phosphine in reactions occurring by associative mechanisms (such as oxidative addition or protonation) by direct steric interactions, and differences in solvation energies due to steric effects in either ground or transition states could also have a great effect on chemical reactivity. Other techniques, such as IR and $^{13}C$ NMR spectroscopy, give conflicting evidence on the relative donor abilities of phenyl- vs. methylphosphines. However, the commonly held view among inorganic and organometallic chemists that methylphosphines are significantly stronger donor ligands than phenylphosphines is, in our opinion, no longer tenable.

**Acknowledgment.** We are very grateful to the University of Waterloo for the use of the Raman spectrometer and to Dr. N. C. Baird for useful discussions. We also wish to acknowledge the NSERC (Canada) for funding.

**Registry No.** dppm, 2071-20-7; $W(CO)_5(PPh_3)$, 15444-65-2; $W(CO)_5(PMePh_2)$, 18534-36-6; $W(CO)_5(PMe_2Ph)$, 42565-94-6; $W(CO)_5(PMe_3)$, 26555-11-3; $W(CO)_4$(dppm), 41830-14-2; $W(CO)_4$(dppe), 29890-05-9; $W(CO)_4$(dmpm), 90624-10-5; $W(CO)_4$(dmpe), 40544-99-8; $W(CO)_4$(depm), 103884-73-7; $W(CO)_4$(depe), 97284-98-5; $^{183}W$, 14265-81-7; $^{13}C$, 14762-74-4.

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# Isomerization Processes Observed for Chromium Compounds by Using the Gas Chromatographic Reactor

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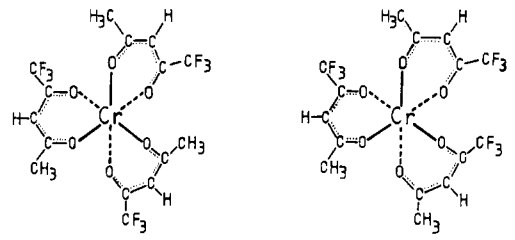
Two volatile chromium compounds, tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) [$Cr(tfa)_3$] and (2-methylnaphthalene)tricarbonylchromium [2-MenaphCr$(CO)_3$], have been studied gas chromatographically. The resolution of geometrical isomers of $Cr(tfa)_3$ using gas chromatography at sufficiently high temperatures (150–200 °C) permitted the dynamic interconversion process of the isomers to be studied. The use of high-resolution capillary columns aided this study. The activation energy for cis → trans isomerization was estimated to be ca. 130 ± 10 kJ mol$^{-1}$, and the twist mechanism was believed to be operative. Successful gas chromatographic separation of isomers of a bicyclic polyene–$M(CO)_3$ system is reported for the first time. The rearrangement of the $-Cr(CO)_3$ group can be followed in the gas chromatographic reactor; however, direct on-column injection is necessary in order to overcome decomposition of the compound, and this makes extraction of thermodynamic data less straightforward. An intramolecular (nondissociative) mechanism for the rearrangement is supported, and activation energies for isomer interconversion were estimated at 94 ± 7 and 100 ± 10 kJ mol$^{-1}$, respectively.

## Introduction

The gas chromatographic resolution of the cis and trans geometric isomers of $Cr(tfa)_3$ (**1a** and **1b**) has been well documented.[1-3] The resolution of the isomers is a function of chromatographic parameters such as temperature, liquid phase, carrier flow rate, and overall plate count (efficiency) of the column; on capillary columns the resolution is much greater by virtue of the higher efficiency achievable. Each geometric isomer is enantiomeric, existing in Δ and Λ optically isomeric forms; however, these are not resolved in the GC experiment since the liquid phase is nondiscriminating toward these isomers [and so cis(Δ) and cis(Λ) coelute]. The mechanism of interconversion from cis to trans and vice versa for $Cr(tfa)_3$ and indeed many analogous systems such as [M(unsymmetrical bidentate)$_3$], [M(unsymmetrical bidentate)$_2$(symmetrical bidentate)], etc. has been the subject of much interest over the past few decades. Thus, these complexes may undergo isomerization as well as racemization. Any mechanism proposed to account for this dynamic behavior must take cognizance of all possible pathways that can lead to isomerization–racemization and fit this to experimental observation. This has been discussed by Gordon and Holm[4] in general terms and also for the Co(III) complex with 5-methylhexane-2,4-dione, and the mechanisms are also presented in advanced-level textbooks.[5]

**1b** **1a**



Nuclear magnetic resonance methods have been applied to study the isomerization process. Fay and Piper used $^{19}F$ and $^{1}H$ NMR to characterize and in some cases obtain coalescence of the trifluoromethyl and methyl resonances, respectively, in $M(tfa)_3$ complexes and $M(tfa)_n(acac)_{3-n}$ systems.[6-8] Time-dependent intensties of NMR signals were also employed to study the inert Co complex. More recently, Grossmann and Haworth used the dynamic $^{1}H$ NMR method to study coalescence of methyl resonances of labile $M(tfa)_3$ ($M = Al^{3+}$, $Ga^{3+}$)[9] and from the activation parameters proposed mechanisms for ligand interchange for *trans*-$M(tfa)_3$. Hence, both time-dependent and dynamic NMR procedures have been utilized.

Gas chromatography has been used almost exclusively for the volatile and thermally stable paramagnetic $Cr(tfa)_3$ complex, for which NMR methods are unsuited. The procedure is essentially a time-dependent one, with $Cr(tfa)_3$ heated at different temperatures and the solution sampled at intervals in order to estimate rate constants and activation parameters for the isomerization. Fontaine et al.[10] dissolved the complex in both 1,2,4-trimethyl-

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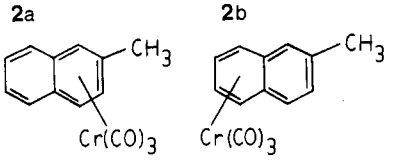
benzene and toluene and sampled solutions heated in the range 80–140 °C. In a gas-phase study,[2] small amounts (ca. $10^{-5}$ g) of isomerically enriched complex were encapsulated in ampules and heated; the contents were analyzed by GC. Likewise, photolysis of *trans*-$Cr(tfa)_3$ in several nonaqueous solvents showed trans → cis isomerization to be the dominant process for irradiation at $\lambda$ = 366 nm,[11] with ratios of cis and trans estimated by GC. The isomerization reaction is first order,[2] and since the above methods are pot reaction processes (forward and reverse reactions occurring simultaneously), pseudo-first-order conditions will be attained in the initial reaction stage.

Recently, we demonstrated[12] the application of the gas chromatographic technique to study conformational interconversions of sterically hindered molecules with high rotational barriers. The method is a dynamic one, since isomerization occurs during the residence of the compound on the column. For use of the GC reactor, the isomers must be chromatographically resolvable and the barrier to interconversion must be of such a magnitude as to be "consistent" with the temperature at which the compounds are chromatographed. Once an isomerization event has occurred, the product immediately begins to separate from the remaining reactant isomer, according to their different partition coefficients. With this condition obtaining, first-order kinetics can be assumed for the decrease in isomer peak measured on the chromatogram. The potential for application of this method to $Cr(tfa)_3$ was apparent from Uden et al.'s comment[3] that slight tailing of *trans*-$Cr(tfa)_3$ at 100 °C on a PLOT column was attributable to slight on-column isomerization, a phenomenon also acknowledged by others.[2,10] The facile resolution of cis–trans isomers on a number of capillary columns was investigated by Sucre and Jennings.[13] No interconversion/isomerization could be discerned at the reasonably low temperatures employed. Excellent resolution at 100 °C, with no peak skewing, was achieved on a Dexsil-coated column. However, it appears that no study has utilized this on-column behavior in order to obtain kinetic data on $Cr(tfa)_3$.

The second application of the GC reactor to the fluxional behavior of chromium compounds deals with the $\pi$-bonded organometallic compound 2-MenaphCr(CO)$_3$. This is expected to exist in two isomeric forms, depending upon which ring the tricarbonylchromium moiety is attached to[14]—**2a** and **2b**. GC of




tricarbonylchromium compounds of benzene derivatives has been reviewed.[15] Interestingly, in a study using a capillary column[16] quantitative decomposition of the compounds occurred. Fewer reports of GC of higher benzenoid analogues have appeared. 3,4-$Me_2$naphCr(CO)$_3$ readily decomposed,[17] and strict temperature control had to be observed in the experiment. The separation of structural isomers has been effected by liquid chromatography;[18] however, such separations by GC do not appear to have been hitherto reported.

It was, therefore, of interest to us to apply our GC reactor method to the above volatile chromium compounds. The aims were broadly (i) to see if the isomerization of the $Cr(tfa)_3$ system was qualitatively similar, in the GC reactor, to the isomerizations of organic molecules we have previously observed, (ii) to attempt to chromatograph and obtain resolution of isomers of 2-MenaphCr(CO)$_3$ and, if successful, to observe the interconversion process for migration of the Cr(CO)$_3$ group should this be possible, and (iii) to estimate rate and activation parameters for the above systems by using the GC reactor, if the requisite data can be obtained.

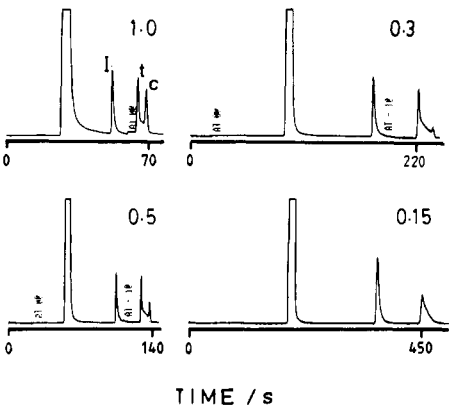



**Figure 1.** Gas chromatograms of $Cr(tfa)_3$ at 175 °C: I = 2-methylnaphthalene, t = *trans*-$Cr(tfa)_3$, c = *cis*-$Cr(tfa)_3$. Carrier gas pressure settings (kg cm$^{-2}$) are indicated on individual traces.

## Experimental Section

**Synthesis.** 1,1,1-Trifluoro-2,4-pentanedione was used as obtained from Tokyo Kasei. $Cr(tfa)_3$ was prepared according to the procedure of Fay and Piper.[7] Although isomer enrichment is not necessarily required for the GC reactor, low abundance for the cis isomer made enrichment of this isomer desirable. Thus column chromatography on silica gel was used to effect partial separation of trans and cis isomers.

2-MenaphCr(CO)$_3$ was prepared from the aromatic ligand (Merck) and hexacarbonylchromium (Alfa) by refluxing in di-*n*-butyl ether for 3 h. The ether was degassed prior to use, and the reaction was carried out under nitrogen. Excess solvent was removed under reduced pressure. TLC (silica) indicated that in benzene/hexane (1:1) the unreacted ligand eluted faster than the chromium complex, which corresponded to two yellow spots, $R_f$ 0.65 and 0.55. The mixture was passed through a silica gel column with petroleum ether as eluent, and the two orange bands were collected. Upon removal of solvent, orange crystals were obtained that were further vacuum-sublimed; mp 68–70 °C. $^1$H NMR (90 MHz): $\delta$ 7.1–7.6 (m, Ar H), 5.9–6.2 and 5.3–5.5 (m, M(CO)$_3$ Ar H), 2.32 and 2.43 (s, $CH_3$). IR (KBr): 1960 (CO), 1480, 1380, 1240, 1163, 850, 755, 668, 635 cm$^{-1}$. MS M$^{\bullet+}$: $m/z$ 278 ($C_{14}H_{10}{}^{52}CrO_3$, 15%, correct isotope pattern), 222 (15), 195 (15), 194 (62), 143 (31), 142 (100), 141 (85), 115 (16), 52 (61). $M_r$: calcd for $C_{14}H_{10}{}^{52}CrO_3$, 278.0005; found (MS), 277.9935.

**Gas Chromatography.** A Hewlett-Packard 5793 gas chromatograph was used throughout, with hydrogen carrier gas and flame ionization detection. A Scientific Glass Engineering (SGE) 5-$\mu$L microsyringe was used for injection into the capillary injector, which was normally operated in split mode. A SGE fused-silica capillary column (dimethylsiloxane bonded phase), 25 m × 0.32 mm, was used for $Cr(tfa)_3$, and in addition to this column a 5-m Hewlett-Packard megabore column (nonpolar) was used for the 2-MenaphCr(CO)$_3$ work. Chromatograms were recorded on a Hewlett-Packard 3390 computing integrator. On-column injection was used for the Cr(CO)$_3$ complex (refer to text for details).

**GC Reactor Methodology.** To obtain kinetic and activation data, the sample is chromatographed at three temperatures, and for each temperature the carrier gas flow rate is altered over at least five different rates. The chosen temperatures depend upon solute volatility and the extent of interconversion at that temperature. The retention time, $t_R$, of each isomer is accurately calculated at each flow, and the abundance of unconverted isomer is measured against an internal, inert standard [tetradecane or 2-methylnaphthalene for $Cr(tfa)_3$]. The abundance after reaction time $t_R$ is then compared with that for zero time, which gives the extent of isomerization each isomer has undergone. Data are analyzed according to usual methods to obtain rates and Arrhenius activation energy.

## Results and Discussion

Typical gas chromatograms, exhibiting the interconversion phenomenon in $Cr(tfa)_3$, are presented in Figures 1 and 2. They clearly show that the relative abundance of unconverted cis isomer

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(18) Greenwood, J. M.; Veening, H.; Willeford, B. R. *J. Organomet. Chem.* **1972**, *38*, 345.

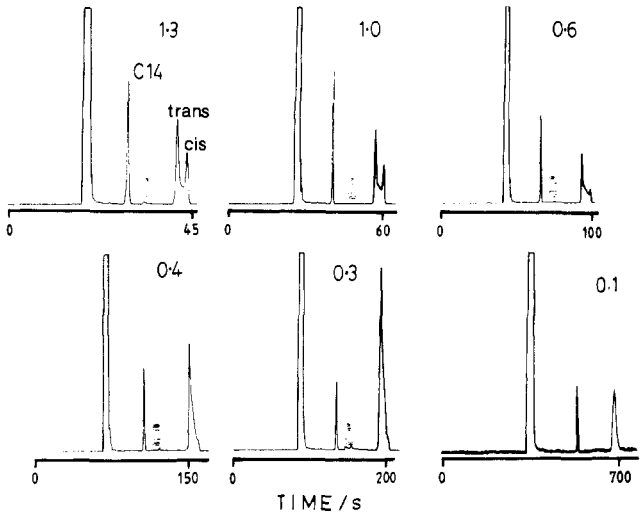


**Figure 2.** Gas chromatograms of $Cr(tfa)_3$ at 185 °C: C14 = tetradecane as internal standard.

**Table I.** Rate and Activation Data for $Cr(tfa)_3$ and 2-MenaphCr(CO)$_3$

| | rate, $10^4$ s$^{-1}$ | | |
|---|---|---|---|
| $T$, K | **1b → 1a** | **2a → 2b** | **2b → 2a** |
| 458 | 240 | | |
| 443 | 76 | | |
| 428 | 20 | 32.9 | 68 |
| 413 | | 16.7 | 30 |
| 398 | | 5.6 | 10 |
| $E_a$, kJ mol$^{-1}$ | 130 ± 10 | 94 ± 7 | 100 ● 10 |

rapidly decreases as the reaction progresses (i.e. as time increases or flow rate decreases). Thus, for 185 °C at 45 s, the ratio trans/cis is about 2.0, but at 100 s it is about 12.0. After 150 s, there is essentially no unconverted cis isomer remaining—all the cis that was originally injected has undergone isomerization into trans. The peak becomes almost symmetrical after 700 s of reaction time. A rather surprising result is that the peak corresponding to the trans isomer does not exhibit such a rapid decrease in peak height with time. The ratio of trans/internal standard is almost constant at all flows at 155 and 170 °C. At 185 °C however the ratio does decrease, albeit slowly, with decreased flow. The analysis of the trans isomer was repeated at 200 and 220 °C, but operating at these temperatures poses difficulties. Since, like most other physical methods, the reactor must effectively separate the species that are to be quantified, the poorer resolution between cis and trans isomers at the elevated temperatures makes analysis more uncertain. The resolution suffers directly as a result of rapid conversion of cis into trans, which causes the cis peak to merge into the trans and to become a shoulder to the longer retention side of trans. The trans peak will eventually become symmetrical and narrow as coalescence progresses [cf. the low-flow (0.1) chromatogram at 185 °C].

These observations imply that the cis isomer undergoes isomerization considerably more readily than the trans isomer; thus cis → trans will have a higher rate constant than trans → cis. This agrees qualitatively with the results of others; Kutal and Sievers[2] found that the rate for trans → cis to be about 5 times slower than cis → trans in the gas phase, and similar comparative values were obtained in nonpolar solvents.[10] In a photolysis study[11] quantum yields for trans → cis were about 5 times lower than those for cis → trans. Rate and activation parameters from the present work are given in Table I. The $E_a$ value of 130 ± 10 kJ mol$^{-1}$ for cis → trans agrees with previously reported calculations.[2,10]

It should be pointed out that in our calculations the time unit is taken to be the total time that the solute is on the column. We do not differentiate between time spent in gas phase and liquid phase and in doing so assume that the thermodynamic parameters are the same in both phases. This assumption is supported by

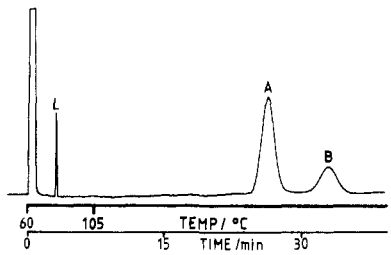


**Figure 3.** Gas chromatograms of isomers of 2-MenaphCr(CO)$_3$ (5-m megabore column, temperature programmed from 60 to 105 °C at 7.5 °C/min with on-column injection): L = trace ligand impurity; A = **2a**; B = **2b**.

conclusions that the role of the solvent in the interconversion mechanisms is small.[2]

While it is not intended to deduce mechanisms from this present work, some general observations can be made. Both twisting (trigonal and rhombohedral twists) and bond rupture (with square-planar or trigonal-bipyramidal intermediates) mechanisms have been invoked to account for the interconversions.[4,5] The only previous gas-phase study[2] concluded that a twist was most likely. For solution studies, the majority of workers interpret their data in favor of bond ruptures, but with the twist not completely ruled out (i.e. a mixture of mechanisms may be possible, which is apparent from Stevenson's work[19]). The twist mechanism is favored when data produce a low frequency factor, since stereochemical rearrangement of ligands aligned in the correct geometry for twisting is a low probability event. The main difference between gas- and liquid-phase studies is the possibility of solvent effects and stabilization of the intermediate in the latter, which would favor bond rupture by stabilization of charge separation. Since the bond rupture energy (Cr–O) may be larger than the activation energy, Kutal and Sievers reason that twisting is the more likely route. From the data available and the lack of evidence for formation of a more polar species in the gas chromatographic analysis (a bond rupture mechanism giving a polar intermediate that might be expected to be retained longer on the column), we likewise conclude that twisting is the main mechanism operative in the gas phase.

Figure 3 illustrates the favorable gas chromatographic analysis of 2-MenaphCr(CO)$_3$. It is apparent that peak shape is very good on the nonpolar column, and also the separation of the positional isomers is good even under the nonoptimal conditions and with the low efficiency megabore column. However, in order to obtain this successful result, some difficulties had to be resolved. First, on the longer column (25 m) using conventional split and splitless injection methods, only a large peak corresponding to free ligand was obtained. There was no evidence of any significant peak later in the chromatogram (GC analysis conditions: injector 200 °C, detector 250 °C, column oven programmed from 100 to 200 °C at 7.5 °C/min). The presence of 2-methylnaphthalene was due to either impurity in the sample or decomposition in the injector block, yielding the free ligand. This latter possibility was not unexpected given earlier experiences.[17] Upon removal of the glass injector liner, considerable decomposition was noted. Lowering the injector temperature did not produce any marked difference. Thermal decomposition of labile compounds may be overcome by cool on-column injection. Since this specific injector was not available, a makeshift procedure was instituted by removal of the column end from the injector and direct injection into the column by insertion of the syringe needle. Reattaching the column and programming the temperature up produced a large peak later in the chromatogram with a retention index of ca. 2000 (eluting with about the same retention as cosane). The free ligand peak was, in comparison, very small. Elution of the large peak was accompanied by a purple emission in the FID flame. Close inspection of the peak shape revealed behavior that from previous experience we reasoned could be an indication of isomer resolution; however,

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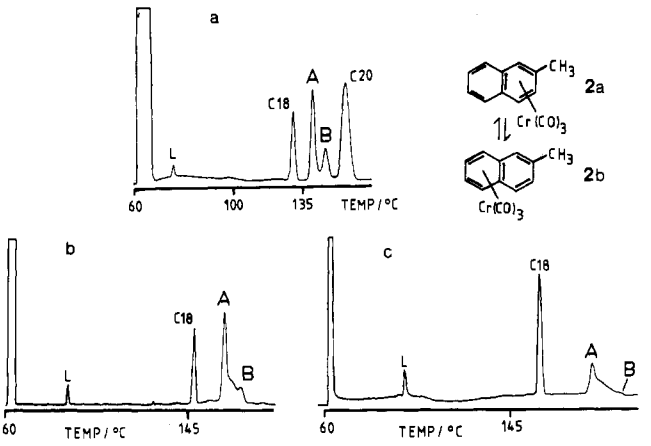


**Figure 4.** Gas chromatograms of 2-MenaphCr(CO)$_3$ on 5-m megabore column (on-column injection method and temperature programming to 135 °C (trace a) and 145 °C (traces b and c, carrier gas pressure setting 0.4 for (a) and (b) and 0.2 for (c)). L, A, and B are according to Figure 3.

the inconvenience of using a long column prompted the use of the wide-bore (530 $\mu$m i.d.) column, which can accommodate large carrier flow rates. This enabled split injection to be used with some success since the solute resides in the injector for only a very short time and good transfer to the column is possible. However, some decomposition still occurred, so on-column injection appears to be necessary. Figure 3 shows base line resolution of isomers **2a** and **2b**. There is no evidence of isomerization at the low temperature (105 °C) used, which would cause a plateau between the unconverted terminal peaks.[12] Retention indices of isomers **2a** and **2b** are 1870 and 1920, respectively (refer to Figure 4a). The earlier eluting isomer, **2a** (the more abundant), is apparently less polar than isomer **2b**, and this conclusion seems to agree with the liquid chromatographic analyses of similar compounds,[18] with the less polar isomer being the one with Cr(CO)$_3$ on the substituted ring.

Chromatograms in Figure 4b,c illustrate that dynamic interchange does occur, and the GC traces are extraordinarily similar to those of other systems we have studied, encompassing rotations about sterically hindered single bonds,[12] the cis–trans isomerization of Cr(tfa)$_3$, and also syn and anti acetaldoxime interconversions.[20]

(20) Marriott, P. J.; Lai, Y.-H.; Abdullah, R., unpublished observations.

Reversible isomerization is indicated by a series of trials against the internal standard, with both **2a** and **2b** decreasing in relative proportion. The mechanism for rearrangements of Cr(CO)$_3$ on naphthalene has been discussed recently, and it proceeds through a non-least-motion pathway, with first-order kinetics.[21a] In the present GC reactor study, the results tend to support the suggestion that the mechanism is an intramolecular one (in coordinating solvents, the exchange was proposed to be intermolecular).[21a] Since the GC method is a high (assumed infinite) dilution method, intermolecular reactions of solute molecules are not favored. If the Cr(CO)$_3$ group dissociates completely from the naphthalene ligand, we would expect an irreversible reaction to result and consequent undesirable phenomena would be seen in the GC profile (such as decomposition effects or peak broadening). Release of the volatile ligand would produce a broad hump in the GC much as that for decomposition of dicyclopentadiene in Langer's GC reactor.[22] Rather, the isomer peaks remain well shaped and no distortion of peak profile is seen.

Kinetic parameters have been estimated for 2-MenaphCr(CO)$_3$ (Table I). Activation energies for **2a** → **2b** and **2b** → **2a** are 94 ± 7 and 100 ± 10 kJ mol$^{-1}$, respectively. These values are only approximate, since the GC procedure had to be modified somewhat in order to obtain rate data. Thus, the on-column injection was made at room temperature, the column quickly reattached to the injector, and the oven rapidly heated to the temperature required (125, 140, 155 °C). This heating period took approximately 1.5 min, and depending upon the reproducibility of the procedure, some error in estimation of times may result. Also, the assumption of isothermal conditions usually made in the Arrhenius method clearly does not apply. However, the errors quoted are believed to be fair estimates of these factors. The calculated activation energies are consistent with those estimated theoretically for Cr(CO)$_3$ migration along the non-least-motion potential energy surface in naphthalene[21a] and also with the $\Delta H^{\ddagger}$ value[21b] of 125 kJ mol$^{-1}$ for 2,3-Me$_2$naphCr(CO)$_3$.

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**Registry No.** **1b**, 21496-95-7; **2a**, 96858-08-1; **2b**, 103837-14-5.

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