

Figure 2. Optimized geometries of an intermediate complex (top), the product (bottom), and the transition state (middle) connecting them in the reaction of germaethene with water, obtained at the HF/DZ level.

calculated for the isomerization of silaethene.^{8b}

The Reaction with Water. The optimized geometries of an intermediate complex, the product, and the transition state connecting them are shown in Figure 2. The reaction with water initiates with the formation of a weak complex (1.5 kcal/mol at the HF/DZ+d level and 2.6 kcal/mol at the MP3/DZ level) in a fairly early stage, in which one of the lone pairs of water is oriented for maximum interaction with the π^* orbital of germaethene localized strongly around Ge. The complex is transformed via a four-center-like transition state to the product, $\text{H}_2(\text{OH})\text{Ge}-\text{CH}_3$. A Mulliken population analysis reveals that the attack of water is first nucleophilic and becomes electrophilic as the reaction reaches the transition state. The reaction with water is calculated to be 68.1 (HF/DZ+d) and 61.7 (MP3/DZ) kcal/mol exothermic. Reflecting the large exothermicity, the transition state rather resembles the complex in structure and is "early", as shown in Figure 2. The calculated values for the overall barrier are 15.1 (HF/DZ+d) and 7.4 (MP3/DZ) kcal/mol. These values are essentially comparable to those of 12.0 (HF/DZ+d) and 8.9 (MP3/DZ) kcal/mol for the silaethene reaction with water,⁹ suggesting that germaethene is kinetically as stable as silaethene.

Compared with the value of 68 (HF/4-31G) kcal/mol for the reaction of ethene,¹⁰ the overall barriers for germaethene and silaethene are much smaller. One may consider that the high reactivity of germaethene and silaethene is simply due to their strongly polarized double bonds, as often pointed out.^{1a,b} However, an overall barrier for the $\text{H}_2\text{Si}=\text{SiH}_2 + \text{H}_2\text{O}$ reaction is calculated to be as small as 3.2 (HF/DZ+d) kcal/mol.¹¹ At this point, it is noteworthy that HOMO levels rise in the order $\text{H}_2\text{C}=\text{CH}_2$

$<< \text{H}_2\text{Si}=\text{CH}_2 \leq \text{H}_2\text{Ge}=\text{CH}_2 < \text{H}_2\text{Si}=\text{SiH}_2$, while LUMO levels drop in the same way along the series.¹² This means that in Klopman's terminology¹³ the reactivity of π -bonded group 4B compounds is significantly "frontier controlled", as well as "charge controlled". This finding would be useful for the design of a kinetically more stable germaethene.

Hydrogenation Energy. Finally, an attempt was made to evaluate and compare the energies released upon addition of H_2 to germaethene and silaethene. The hydrogenation energies calculated at the HF/DZ+d level are 65.6 ($\text{H}_2\text{Ge}=\text{CH}_2$) and 67.9 ($\text{H}_2\text{Si}=\text{CH}_2$) kcal/mol, while those at the MP3/DZ level are 48.7 ($\text{H}_2\text{Ge}=\text{CH}_2$) and 49.0 ($\text{H}_2\text{Si}=\text{CH}_2$) kcal/mol.¹⁴ Obviously, these results indicate that germaethene is as stable as silaethene in a thermodynamic sense.

The present work predicts that germaethene resembles silaethene closely in stability and reactivity except the relative stability of the doubly bonded and divalent forms. It is hoped that successful schemes for the synthesis of germaethene are soon devised. We are currently studying the reactivity toward self-dimerization.

Acknowledgment. All calculations were carried out at the Computer Center of the Institute for Molecular Science, using an IMS version of the GAUSSIAN80 series of programs¹⁵.

Registry No. $\text{H}_2\text{Ge}=\text{CH}_2$, 60188-36-5; $\text{H}\ddot{\text{G}}\text{e}-\text{CH}_3$, 78800-76-7; $\text{H}_2(\text{OH})\text{Ge}-\text{CH}_3$, 88181-62-8; H_2O , 7732-18-5.

(12) Nagase, S.; Kudo, T. *J. Mol. Struct.* **1983**, *103*, 35-44 (a special issue of THEOCHEM in honor of Prof. Fukui and his Nobel prize awarded in chemistry).

(13) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223-237. Klopman, G. "Chemical Reactivity and Reaction Paths"; Wiley: New York, 1974; pp 55-165.

(14) The optimized geometries and energies for $\text{H}_3\text{Ge}-\text{CH}_3$ and $\text{H}_3\text{Si}-\text{CH}_3$ are available from the authors on request.

(15) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *10*, 406.

Self-Catalysis in Arene Exchange Reactions of (Arene)tricarboxylchromium Complexes

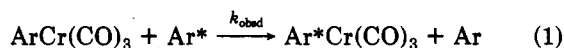
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Summary: The replacement of *p*-xylene from its tricarboxylchromium complex by benzene is catalyzed by (hexamethylbenzene)tricarboxylchromium without the replacement of hexamethylbenzene. This and other observations suggest that the bound carbonyl group acts as a nucleophilic catalyst in arene exchange.

The tricarboxylchromium complexes of substituted benzenes were observed to exchange with ¹⁴C-labeled arene at 140-180 °C by Strohmeier and co-workers.¹



(1) (a) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem.* **1961**, *29*, 339-346. (b) Strohmeier, W.; Muller, R. *Ibid.* **1964**, *40*, 85-95. (c) Strohmeier, W.; Staricco, E. H. *Ibid.* **1963**, *38*, 315-325.

(9) Hanamura, M.; Nagase, S.; Morokuma, K., to be submitted for publication.

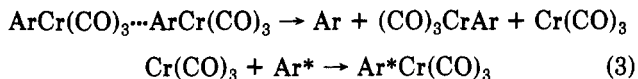
(10) Koizumi, M.; Yamashita, K.; Yamabe, T.; Fukui, K. Abstract of a Symposium on Molecular Structures held in Kyoto, Japan, 1981, pp 768-769.

(11) The subject will be discussed in detail in a future publication by Nagase and Kudo.

The kinetics of these reactions were described by a two-term rate law in which one term is second order in the complex.

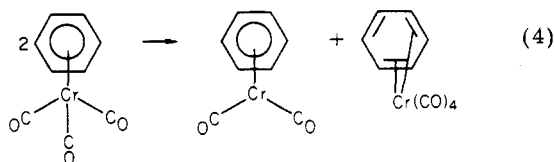
$$\frac{d[\text{Ar}^*\text{Cr}(\text{CO})_3]}{dt} = k_{\text{II}}[\text{ArCr}(\text{CO})_3]^2 + k_{\text{IV}}[\text{ArCr}(\text{CO})_3][\text{Ar}^*] \quad (2)$$

The mechanism proposed for this process, involving simultaneous exchange of two complex molecules (eq 3), has

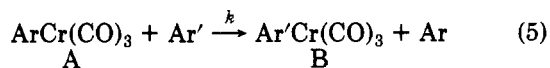


been criticized on general mechanistic² and experimental grounds.^{3,4} For example, Jackson et al.⁵ observed that *cis*- and *trans*-(1-methylindane)tricarbonylchromium isomerizes in the presence but not in the absence of excess ligand.

Mahaffy and Pauson³ suggested the alternative mechanism of eq 4 in which either intermediate could lead to exchange.



The observed rate law (eq 2), in its general application to eq 5, is deceptive. The initial rate method used by



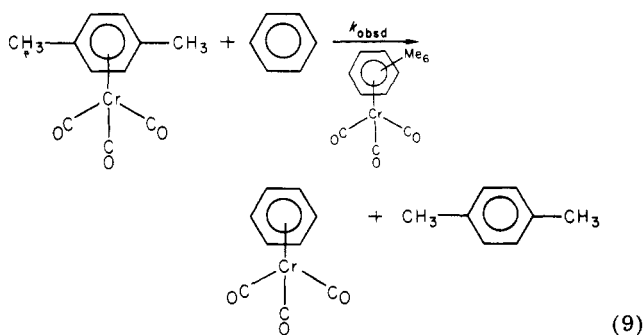
$$\frac{d[\text{Ar}'\text{Cr}(\text{CO})_3]}{dt} = k_{\text{II}}[\text{A}]^2 + k_{\text{IV}}[\text{A}][\text{Ar}'] \quad (6)$$

$$\frac{d[\text{Ar}'\text{Cr}(\text{CO})_3]}{dt} = k_{\text{II}}[\text{A}][\text{A} + \text{B}] + k_{\text{IV}}[\text{A}][\text{Ar}'] \quad (7)$$

Strohmeier does not differentiate between a true bimolecular term (eq 6) and a term in which all chromium carbonyl compounds act as catalysts (eq 7). If the kinetics are actually described by eq 7, then addition of a third, unreactive, complex (C) should lead to eq 8. In this case

$$\frac{d[\text{B}]}{dt} = k_{\text{IV}}[\text{A}][\text{A} + \text{B} + \text{C}] + k_{\text{IV}}[\text{A}][\text{Ar}'] \quad (8)$$

the rate should be proportional to the concentration of C.



(2) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* 1979, 178, 197-216.

(3) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Synop.* 1979, 126; *J. Chem. Res., Miniprint* 1979, 1752-1775.

(4) Zimmerman, C. L.; Shaner, C. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res., Synop.* 1980, 108; *J. Chem. Res., Miniprint* 1979, 1289-1297.

(5) Gracey, D. E. F.; Jackson, W. R.; McMullen, C. H.; Thompson, N. *J. Chem. Soc. B* 1969, 1197-1203.



Figure 1. ¹H NMR spectra of a solution of 0.1 M (*p*-xylene)-Cr(CO)₃ and 0.12 M (hexamethylbenzene)Cr(CO)₃ in benzene at 0, 105, and 208 h of heating at 170 °C. In addition to resonances of reactive species (see text), peaks at 1.4 and 1.8 ppm represent cyclohexane and (hexamethylbenzene)tricarbonylchromium, respectively.

We have studied the kinetics of displacement of *p*-xylene from (*p*-xylene)tricarbonylchromium by benzene in the presence of (hexamethylbenzene)tricarbonylchromium which is relatively unreactive toward displacement (eq 9).^{3,4}

The *p*-xylene complex (0.1 M) was heated at 170 °C in a sealed NMR tube in benzene solvent containing various concentrations of the hexamethylbenzene complex.⁶ Figure 1 shows the ¹H NMR of this solution containing 0.12 M (hexamethylbenzene)tricarbonylchromium at times 0, 105, and 208 h. The disappearance of *p*-xylene complex methyl protons, δ 1.6, and aromatic protons, δ 4.5, and the appearance of benzene complex, δ 4.4, and free arene (*p*-xylene and hexamethylbenzene) protons, δ 2.2, provided four measures of the rate of the exchange. Kinetics of exchange, determined by all four measures of the rate, appear in Table I. The fact that the rate constants from the production of free methyl protons (δ 2.2) differ only slightly from those calculated from the other resonances indicated that the hexamethylbenzene complex was relatively inert toward exchange under the reaction conditions and therefore was functioning only as catalyst.

Each of the kinetic plots are accurately first order in (*p*-xylene)tricarbonylchromium. The slope of Figure 2, indicating a process first order in (hexamethylbenzene)-

(6) The NMR tubes were removed from the heating bath at specified times and cooled to room temperature and NMR spectra determined with at least eight repetitive integrations. Concentrations of each species were calculated from the ratio of a specific NMR resonance to that of a cyclohexane standard.

Table I. Rate Constants for the Exchange Reaction of 0.1 M (*p*-Xylene)tricarbonylchromium with Benzene at 170 °C in Benzene Containing (Hexamethylbenzene)tricarbonylchromium^a

concn of HMBCr(CO) ₃ , M	10 ⁷ k _{obsd} , s ⁻¹			
	b	c	d	e
0.18	12.4 ± 0.3	11.5 ± 0.3	12.1 ± 0.5	12.9 ± 0.8
0.155	9.5 ± 1.3	8.8 ± 0.3	9.7 ± 1.2	9.7 ± 0.6
0.12	7.5 ± 1.0	8.5 ± 0.3	8.2 ± 1.3	10.0 ± 0.5
0.08	6.8 ± 0.7	6.5 ± 0.1	6.7 ± 0.7	7.2 ± 0.4
0.055	4.0 ± 0.9	4.4 ± 0.3	4.4 ± 0.6	4.4 ± 0.2
0.00	2.0 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	2.0 ± 0.1

^a Cyclohexane was employed as internal standard. ^b Obtained from disappearance of *p*-xylene complex CH₃ protons. ^c Obtained from appearance of (benzene)tricarbonylchromium. ^d Obtained from disappearance of *p*-xylene complex ArH protons. ^e Obtained from appearance of free CH₃ protons (*p*-xylene and hexamethylbenzene).

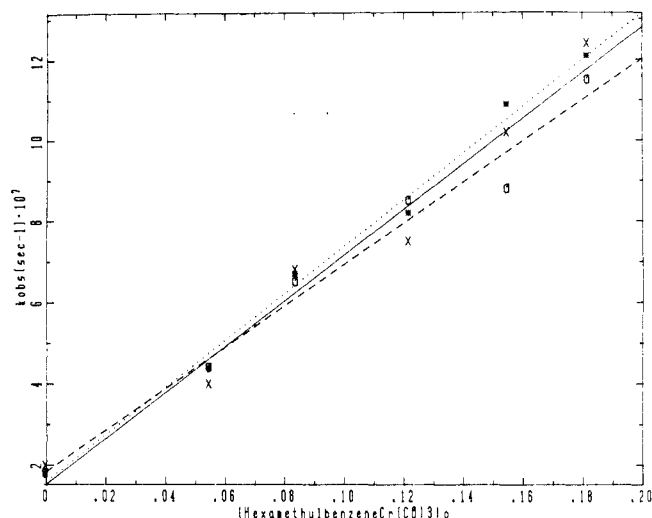


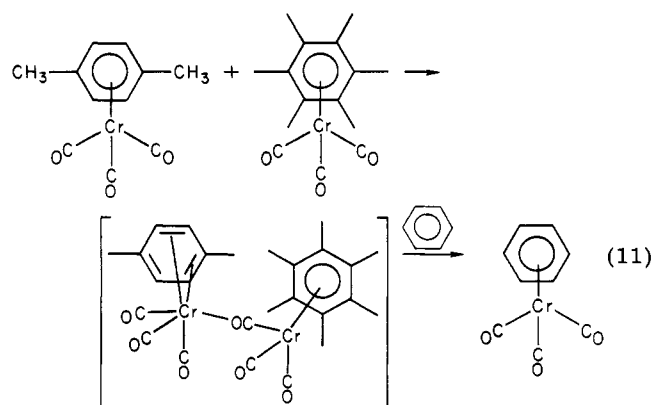
Figure 2. Plot of k_{obsd} vs. concentration of (hexamethylbenzene)tricarbonylchromium for arene exchange between (*p*-xylene)tricarbonylchromium and benzene in the presence of (hexamethylbenzene)tricarbonylchromium at 170 °C: × (—), k_{obsd} disappearance of (*p*-xylene)Cr(CO)₃-CH₃; ○ (---), k_{obsd} appearance of (benzene)Cr(CO)₃; * (···), k_{obsd} disappearance of (*p*-xylene)Cr(CO)₃-ArH.

tricarbonylchromium, affords a mean second-order rate constant of $5.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for the term

$$\frac{d[\text{BZCr}(\text{CO})_3]}{dt} = k_2[(p\text{-xylene})\text{Cr}(\text{CO})_3][\text{HMBCr}(\text{CO})_3] + \dots \quad (10)$$

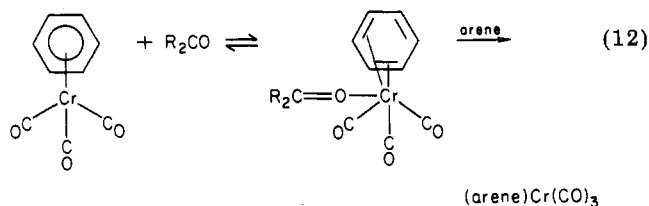
This value compares well with Strohmeier's values of $k_{\text{II}} = 1.5 \times 10^{-6}$ and $3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for the second-order terms in eq 1 for Ar = benzene and toluene, respectively.

We suggest a novel catalytic function of an (arene)tricarbonylchromium complex illustrated for our reaction shown in eq 11. Thus we have confirmed Strohmeier's

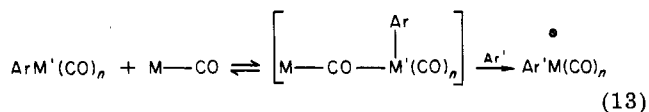


kinetic studies but eliminated both the proposed mecha-

nisms.⁷ In this catalysis the lone pairs on the bound CO are proposed to function in the manner suggested for the catalysis of these reactions by ketones, ethers, and nitriles (eq 12).^{3,8}



The increase of k_{II} in the order benzene complex < toluene complex < HMB complex accords with this proposal. It seems likely that such metal carbonyl catalysis is a general phenomenon.



Further details of catalyzed and uncatalyzed exchange reactions are discussed elsewhere.⁸

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Registry No. (*p*-Xylene)Cr(CO)₃, 12129-27-0; (hexamethylbenzene)Cr(CO)₃, 12082-08-5; (benzene)Cr(CO)₃, 12082-08-5; benzene, 71-43-2.

(7) We have shown that a labeled Cr(¹³CO)₃ group can be exchanged intact in the presence of ¹²CO, eliminating the mechanism of eq 4.⁸

(8) Traylor, T. G.; Stewart, K.; Goldberg, M., submitted for publication.

High-Yield Acyl Anion Trapping Reactions. Nucleophilic Acylation of Dialkyl Disulfides, *S*-Alkyl Thioesters, and Elemental Sulfur

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Summary: Organic disulfides may be acylated to give *S*-alkyl thioesters in good yield by the RLI/CO in situ procedure at very low temperatures. Similar nucleophilic acylation, at -78 °C, of elemental sulfur, followed by addition of iodomethane, gives RC(O)SMe.