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Preliminary Communication

Fluxional behavior of 7-substituted cycloheptatriene iron tricarbonyls

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Summary

The reaction between $C_7H_7Fe(CO)_3^-$ and Me_3MCl, M = Si and Ge, produces 7-substituted cycloheptatriene iron tricarbonyl derivatives. Both compounds, unlike the parent molecule, are fluxional. It is shown that an oscillatory motion of the $Fe(CO)_3$ group, having the effect of a 1,3-shift with respect to the ring, is responsible for the observed fluxionality.

The fluxional behaviour of several classes of organometallic compounds has attracted considerable interest over the past decade [1]. One of the overriding principles that has emerged from the numerous studies on cyclopolyene metal systems is that while 1,2-shifts are allowed, 1,3-shifts are forbidden processes. There are indeed several non-fluxional molecules which seem to confirm the above mentioned rule. One such species is $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ which shows no nmr line broadening up to 373°K [2]. Here we wish to report our observation on (7-RC_7H_7)Fe(CO)$_3$, R = $SiMe_3$ and $GeMe_3$, derivatives which show that rather subtle substitutional changes are apparently sufficient to induce fluxionality in these complexes.

The reactivity of cycloheptatrienyltricarbonylferrate(1−), (C_7H_7)Fe(CO)$_3^-$, toward transition metal carbonyl halides [3] and main group electrophiles [4] has recently been investigated. The reaction with Me_3MCl, M = Si and Ge, yields 7-substituted cycloheptatrieneirontricarbonyl derivatives. The room temperature ^1H-nmr spectra of the complexes are entirely

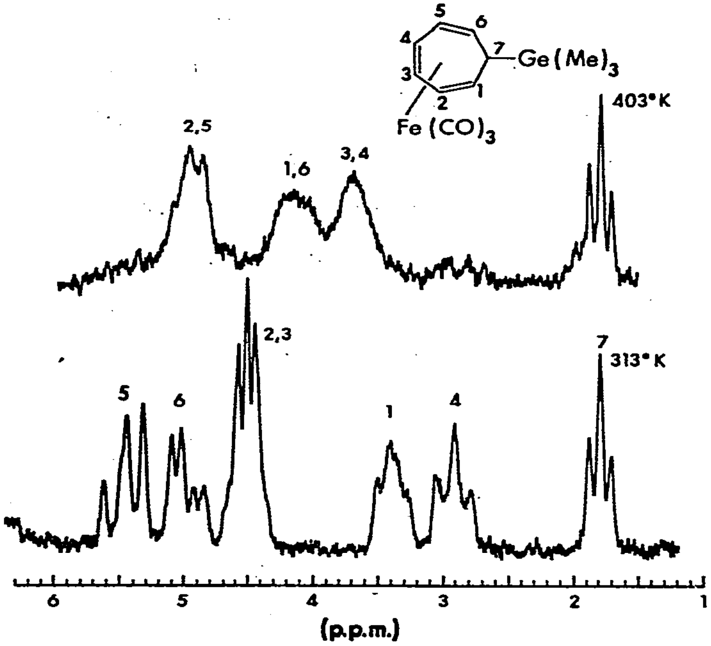
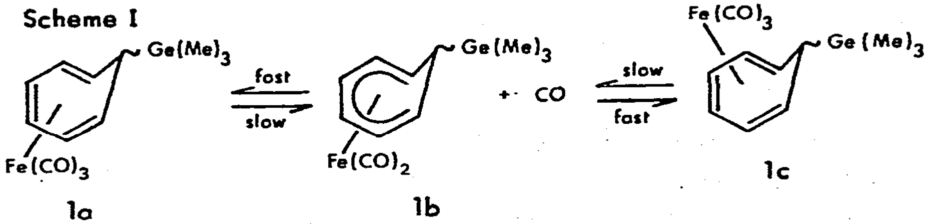


Figure 1 Variable temperature 60 MHz ^1H nmr spectra of (7-$GeMe_3C_7H_7$)Fe(CO)$_3$. Assignments are based on decoupling experiments.

consistent with such formulation*. However, the compounds, quite unlike the parent unsubstituted $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ molecule, exhibit fluxional behavior. Figure 1 shows the behavior of the trimethylgermyl substituted derivative. It is seen that as the temperature is raised all the resonances, except that due to H-7, broaden, coalesce and finally reform into three new sets of peaks. Similar behavior is also exhibited by the ^{13}C-nmr spectra of the compound, figure 2. Because of the larger chemical shift differences, the high temperature limiting spectrum could not be reached in this case. Nevertheless, the uniqueness and non-participation of C-7 in the fluxional process is unmistakable. The analogous trimethylsilyl substituted compound is also fluxional. The process, however, is somewhat slower, as evidenced by the higher coalescence temperature with this molecule, T_c = 388°K as opposed to 373°K for the germanium derivative.

We can envisage four distinct processes in these compounds that could cause temperature dependence of the nmr spectra: 1) hydrogen migration; 2) Me_3M, M = Si or Ge, group migration; 3) reversible CO dissociation, Scheme I;

Scheme I



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*full details on the preparation and physical properties of these compounds will be the subject of a forthcoming publication

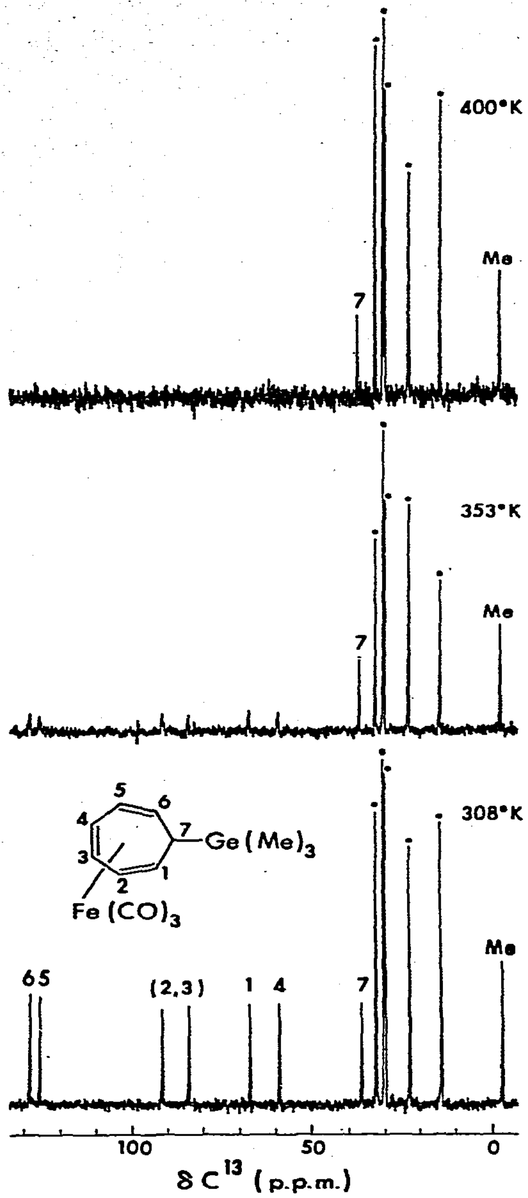
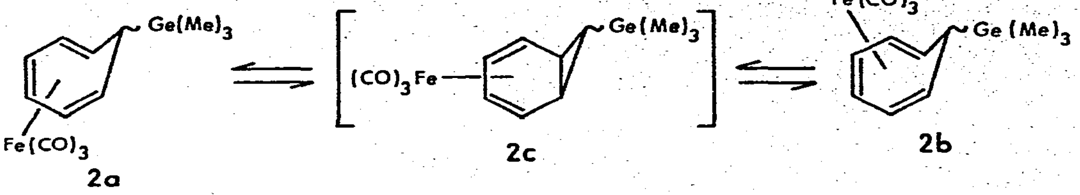


Figure 2 Variable temperature 22.628 MHz ^{13}C nmr spectra of $(7\text{-GeMe}_3C_7H_7)Fe(CO)_3$ in n-decane. The peaks marked with asterisks are due to the solvent.

4) oscillatory motion of the $Fe(CO)_3$ moiety, Scheme II. The

Scheme II



temperature independence of the H-7 and C-7 nuclei immediately rules out processes 1 and 2*. Furthermore, our failure to induce ^{13}CO enrichment of the germanium derivative under thermal conditions (1 atm. of ^{13}CO, 388°K and 1 hour reaction time) allows us to eliminate process 3 as a possibility. We are therefore left with process 4, oscillatory motion of the $Fe(CO)_3$ moiety having the effect of a 1,3-shift, as the only viable explanation for the observed fluxionality of the complexes. We hasten to add that whether the fluxional process is a genuine 1,3-shift, **2a** $\rightleftharpoons$ **2b**, or occurs by successive 1,2-shifts with the intermediacy of norcaradiene structure **1c**, is not known with certainty. To further probe this question the effect of substituents on the C-7 carbon on the fluxionality of the complexes is being investigated. We are also attempting to grow suitable crystals to ascertain the stereochemistry of the Me_3M substituents in the present compounds.

Finally we should note that attempts to further promote

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[*] Hydrogen migrations are seen to occur above 373°K, the facility of this process is Si > Ge.

the fluxionality by Me_3Sn substitution at the C-7 position proved so far unsuccessful. Although the reaction between $C_7H_7Fe(CO)_3^-$ and Me_3SnCl proceeds readily, the resulting material is apparently a mixture of $Me_3SnC_7H_7Fe(CO)_3$, the desired compound, and $C_7H_7Fe(CO)_2SnMe_3$, an Sn-Fe containing complex. All our attempts to separate these two components so far proved fruitless. Work is also continuing on this intriguing reaction.

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