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Metal Inter-ring Movement in Fluorenechromium Tricarbonyl and Its Anion

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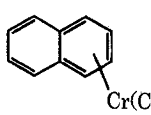
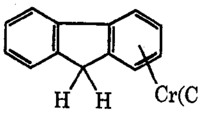
The phenomenon of valency tautomerism has been recognized in organometallic compounds for several years.[2] In many of these molecules an $M(CO)_3$ fragment migrates between chemically equivalent sites of a large organic ligand. A related type of process is the movement of a metal-containing fragment from one site to another (nonequivalent) site on an organic ligand. To our knowledge, these phenomena have not been found for polynuclear arenemetal tricarbonyl species, where they would manifest themselves as inter-ring movement of the $M(CO)_3$ moiety.[3] This is not surprising, as it is difficult to conceive of a simple intramolecular mechanism whereby the metal might move between rings while maintaining a reasonable degree of bonding. Furthermore, in all arene complexes the metal tricarbonyl moiety shows a distinct preference for a particular ring in a fused-ring aromatic system.[4]

In this paper we look at the nmr, infrared, and electronic spectral characteristics of three species. These are naphthalenechromium tricarbonyl (I), fluorenechromium tricarbonyl (II), and the species believed to be the fluorenylchromium tricarbonyl anion (III). Specifically, we present evidence for the lack of rapid inter-ring movement in I and for the migration of the $Cr(CO)_3$ fragment from the six- to the five-membered ring as II is converted to III by strong base.


I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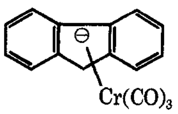
III

Results and Discussion

Naphthalenechromium tricarbonyl was prepared according to Fischer;[5] its nmr spectrum (τ 2.5, 3.8, 4.4; 4:2:2) at room temperature was consistent with $Cr(CO)_3$ being bound to one of the rings. Thus, at room temperature there is no evidence for the migration of $Cr(CO)_3$ between rings on the nmr time scale. Heating $(C_{10}H_8)Cr(CO)_3$ to 110° in either dibutyl ether or sulfolane led to no broadening or coalescence of the pattern.[6] Thus, in this system where the two rings are equivalent, exchange occurs relatively slowly, if at all.

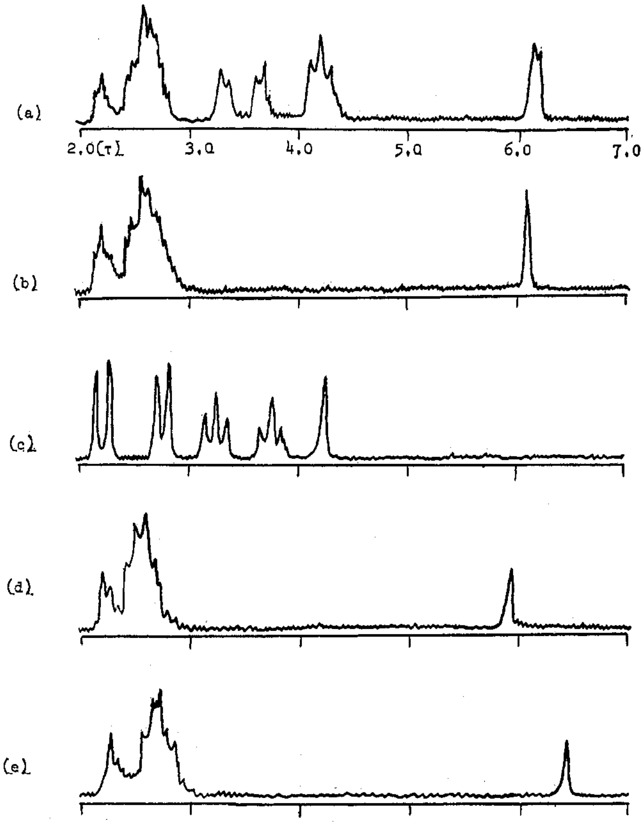

Figure 1.—The proton nmr spectra of (a) (fluorene)$CrCO_3$, (b) fluorene, (c) $K^+(fluorenyl)^-$, (d) $K^+(fluorenyl)Cr(CO)_3^-$, and (e) $K^+(fluorenyl)Mo(CO)_3^-$.

(Fluorene)$Cr(CO)_3$ (II) was also prepared after Fischer.[7] Its nmr spectrum,[7] shown in Figure 1a, clearly shows the placement of the $Cr(CO)_3$ on one of the terminal six-membered rings. This is not surprising since the central five-membered ring formally possesses no π electrons of its own. In Figure 1b, the spectrum of fluorene is shown for comparison. Addition of potassium *tert*-butoxide to either fluorene or fluorenechromium tricarbonyl in DMSO (or DMSO-d_6) leads to an immediate darkening of the solution. In the fluorene case, the species produced is the anion left after facile removal of a 9 proton. The fluorene anion's nmr spectrum differs drastically from that of either free or complexed fluorene and is shown in Figure

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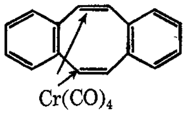
[2] T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 366 (1960); C. G. Kreiter, A. Masabol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

[3] A process closely related to that described here has been recently reported. Thus, Muller, *et al.*, prepared



and, by heating, caused the loss of CO and the movement of a chromium tricarbonyl moiety to a six-membered ring: J. Muller, P. Goser, and M. Elian, *Angew. Chem., Int. Ed. Engl.*, **8**, 374 (1969).

[4] B. J. Nicholson, *J. Amer. Chem. Soc.*, **88**, 5156 (1966), and references therein.

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

[6] Nmr spectra of benz[*a*]anthracene- and benzo[*b*]fluorenechromium tricarbonyl complexes at 110° in diglyme also show the chromium tricarbonyl group tightly bound to a single (terminal) ring: B. Deubzer, E. O. Fischer, H. P. Fritz, C. G. Kreiter, N. Kriebitzsch, H. D. Simmons, Jr., and B. R. Willeford, Jr., *ibid.*, **100**, 3084 (1967).

[7] E. O. Fischer, *Z. Naturforsch. B*, **15**, 465 (1960); E. O. Fischer, H. A. Goodwin, C. G. Kreiter, H. D. Simmons, Jr., K. Sonogashira, and S. B. Wild, *J. Organometal. Chem.*, **14**, 359 (1968).

1c. Of particular note is the 9 proton, which now integrates to half its relative value in fluorene. The spectrum of the anion is somewhat solvent and counterion sensitive, but the spectrum we obtain is in agreement with that obtained using other methods of generating the anion.[8] Upon adding base to the (fluorene)Cr(CO)$_3$ a red-brown color immediately appears, and the nmr spectrum shown in Figure 1d is obtained. There are no peaks in the complexed aromatic region (τ 3.5–5) of the spectrum. Furthermore, the pattern integrates in the ratio 8:1, indicating loss of a 9 proton. Additionally, the τ value for the lone 9 proton (τ 5.9) has shifted upfield from that of the 9 proton in the fluorene anion (τ 4.1). This spectrum can be interpreted in terms of the structural transformation II $\rightarrow$ III; *i.e.*, the Cr(CO)$_3$ fragment has been induced to migrate from the six- to the five-membered ring. (Although not shown in the spectra of Figure 1c and 1d, a peak due to the O–H proton now on $(CH_3)_3COH$ is also present.) Results similar to the above have been found using other bases (NaOH or $(CH_3)_4NOH$) and other solvents (THF, DMSO-d_6, and dioxane). Quite recently,[9] King and Efraty prepared (fluorenyl)Mn(CO)$_3$ from the reaction between sodium fluorenide and Mn(CO)$_5$Br. Our nmr results are comparable to theirs and together they provide good evidence for the existence of the *pentahapto*(fluorenyl)chromium tricarbonyl anion.

To establish unequivocally the nature and details of the process we describe would require either isolation of the complex anion as an appropriate salt or synthesis of a derivative which would require the previous existence of the free anion. Attempts to isolate solid compounds as salts failed to yield pure compounds. Thus, addition of numerous salts such as $N(CH_3)_4Cl$, $N(C_2H_5)_4Cl$, $N(C_3H_7)_4Cl$, $N(C_4H_9)_4Cl$, and $As(C_6H_5)_4Cl$ produced the expected chloride salt but failed on work-up to give a pure sample of the appropriate salt of the complex. Invariably, paramagnetic impurities were found in the isolated product. Attempts at reaction of the anion III with CH_3I, $Hg(CN)_2$, and $Sn(CH_3)_3I$ [in anticipation of its reacting in a similar manner to $C_5H_5Cr(CO)_3^-$][10,11] led to distinct reactions, but again a pure product could not be isolated.[12] We therefore turned to further spectroscopic methods to characterize the solution species.

The infrared spectrum of III in THF exhibits bands at 1980 and 1910 cm^{-1} typical of a metal tricarbonyl complex. Thus, we conclude that the metal tricarbonyl fragment has not dissociated from the arene ligand. Further evidence for the presence of III is provided by the electronic absorption spectrum. Thus, all arene-metal tricarbonyl complexes show absorption in the region 310–350 nm.[13] This absorption is believed to be a Cr $\rightarrow$ ring transition in $C_6H_6Cr(CO)_3$[14] and thus should be characteristic of (arene)Cr(CO)$_3$ bonding. For example, (naphthalene)Cr(CO)$_3$ has a band at 342 nm (ϵ 6×10^3) while (fluorene)Cr(CO)$_3$ has a band at 333 nm (ϵ 10^4). The spectrum of III similarly exhibits a peak at 336 nm (ϵ 7×10^3) again indicating the presence of a Cr(CO)$_3$ complex. The combined nmr, ir, and electronic spectral results indicate that III is indeed a complex anion containing Cr(CO)$_3$ bonded to the central five-membered ring.

If our interpretation is correct, it should be possible to prepare III by direct reaction of Cr(CO)$_3$ and the fluorenide anion. [This would be directly analogous to the preparation of $(C_5H_5)Cr(CO)_3^-$ from $C_5H_5^-$ and $Cr(CO)_6$.[9]] We attempted this reaction in refluxing THF and obtained a brown product which could not be freed of paramagnetic impurities. This same reaction was also attempted using sodium fluorenide and $(CH_3CN)_3Mo(CO)_3$.[15] The product of the latter reaction showed the nmr spectrum in Figure 1e, which is quite similar to the spectrum of III (Figure 1d). It thus appears that the anionic complex (fluorene)Mo(CO)$_3^-$ can be produced by this alternate approach. (Fluorene)Mo(CO)$_3$ has never been successfully prepared and so the first method of generating this anion cannot be applied in this case.

Conclusions

We have reported some of our experiments which provide information on the question of inter-ring movement in arenemetal tricarbonyl complexes. We have shown that in complexes where there is no free energy change associated with inter-ring movement, this movement is found to be slower (at least) than the nmr time scale. On the other hand, for (fluorene)Cr(CO)$_3$, treatment with base induces the metal to move from the six- to the five-membered ring. Various attempts to reverse the reaction by adding acid were unsuccessful. Thus, addition of aqueous acid led to slow decomposition of III, with fluorene and inorganic materials as ultimate products. By making the five-membered ring cyclopentadienyl in nature, we have given the one-way inter-ring movement a favorable free energy change. One question to which we have not addressed ourselves is the mechanism of the ring shift. Both intra- and intermolecular mechanisms must be considered as possible.

Experimental Section

Nonpolar solvents such as CCl_4, $CDCl_3$, and $CHCl_3$ were used directly from the reagent bottle (reagent grade). THF was distilled over $LiAlH_4$ and stored over molecular sieves. DMSO and DMSO-d_6 were stored over molecular sieves. All organometallic samples were prepared in the glove bag under an atmosphere of nitrogen. Nmr spectra were recorded on a Varian A-60 nmr spectrometer using TMS as the internal standard. For the high-temperature studies, the Varian V-6057 high–low temperature system containing the V-6031 variable-temperature probe, the V-6040 variable-temperature controller, and the V-6060 low-temperature kit was utilized. The ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. All infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrometer using NaCl plates and a solvent reference sample.

Cr(CO)$_6$ and Mo(CO)$_6$ were obtained from Pressure Chemical Co. while fluorene was obtained from K & K Laboratories and resublimed prior to use. Li$^+$(fluorene)$^-$ and K$^+$(fluorene)$^-$ were prepared by the method of Scherf and Brown[16] while $Mo(CH_3CN)_3(CO)_3$ was prepared after Tate, *et al.*[17] (Naphthalene)Cr(CO)$_3$ was prepared by the method of Fischer[5] except that ethylcyclohexane was employed as solvent and the method of purification involved sublimation of the product at 75° (1 mm). (Fluorene)Cr(CO)$_3$ was also synthesized after Fischer[7] except that in purification sublimation at 75° (1 mm) led to removal of impuri-

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[8] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 973 (1963).

[9] R. B. King and A. Efraty, *J. Organometal. Chem.*, **23**, 527 (1970).

[10] G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[11] R. B. King, *Inorg. Syn.*, **7**, 99 (1963).

[12] In each case the other product of the expected reaction (NaI, NaCN, or NaI) was obtained and identified.

[13] D. A. Brown, *Transition Metal Chem.*, **3**, 1 (1966).

[14] D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).

[15] R. B. King, *J. Organometal. Chem.*, **8**, 287 (1967).

[16] G. W. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

[17] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, **1**, 433 (1962).

ties with pure (fluorene)$Cr(CO)_3$ left remaining. Solutions containing K^+(fluorenyl)$Mo(CO)_3^-$ were prepared as follows. Equimolar quantities of fluorenylpotassium and tris(acetonitrile)molybdenum tricarbonyl were placed in a 100-ml round-bottom flask under nitrogen. Fifty milliliters of freshly distilled dioxane (from Na) was placed in the flask. The mixture was then refluxed under nitrogen for 22 hr. After allowing the mixture to cool, it was filtered to remove unreacted starting materials. The amber yellow filtrate was used for the nmr spectrum discussed above.

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A Hydrogen-1 Nuclear Magnetic Resonance Study of Unsymmetrical Mercury Compounds from Bis(trimethylsilyl)mercury and Diorganomercurials

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In equilibrium systems containing two mercury compounds (A_2Hg, B_2Hg) the unsymmetrical species (AHgB) is usually the major product of the reaction

$$A_2Hg + B_2Hg \rightleftarrows AHgB \qquad (1)$$

particularly if A and B are of different electronegativity.[1,2] The situation is less clear when one of the substituents is a triorganosilyl group.

Bis(trimethylsilyl)mercury and dimethylmercury have been reported not to give the unsymmetrical compound $(CH_3)_3SiHgCH_3$ at room temperature.[3] Vyazankin, *et al.*, have reported that $(C_2H_5)_3SiHgC_2H_5$ slowly symmetrizes, although the compound is stable enough to be distilled under vacuum.[4] These reports imply that the symmetrical compounds are favored in diorganomercury–bis(triorganosilyl)mercury systems. However, Marano and MacDiarmid have reported low yields of $Cl_3SiHgC_2H_5$ from diethylmercury and bis(trichlorosilyl)mercury.[5]

To investigate the apparently anomolous behavior of these systems, the reactions of bis(trimethylsilyl)mercury with diorganomercury species were followed by pmr spectroscopy.

Experimental Section

Organomercury compounds either were commercial products or were prepared by standard methods. Bis(trimethylsilyl)mercury was made by Eaborn's method[6] and was sublimed before use. All manipulations involving silylmercury compounds were performed on a vacuum line or under a nitrogen or argon atmosphere dried by sodium–potassium alloy. Solvents were dried over alkali metal and stored on the vacuum line. Solvents used for the reactions are those indicated in Table I.

TABLE I

NMR DATA FOR TRIMETHYLSILYLMERCURY AND METHYLMERCURY SPECIES

R	$(CH_3)_3SiHgR$		CH_3HgR
	τ	$J_{^{199}Hg-Si-C-^1H}$, Hz	$J_{^{199}Hg-C-^1H}$, Hz
Trimethylsilyl	9.80[a]	40.8[a]	76.8[a]
Methyl	9.86[a]	53.5[a]	102.5[d,e]
Phenyl	9.79[b]	55.4[b]	108.5[d,e]
Vinyl	9.83[a]	54.2[a]	107.0[d,e]
Cyclopropyl	9.89[b]	52.4[b]	103.5[d,e]
1-Propynal	9.82[b]	70.6[b]	148[b]
Bis(trimethylsilyl)amido	9.73[b]	79.2[b]	157.2[b]
Benzyl	9.87[b]	55.0[b]	107.2[b]
Pentachlorophenyl	9.83[c]	72.2[c]	...[f]

[a] In cyclopentane. [b] In 1,2-dimethoxyethane. [c] In benzene. [d] In Freon 11. [e] H. D. Visser, Ph.D. Thesis, Wayne State University, 1969. [f] Not measured.

Samples were prepared by placing the diorganomercurial and the bis(trimethylsilyl)mercury in an nmr tube, adding solvent from the vacuum line, and sealing off the tube under vacuum.

The appearance of unsymmetrical species could be easily observed by pmr. Significant quantities of the mixed species could be observed when the samples were left at room temperature: 2 min for bis[(trimethylsilyl)amido]mercury, 1 hr for dipropynal- and dibenzylmercury, 1 day for diphenyl- and divinylmercury, several days for dicyclopropylmercury, and several weeks for bis(pentachlorophenyl)- and dimethylmercury. Except for $(CH_3)_3SiHgCH_3$, decomposition of the unsymmetrical compounds was more rapid than for the bis(trimethylsilyl)mercury. Mercury was precipitated and resonances assignable to $(CH_3)_3SiR$ were observed.

Nmr spectra were obtained on a Varian Associates A-60A spectrometer at ambient temperatures unless otherwise noted. Coupling constants should be considered accurate to ± 0.3 Hz.

Results and Discussion

Mixed species were detected when the organic group was methyl, phenyl, cyclopropyl, propynal, vinyl, pentachlorophenyl, benzyl, and the amide group bis(trimethylsilyl)amido. With dimethylmercury the equilibrium constant appeared to be close to the random value of 4.0, but decomposition of bis(trimethylsilyl)mercury prevented an accurate determination. With the other diorganomercurials the fairly rapid decomposition of the symmetrical compounds, probably by the reaction

$$RHgSi(CH_3)_3 \longrightarrow (CH_3)_3SiR + Hg \qquad (2)$$

prevented determination of the equilibrium constants, although they appeared to be much larger than the random value. The decomposition of $(CH_3)_3SiHgN(Si(CH_3)_3)_2$ was very rapid (within a few minutes at room temperature) and it was not possible to tell if the mixed species was favored.

These results show that, contrary to implications in the literature, unsymmetrical triorganosilylorganomercurials are the favored species in mixtures of bis(triorganosilyl)mercurials and diorganomercurials. In this regard silylmercury compounds more closely resemble organomercury compounds than may have been previously believed.

As expected the value of the $^{199}Hg-Si-C-^1H$ coupling in $(CH_3)_3SiHgR$ increases as the electronegativity of R increases (Table I). An interesting linear relationship was found between the values of $J_{^{199}Hg-Si-C-^1H}$ and $J_{^{199}Hg-C-^1H}$ in the related methyl compound CH_3HgR.

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(1) M. D. Rausch and J. R. VanWazer, *Inorg. Chem.*, **3**, 761 (1964).

(2) Y. Marcus and I. Eliezer, *J. Phys. Chem.*, **66**, 1661 (1962).

(3) A. G. Lee, *J. Organometal. Chem.*, **16**, 321 (1969).

(4) N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, and T. G. Gurikova, *Dokl. Akad. Nauk SSSR*, **155**, 1108 (1964).

(5) G. A. Marano and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 621 (1969).

(6) C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc. C*, 2188 (1967).