was filtered under suction and dried under oil-pump vacuum. Recrystallization of this crude product from acetone at 0° C gave colorless crystals of **16.**

Preparation of Bis(toluene-3,4-dithiolato)germanium(IV) (4). A solution of germanium tetrachloride (0.642 **g,** 3 mmol) in benzene (10 mL) was added dropwise under vigorous stirring to a solution of toluene-3,4-dithiol (0.94 **g,** 6 mmol) and triethylamine (1.22 **g,** 12 mmol) in benzene (50 mL) at room temperature. A curdy white precipitate formed, and the color of the reaction mixture turned yellow. The resulting reaction mixture was heated under reflux for 1 h to obtain a tan solution containing an insoluble white precipitate. Evaporation of solvent from the reaction mixture gave a light purple crystalline residue, which was treated with water (50 mL) to dissolve the triethylammonium chloride byproduct. The water-insoluble crystalline precipitate left behind was filtered under suction and air-dried to obtain an almost pure sample of **bis(toluene-3,4-dithiolato)germanium(IV) (4)** (1.2 9). *An* analytically pure sample of **4** was prepared as follows: To a suspension of the crude product of 4 in acetonitrile at 81 °C was added tetraethylammonium chloride in small amounts until a clear orange solution was obtained. The solution was filtered hot to remove traces of suspended material. When the solution was cooled to room temperature, needle-shaped crystals of bis(toluene-3,4-dithiolato)germanium(IV) (4) were obtained; mp 200-201 °C (lit.²⁹

mp 195-196 °C). Anal. Calcd for C₁₄H₁₂S₄Ge: C, 44.12; H, 3.17. Found: C, 44.21; H, 2.93.

Preparation of Methyltriphenylphosphonium Fluorobis(4-methylbenzene-1,2-dithiolato)germanate, $[Ph_3PMe]$ $((F)Ge(C_7H_6S_2)_2]$ (19) . Ge(tdt)₂ (4) $(0.38 \text{ g}, 1 \text{ mmol})$ and $KF-2H_2O$ $(0.19 \text{ g}, 2 \text{ mmol})$ were suspended in a solution of **methyltriphenylphosphonium** bromide (0.36 **g,** 1 mmol) in acetonitrile (50 mL). The resulting heterogeneous reaction mixture was heated under reflux for 3 h to obtain a yellow solution. The reaction mixture was cooled to room temperature and filtered to remove the insoluble potassium halide. The filtrate was concentrated (10 mL) and cooled to $0 °C$ to obtain pale yellow crystals of $[Ph_3PMe] [(F)Ge(C_7H_6S_2)_2]$ (19).

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Registry No. 2, 76375-54-7; **4,** 79084-23-4; **5,** 79084-27-8; **7,** 79084-28-9; **8,** 76375-58-1; *9,* 76375-56-9; **10,** 79084-29-0; **11,** 79084-30-3; **14,** 79084-32-5; **15,** 79084-34-7; **16,** 79084-36-9; **18,** 79084-38-1; **19,** 79084-39-2; GeCI4, 10038-98-9.

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Molecular Complex Formation of Tricarbonyl(~6-[2.2]paracyclophane)chromium and 1,3,5-Trinitrobenzene

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 $Triachonyl(\eta^6-[2.2]paracyclophane)chromium (([2.2]paracyclophane)Cr(CO)₃) forms a charge-transfer complex with 1,3,5-trinitrobenzene (1,3,5-TNB) in 1,2-dichloroethane. The ionization potential of ([2.2]paracyclophane)Cr(CO)₃ was$ determined to be 7.2 eV from the observed intermolecular charge-transfer transition energy. The value was close to those obtained for the usual chromium tricarbonyl complexes with η^6 -coordinated benzene derivatives. In solution, the acceptor molecule **is** more likely to interact directly with the chromium d orbital lobes by sitting beneath the base of the pyramid formed by three metal-carbonyl bonds rather than by stacking on the aromatic ring as in the usual aromatic molecular complexes. This is also supported by the fact that some other chromium-carbonyl complexes without an η^6 -coordinated aromatic ring also exhibit spectral evidence of complex formation with 1,3,5-TNB.

 $(\eta^6$ -Arene)tricarbonylchromium ((arene)Cr(CO)₃) forms a charge-transfer complex with electron acceptors such as 1,3,5-trinitrobenzene (1,3,5-TNB) and tetracyanoethylene. $1-3$ It has been assumed that the bulky acceptor 1,3,5-TNB forms a molecular complex by a charge-transfer interaction of 1,3,5-TNB with the central chromium through the η^6 -coordinated benzene ring in a "face-to-face" stack, which has been found in the molecular complexes of 1,3,5-TNB and aromatic compounds.⁴ A study by X -ray crystallography of the molecular complex of $(\eta^6$ -anisole)Cr(CO)₃ and 1,3,5-TNB has revealed a structure of "face-to-face" stacking of the benzene rings of coordinated anisole and 1,3,5-TNB. In the crystal, however, a molecule of (anisole) $Cr(CO)$ ₁ is sandwiched between two 1,3,5-TNB molecules. This implies that 1,3,5-TNB molecules may accept a charge of the chromium $d\pi$ orbitals not only through the "face-to-face" stack of the benzene rings but also through a direct interaction with the chromium or-

(1) Huttner, G.; **Fischer, E. 0.; Fischer, R. D.; Carter, 0. L.; McPhail, A. T.; Sim,** *G.* **A.** *J. Organomel. Chem.* **1966,** *6,* **288.**

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- **(2) Kobayashi, H.; Kobayashi, M.; Kaizu,** *Y. Bull. Chem.* **SOC.** *Jpn.* **1973,** *46,* **3109.**
- **(3) Kobayashi, H.; Kobayashi, M.; Kaizu,** *Y. Bull. Chem.* **SOC.** *Jpn.* **1975,** *48,* **1222.**
- **(4) Carter, 0. L.; McPhail, A. T.; Sim,** G. **A.** *J. Chem.* **SOC.** *A* **1966, 822.**

bitals extending between three metal-carbonyl bonds. In fact, the distance (4.70 **A)** between chromium and the center of the 1,3,5-TNB in contact with carbonyl groups is shorter than the distance (5.14 **A)** between chromium and the 1,3,5-TNB located on η^6 -coordinated arene (Figure 1). Since the tricarbonylchromium group is electron withdrawing, it confers on the coordinated arene a higher acidity and a higher susceptibility to nucleophilic substitution but a lower susceptibility to electrophilic substitution.⁵⁻⁹ In fact, a greater dipole moment observed indicates an appreciable migration of the arene π electron into the tricarbonylchromium group.¹⁰ $(\text{arene})Cr(CO)$ ₃ forms a molecular complex with electron acceptors rather than electron donors. The ionization potential of $(\text{aree})Cr(CO)$, can be evaluated from the charge-transfer excitation energy in the molecular complexes with electron

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- **(6) Nicholls, B.; Whiting, M. C.** *J. Chem. SOC.* **1959, 551. (7) Riemschneider, R.; Becker, 0.; Franz, K.** *Monatsh. Chem.* **1959,** *90,* **571.**
- **(8) Brown, D. A.; Raju, J. R.** *J. Chem.* **SOC.** *A* **1966, 40.**
- **(9) Semmelhack, M. F. "New Applications** of **Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; p 361.**
- **(10) Fischer, E. 0.; Schreiner, S.** *Chem. Ber.* **1959,** *92,* **938.**

⁽⁵⁾ Fisher, E. *0.;* **Ofele, L.; Essler, H.; Frohlich, W.; Mortensen, J. P.; Semmlinger, W.** *Chem. Ber.* **1958,** *91,* **2763.**

$$
\bigcirc(C,C;N\;,\; \bigcirc(C)\;,\; \bigcirc(C;C\;)
$$

Figure 1. Geometry of the molecular complex of (anisole)Cr(CO), and 1,3,5-TNB (drawn by use of the data given in ref **4).**

acceptors. An electron detachment of $(\text{are}^{\text{ne}})Cr(CO)$ ₃ occurs upon charge-transfer excitation from one of the chromium filled $d\pi$ orbitals rather than from the highest occupied arene *r* orbitals. In a previous paper, we assumed that the acceptor 1,3,5-TNB was in contact with the η^6 -coordinated benzene.² Fischer et al. also assumed that the "face-to-face" stack of the benzene rings of 1,3,5-TNB and coordinated arene found in the crystals is preserved even in solution.' In this paper, we present evidence that the charge-transfer interaction of 1,3,5-TNB with the central chromium atom of η^6 -arene-tricarbonyl complexes arises in a highly charge-populated region between the chromium-carbonyl bonds.

Experimental Section

Chromium carbonyls, except pentacarbonyl(trimethy1 phosphine)chromium $((H_3C)_3PCr(CO)_5)$, were prepared by refluxing hexacarbonylchromium (Strem Chemicals Inc.) with the corresponding aromatic derivatives in appropriate solvents under dry nitrogen at mosphere.^{5,6,11-14} The refluxed mixtures were filtered, and the filtrates were condensed by vacuum distillation. The residue was purified by recrystallization. $(H_3C)_3PCr(CO)_5$ was prepared from $(H_3C)_3P-$ AgNO₃ and $(H_3C_2)_4N[CrCl(CO)_5]$ in dichloromethane.¹⁵ The product was purified twice by sublimation. The complexes were identified by elemental analyses and IR spectra.

1,3,5-TNB (Tokyo Kasei Co.) was recrystallized from ethanol and then from carbon tetrachloride. The solvent used for absorption measurements was 1,2-dichIoroethane (Wako Pure Chemical Co.) purified and dried by the usual procedurei6 and saturated with dry nitrogen gas by bubbling just before use.

Spectral Measurements. Infrared spectra of (arene)tricarbonylchromium in 1,2-dichIoroethane and in KBr disks were taken on a Hitachi spectrometer, Model EPLG3. NMR spectra of the complexes in CDCI₃ were recorded on a Varian spectrometer, Model T-60 (60 MHz), and/or a JEOL spectrometer, JNM-PS-100 (100 MHz). Tetramethylsilane was used as an internal standard. **I3C** NMR spectra of the complexes in 1,2-dichloroethane were taken on a JEOL spectrometer, Model JNM-FX60 (15 MHz).

Electronic absorption spectra were recorded on a Shimadzu au- tomatic recording spectrophotometer, Model MPS-50. The cell compartment was maintained at a constant temperature by circulating water regulated by a Haake thermostat, Model FK.

- (1 1) Fischer, E. *0.;* Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959,** *92,* 3214.
- (12) Cram, D. J.; Wilkinson, D. I. *J. Am. Chem. SOC.* **1960,** *82,* 5721.
- (13) Zingales, F.; Canziani, F. *Gazz. Chim. Ifal.* **1962,** *92,* 343.
- (14) Magee, T. A.; Matthews, C. N.; Wang, T. **S.;** Wotiz, J. H. *J. Am. Chem. SOC.* **1961, 83,** 3200.
- (15) Connor, J. A.; **Jones,** E. M.; McEwen, G. K. *J. Organomef. Chem.* **1972,** 43, 357.
- (16) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

Determinations of the Complex Formation Comtants. The formation of molecular complexes was detected by observation of a chargetransfer absorption band. Since the charge-transfer band of the molecular complex overlaps the absorption bands due to free donor and acceptor, the observed absorbance $E(\tilde{v})$ at a given wavenumber $\tilde{\nu}$ is given by

$$
(E(\tilde{\nu}))/l = (\epsilon_{\text{DA}}(\tilde{\nu}))[D \cdot A] + (\epsilon_A(\tilde{\nu}))[A] + (\epsilon_D(\tilde{\nu}))[D] \quad (1)
$$

where ϵ denotes the molar absorption coefficient, l is the optical path length, brackets denote concentration, and D, A, and D-A imply donor, acceptor, and molecular complex, respectively. We define $\epsilon_{CT}(\tilde{\nu})$ as

$$
\epsilon_{\text{CT}}(\tilde{\nu}) \equiv \epsilon_{\text{D-A}}(\tilde{\nu}) - \epsilon_{\text{D}}(\tilde{\nu}) - \epsilon_{\text{A}}(\tilde{\nu}) \tag{2}
$$

Then (1) is rewritten as

$$
(E(\tilde{v}))/l = (\epsilon_{\text{D}}(\tilde{v}))[D]_0 + (\epsilon_{\text{A}}(\tilde{v}))[A]_0 + (\epsilon_{\text{CT}}(\tilde{v}))[D\cdot A]
$$
 (3)

Here $\epsilon_{CT}(\tilde{\nu})$ arises from the intermolecular charge-transfer band, since $\epsilon_{DA}(\tilde{v})$ is assumed to be a superposition of $\epsilon_D(\tilde{v})$, $\epsilon_A(\tilde{v})$, and $\epsilon_{CT}(\tilde{v})$ in the case of weak interactions such as in molecular complex formations. Thus the shape function of the charge-transfer band $f(\tilde{\nu})$ is given as

$$
f(\tilde{\nu}) = (\epsilon_{\text{CT}}(\tilde{\nu}))[D \cdot A] = (E(\tilde{\nu}))/l - (\epsilon_{\text{D}}(\tilde{\nu}))[D]_0 - (\epsilon_A(\tilde{\nu}))[A]_0
$$
 (4)

where $\epsilon_{\mathbf{D}}(\tilde{\nu})$, $\epsilon_{\mathbf{A}}(\tilde{\nu})$, *I*, [D]₀, and [A]₀ are experimentally known and $E(\tilde{\nu})$ is measured. In the case of an exclusive formation of the 1:1 complex, the shape of log $(f(\tilde{\nu}))$ does not vary with $[D]_0$ and $[A]_0$.

The formation constant K of a 1:1 complex D-A is given by

$$
K = \frac{[D \cdot A]}{[A][D]} = \frac{[D \cdot A]}{([A]_0 - [D \cdot A])([D]_0 - [D \cdot A])}
$$
(5)

From **(4)** and *(9,* it follows that

$$
\frac{[\mathbf{D}]_0[\mathbf{A}]_0}{f(\tilde{\mathbf{p}})} = \left\{ [\mathbf{D}]_0 + [\mathbf{A}]_0 - \frac{f(\tilde{\mathbf{p}})}{\epsilon_{\text{CT}}(\tilde{\mathbf{p}})} \right\} \frac{1}{\epsilon_{\text{CT}}(\tilde{\mathbf{p}})} + \frac{1}{K(\epsilon_{\text{CT}}(\tilde{\mathbf{p}}))} \tag{6}
$$

In the present work, the initial concentrations were set so that $[A]_0$ $> [D]_0 \gg [D-A] (= (f(\tilde{\nu}))/(\epsilon_{CT}(\tilde{\nu})))$, and thus the term $(f(\tilde{\nu}))/(\epsilon_{CT}(\tilde{\nu}))$ in (6) can be ignored. Plots of $[D]_0[A]_0/(\tilde{\tau})$ vs. $([D]_0 + [A]_0)$ give a straight line. K and $\epsilon_{CT}(\tilde{\tau})$ can be determined from the slope of the straight line $(1/(\epsilon_{CT}(\tilde{\nu})))$ and the intercept $(1/K(\epsilon_{CT}(\tilde{\nu})))$. It is noted that neglect of $\epsilon_D(\tilde{\nu})$ and $\epsilon_A(\tilde{\nu})$ as employed in our previous work^{2,3} resulted in an appreciable overestimate of K 's.

Thermodynamic data of the molecular complex formations *AH* and ΔS were obtained by measurements of *K* for a variety of temperatures in the -10 to +25 °C range. The slope of the plots of ln K vs. $1/T$ gives $-\Delta H/R$, and the intercept gives $\Delta S/R$.

The ionization potentials I_n of the donor molecules can be estimated from the charge-transfer transition energies in the molecular complexes with a common acceptor by means of an empirical relationship

$$
hv_{\rm CT} = I_{\rm p} - C_1 + C_2/(I_{\rm p} - C_1) \tag{7}
$$

where hv_{CT} is the transition energy in units of electronvolts at the maximum of $\epsilon_{CT}(\bar{v})$ and C_1 and C_2 depend only on the common acceptor. In this work, it was assumed that $C_1 = 5.00$ eV and $C_2 =$ 0.70 eV², which were obtained for a series of the molecular complexes of 1,3,5-TNB.I7

Results and Discussion

For a variety of initial concentrations of $(\text{arene})Cr(CO)$ ₃ and 1,3,5-TNB in 1,2-dichloroethane, log $(f(\tilde{\nu}))$ was plotted against $\tilde{\nu}$. Since no shape change of log $(f(\tilde{\nu}))$ was observed, as exclusive formation of 1:l molecular complex was concluded. Figure 2A shows the plots of $[D]_0[A]_0/(f(\tilde{\nu}))$ against $([D]_0 + [A]_0)$. The slope of the plots $(1/(\epsilon_{CT}(\tilde{\nu})))$ was practically constant for a variety of temperatures, whereas the intercept of the plots $(1/K(\epsilon_{CT}(\tilde{\nu})))$ was temperature dependent. With the assumption that $\epsilon_{CT}(\tilde{\nu})$ is temperature independent, the formation constants K for $([2.2]$ paracyclophane) $Cr(CO)$, and 1,3,5-TNB were determined to be as follows: 0.260 (25 "C), 0.299 (10 "C), 0.332 **(-4.5** "C), and 0.367 (-10.5 °C). The molar absorption coefficient of the molecular complex $\epsilon_{CT}(\tilde{v})$ was evaluated as 1000 at the absorption maximum. Figure 2B shows the plot of In *K* against $1/T$.

⁽¹⁷⁾ Briegleb, G.; Czekalla, J. *Z.* Elekfrorhem. **1959, 63,** 6.

Table I. Thermodynamic Data of the Molecular Complexes Formations with 1,3,5-TNB, the Energies and Intensities of the Charge-Transfer Band of the Molecular Complexes, and the Ionization Potentials of (arene)Cr(CO), Evaluated from the Charge-Transfer Transition Energies

compd	K (at 25 °C). L/mol	$-\Delta H$, kcal/ mol	$-\Delta S$, eu	$hv_{\text{CT}},$ 10^3 cm ⁻¹	$\epsilon_{\rm max}$ L/(mol·cm)	$I_{\rm p}$, eV
(benzene) $Cr(CO)$,				22.0		7.43
$(toluene)Cr(CO)$,	0.42	1.02	5.16	21.8	900	7.41
$(mesitylene)Cr(CO)$,	0.31	1.16	6.20	21.4	1000	7.36
$(hexamethylbenzene)Cr(CO)$,	0.19	1.23	7.42	20.7	1500	7.26
$(dipheny)Cr(CO)$,	0.28	1.27	6.78	20.3	950	7.20
(naphthalene) $Cr(\overline{CO})_3$				20.0		7.16
$([2.2]$ paracyclophane) $Cr(CO)$	0.26	1.43	7.48	20.3	1000	7.20
$(1, 2-bis(diphenylphosphino)ethane)Cr(CO)4$	0.27	0.87	5.55	22.1	1100	7.44
$(\text{triphenylphosphine})Cr(CO)_{s}$		0.90		23.2		7.62
$(\text{trimethylphosphine})Cr(CO)$.	0.19	1.03	6.9	23.7	800	7.67

Figure 2. Plots of (A) $[D]_0[A]_0/(\mathcal{F}(v))$ vs. $([D]_0 + [A]_0)$ and (B) ln K vs. $1/T$: O, 25 °C; 0, 10 °C; 0, -4.5 °C; Θ , -10.5 °C. $[(2.2]$ paracyclophane)Cr(CO)₃], mol·L⁻¹: (I) 3.07 × 10⁻³, (II) 3.10 \times 10⁻³, (III) 3.16 × 10⁻³, (IV) 3.19 × 10⁻³, (V) 3.24 × 10⁻³,
[1,3,5-TNB], mol-L⁻¹: (I) 0.414, (II) 0.338, (III) 0.207, (IV) 0.131, (V) 0.105.

Table I summarizes the values obtained by the present work including the equilibrium constants at $25 \text{ °C } (K)$, the enthalpies and entropies of complex formation (ΔH , ΔS), the transition energies and absorption coefficients of the molecular-complex charge-transfer band (hv_{CT} , ϵ_{max}), and the ion-

ization potentials of $(\eta^6$ -arene)Cr(CO)₃ (I_p).
Figure 3 shows the plots of $h\nu_{CT}$ vs. $-\Delta H$. An increase in
the electron-donating power of (arene)Cr(CO)₃ gives rise to an enhancement of exothermic complex formation. Figure 3 also indicates that the molecular interaction depends mainly on the diagonal energies rather than the off-diagonal terms, and thus the geometry of the interactions is similar from complex to complex. This is also supported by a compensation effect between ΔH and ΔS shown in Figure 4.

The ionization potential of $(\eta^6$ -benzene)Cr(CO)₃ obtained from $h\nu_{CT}$ is 7.42 \pm 0.04 eV. This is in good agreement with the value 7.4 eV determined by photoelectron spectroscopy.¹⁸ The ionization arises from an electron detachment from the highest filled d orbitals, since the ionization potential of the coordinated arene becomes higher for a stabilization of the

Figure 3. Plots of hv_{CT} vs. $-\Delta H$: (1) (toluene)Cr(CO)₃; (2) (mesitylene)Cr(CO)₃; (3) (hexamethylbenzene)Cr(CO)₃; (4) (diphenyl)Cr(CO)₃; (5) ([2.2] paracyclophane)Cr(CO)₃; (6) (1,2bis(diphenylphosphino)ethane) $Cr(CO)₄$; (7) (triphenylphosphine)- $Cr(CO)_{5}$, (8) (trimethylphosphine) $Cr(CO)_{5}$.

Figure 4. Compensation effect between ΔH and ΔS (at 298 K): (1) (toluene) $Cr(CO)_3$; (2) (mesitylene) $Cr(CO)_3$; (3) (hexamethylbenzene) $Cr(CO)_3$; (4) (diphenyl) $Cr(CO)_3$; (5) ([2.2]paracyclophane) $Cr(CO)$ ₃.

 (18) Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. Mol. Phys. 1975, 29, 113.

Figure 5. ¹H NMR spectra of ([2.2]paracyclophane)Cr(CO)₃ and [2.2] paracyclophane in CDCl₃ with reference to $(CH_3)_4Si$.

highest filled arene orbitals by interactions between chromium and arene. Guest et al. assigned the peaks of 7.4 and 10.7 eV observed in photoelectron spectroscopy to the ionizations of d electrons and the peaks higher than 12.7 eV to the ionizations of coordinated benzene and carbonyl groups on the basis of ab initio SCMO.'*

The ionization potential of $([2.2]$ paracyclophane) $Cr(CO)$, is close to those obtained for the usual (arene) $Cr(CO)$, complexes with single η^6 -benzene ring. This indicates that a similar interaction of 1,3,5-TNB arises with chromium $d\pi$ orbitals in $([2.2]$ paracyclophane)Cr(CO)₃ as well as in other (arene)- $Cr(CO)$ ₃ complexes. When ([2.2] paracyclophane) $Cr(CO)$ ₃ forms a charge-transfer complex with 1,3,5-TNB, the counterpart 1,3,5-TNB cannot directly interact with the phenylene ring immediately coordinated to the central chromium. Since an electronic interaction between two phenylenes in paracyclophane is crucial, a charge in the highest d orbital can migrate through the outer phenylene. However, it should be less probable that 1,3,5-TNB can accept a sufficient charge of the highest d orbital by such an indirect interaction so as to give the highest value of ΔH among the (arene)Cr(CO), complexes. 'H and 13C NMR spectra of ([2.2]paracyclopyhane)Cr(CO), are shown in Figures 5 and *6,* respectively. The upfield shift occurs only in the phenylene ring directly coordinated to chromium. This indicates that the interaction between chromium and the aromatic ring is rather localized in the ring directly bonded to chromium. Thus 1,3,5-TNB is more likely to accept an electronic charge directly from the highest filled chromium $d\pi$ orbital lobes by contact with the base of the pyramid of these chromium-arbonyl bonds rather than by stacking on the benzene ring as in the usual aromatic molecular complexes. In fact, the ab initio calculation predicts that the highest filled d orbital has a population between chromium-carbonyl bonds but to a lesser extent on η^6 -coordinated benzene in (benzene)Cr(CO)₃.¹⁸ Furthermore, a high charge distribution was observed between the chromiumcarbonyl bonds by high-resolution X-ray and neutron diffractions at 78 K.¹⁹

 $(H₃C)₃PCr(CO)₅$, $(C₆H₅)₃PCr(CO)₅$, and $[(C₆H₅)₂PC H_2CH_2P(C_6H_5)_2]Cr(CO)_4$ also form charge-transfer molecular complexes with 1,3,5-TNB. Table I also includes *K*, ΔH , ΔS , $h\nu_{\text{CT}}$, ϵ_{max} , and I_{p} observed for the carbonyl(phosphine)chromium complexes. The ionization is assigned to an electron detachment from the highest filled d orbital. Photoelectron spectroscopy reveals the ionization potentials of 7.90 and 7.58 eV for $H_3PCr(CO)$ ₅ and $(H_3C)_3PCr(CO)$ ₅, respectively.²⁰

Figure 6. ¹³C NMR spectra of (2.2) paracyclophane)Cr(CO), and [2.2]paracyclophane in 1,2-dichloroethane. Chemical shifts were measured relative to the internal 1,2-dichloroethane solvent resonance: C, CDC13 used as an internal **lock** signal source; D, 1,2-dichloroethane.

The ab initio calculation also predicts a d ionization for the lowest ionization.20 Thus 1,3,5-TNB accepts an electronic charge directly from chromium d orbitals in the carbonyl- (phosphine)chromium complexes. The ionization potentials and the $-\Delta H$ values of complex formation are largely independent of the bulkiness of the substituents and the absence of an aromatic ring in the coordinated phosphine. The interaction of 1,3,5-TNB is possible only in a position somewhere between the coordinated carbonyls rather than through the coordinated phosphine. Since the chromium atom in (arene) $Cr(CO)$, is more electron donating than that of the car**bonyl(phosphine)chromium** complexes, a direct interaction of 1,3,5-TNB with the chromium orbital should be promoted.

 $(\mu$ ^{- $(\eta^{12}$ -[2.2] Paracyclophane)) - bis (tricarbon ylchromium),} which lacks stackable free phenylene, also shows a remarkable enhancement of spectral intensity due to the complex formation with 1,3,5-TNB. Because of the insolubility in 1,2-dichloroethane, it was mixed with 1,3,5-TNB in KBr for spectral measurements. In some cases of the usual $(\eta^6$ -arene)Cr(CO)₃, the charge-transfer band of molecular complex could be detected with the KBr disks. **(Paracyclophane)bis(tricarbo**nylchromium), however, showed only a definite increase of the spectral intensity instead of an absorption peak.

In conclusion, the complex formation of ([2.2]paracyclophane $Cr(CO)$, with $1,3,5$ -TNB studied in the present work provides sound evidence of the direct interaction of 1,3,5-TNB with the chromium orbital of (arene) $Cr(CO)_{3}$.

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Registry No. ([2.2] paracyclophane)Cr(CO)₃·1,3,5-TNB, 78871-17-7; (benzene)Cr(CO)₃.1,3,5-TNB, 12275-73-9; (toluene)Cr-(CO)3.1,3,5-TNB, 12083-25-9; **(mesitylene)Cr(C0)3.1,3,5-TNB,** 12276-57-2; **(hexarnethylben~ene)Cr(C0)~.1,3,5-TNB,** 12277-28-0; **(diphenyl)Cr(CO),*l,3,5-TNB,** 12277-22-4; (naphtha1ene)Cr- (CO)3.1 ,3,5-TNB, 78871- 13-3; **(1,2-bis(diphenylphosphino)** ethane)Cr(CO)₄.1,3,5-TNB, 78871-11-1; (triphenylphosphine)Cr- $(CO)_{5}$ -1,3,5-TNB, 78871-15-5; (trimethylphosphine)Cr(CO) $_{5}$ -1,3,5-TNB, 78871-19-9; (benzene)Cr(CO)₃, 12082-08-5; (toluene)Cr(CO)₃, 12083-24-8; (mesitylene)Cr(CO)₃, 12129-67-8; (hexamethylbenzene)Cr(CO)₃, 12088-11-8; (diphenyl)Cr(CO)₃, 12111-60-3; (naphthalene) Cr(CO)₃, 12110-37-1; ([2.2] paracyclophane) Cr(CO)₃, 41 354-64-7; **(1,2-bi~(diphenylphosphino)ethane)Cr(CO)~,** 29890-04-8; (triphenylphosphine)Cr(CO)₅, 14917-12-5; (trimethylphosphine)- $Cr(CO)$ ₅, 26555-09-9; [2.2] paracyclophane, 1633-22-3.

⁽¹⁹⁾ Rees, *B.;* **Coppens, P.** *Acta Crystallogr. Sect. B.* **1973,** *B29,* **2515. (20)** Higginson, **B. R.;** Lloyd, **D.** R.; Connor, J. **A.;** Hillier, **I.** H. *J. Chem. SOC., Faraday Trans. 2* **1974,** *70,* **1418.**