-proton observed in the coordinated arenes arises from a quenching of the ring current upon the formation of molecular orbitals between the central metal atom and its coordinated arene. This effect is enhanced in the order Cr>W>Mo. Such an upfield shift has been observed also in the ^{13}C NMR of ring carbons of the corresponding mesitylene metal tricarbonyls.[21]

Since an increase in the charge density on carbonyl groups in arenetricarbonylmolybdenum and -wolfram causes no enhancement of the molecular-complex formation with electron acceptor, the molecular-complex formation cannot be attributed to a charge-transfer interaction between the carbonyl groups and the acceptor. Arenetricarbonylchromium forms a molecular complex with 1,3,5-TNB in "face-to-face" stack of the counter benzene rings, and thus an increase in the intramolecular charge migration from arene to carbonyl groups in arenetricarbonylmolybdenum and -wolfram inhibits the formation of the 1,3,5-TNB molecular complexes.

An increase in the number of methyl groups in coordinated arene promotes the intramolecular charge migration. However, the ionization potential of arene metal tricarbonyls in the TCNE molecular complexes is almost independent of the methyl substitutions. This indicates that the molecular orbital involved in an intermolecular charge transfer arising from the formation of TCNE molecular complexes is different from the molecular orbital participating in the intramolecular charge migration from coordinated arene to carbonyl groups.

The antibonding molecular orbitals predominantly localized on metal d orbitals are given by

$$\phi_+ = -\frac{1}{\sqrt{3}}\{\sqrt{2}\,|d_{-2}\rangle + |d_{+1}\rangle\}$$

$$\phi_- = \frac{1}{\sqrt{3}}\{\sqrt{2}\,|d_{+2}\rangle - |d_{-1}\rangle\}$$

$$\phi_0 = |d_0\rangle$$

$$\phi_+' = -\frac{1}{\sqrt{3}}\{|d_{-2}> - \sqrt{2}|d_{+1}>\}$$

$$\phi_-' = \frac{1}{\sqrt{3}}\{|d_{+2}> + \sqrt{2}|d_{-1}>\},$$

where $|d_0>$, $|d_{\pm 1}>$ and $|d_{\pm 2}>$ are the basis set for C_3 symmetry axis. By the ligand field of carbonyl groups, ϕ_+, ϕ_- and ϕ_0 are stabilized by $2\varepsilon_\pi$ for π back-donation while ϕ_+' and ϕ_-' are destabilized by $\varepsilon_\sigma 3/2$ for σ donation. Thus a splitting between (ϕ_+, ϕ_-, ϕ_0) and (ϕ_+', ϕ_-') is $(3/2\varepsilon_\sigma+2\varepsilon_\pi)$, which is approximately a half of the ligand field splitting in the corresponding metal hexacarbonyl. The molecular orbitals formed in the arene metal tricarbonyl are shown in a schematic fashion as in Fig. 4.

The top filled degenerate molecularo rbital pair of benzene is $|\pm 1>$ and the lowest vacant degenerate molecular orbital pair is $|\pm 2>$. Thus $|d_{\pm 1}>$ can accept an electronic charge from $|\pm 1>$, and $|d_{\pm 2}>$ can donate an electronic charge into $|\pm 2>$. Since the overlap $<d_{\pm 1}|\pm 1>$ is greater than $<d_{\pm 2}|\pm 2>$, a charge transfer from $|\pm 1>$ toward $|d_{\pm 1}>$ is predominant. 1,3,5-TNB can accept a dπ-electronic charge in the $|\pm 2>$ orbital of the coordinated arene in the chromium derivatives. The methyl-proton signal exhibits an upfield shift in the chromium and molybdenum derivatives while it shows a downfield shift in the wolfram derivatives. This indicates that a charge transfer from $|\pm 1>$ to $|d_{\pm 1}>$ is exclusive in the wolfram derivatives while the charge transfer from $|d_{\pm 2}>$ to $|\pm 2>$ cannot be eliminated in the chromium and molybdenum derivatives. The resultant intramolecular charge migration from coordinated arene to carbonyl groups is enhanced in the order W>Mo>Cr as revealed by the CO-stretching frequency. Since an electronic charge in $|\pm 1>$ of the coordinated arene is transferred into $|d_{\pm 1}>$ of the central metal, the coordinated arene displays chemical properties which the corresponding free arene can exhibit only when substituted by more electron-withdrawing groups. The orbital ϕ_0 is not directly participating in the intramolecular charge migration, and thus less depends upon methyl substitutions in the coordinated arene. The energy of ϕ_0, however, is stabilized as a result of the countercurrent intramolecular charge transfers in the case of the chromium and molybdenum derivatives while destabilized for a one-way intramolecular charge transfer from arene to metal in the case of the wolfram derivatives. In fact, the observed ionization potentials of arene metal tricarbonyls in their TCNE molecular complexes were 7.4 eV, 8.1 eV and 8.1 eV for chromium, molybdenum and wolfram, respectively (Table 3), while the dπ-ionization potentials of CrI and MoI are estimated as 3.97 eV and 4.92 eV and are lower than 8.46 eV of WI.$^{22)}$

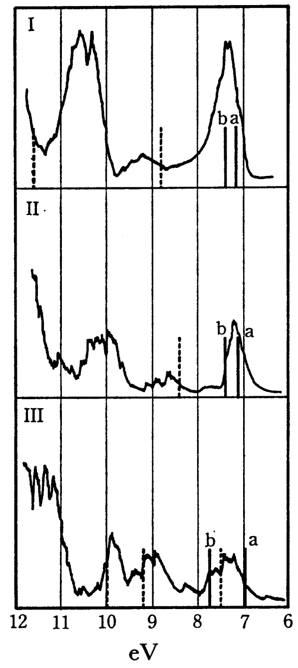

Fig. 5. The He(584 Å) photoelectron spectra of toluene $Cr(CO)_3$, mesitylene $Cr(CO)_3$ and dimethylaniline $Cr(CO)_3$.

I: toluene $Cr(CO)_3$
II: mesitylene $Cr(CO)_3$
III: dimethylaniline $Cr(CO)_3$
——: the ionization potentials of the metal complex determined by the charge-transfer excitation energies in the molcular complexes with 1,3,5-TNB (a) and TCNE (b).
……: the ionization potentials of the corresponding free arenes.

(The values for toluene and dimethylaniline were directly observed by Turner and his coworkers$^{25)}$ and the value for mesitylene was determined by Watanabe.$^{26)}$)

The oxidation state of the central metal atom in the arene metal tricarbonyls is zero, and thus the energy of 4s orbital should be comparable to that of 3d orbital.$^{23)}$ Although the σ bond formation between metal and carbonyl groups raises the energy of 4s orbital, a participation of 4s orbital in the outer-shell electronic structure of arene metal tricarbonyl could be sizable.$^{24)}$ A mixing between ϕ_0 and 4s gives rise to an extra stabilization of the occupied counterpart orbital, which extends in a space between coordinated arene and carbonyl groups. TCNE accepts an electronic charge of this occupied hybrid orbital upon molecular-complex formation.

Figure 5 shows the He (584 Å) photoelectron spectra of toluene $Cr(CO)_3$, mesitylene $Cr(CO)_3$, and dimethylaniline $Cr(CO)_3$. The lowest ionization is attributed to an electron detachment from the filled molecular orbital predominantly localized on the metal d orbitals. A splitting of d orbitals $\phi_\pm$ and ϕ_0 was observed, although a more resolved splitting of d orbitals in some other transition-metal sandwich complexes was recently reported.$^{27,28)}$ The spectrum also indicates that the top filled orbitals of the coordinated arene are more stabilized than those of the corresponding free arene.

Methyl substitutions in the coordinated arenes do not change the ionization potentials of arene metal tricarbonyls, whereas the substitutions reduce the stability of the molecular complexes with TCNE. This might be due to a steric hindrance of the methyl groups introduced to the coordinated arene. The molecular complexes with TCNE are the most stabilized in the molybdenum derivatives, although the intramolecular charge migration increases in the order W>Mo>Cr and the ionization potentials of the molybdenum and wolfram derivatives are almost equal. This should arise from a high charge density on the molybdenum occupied hybrid orbital.

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