

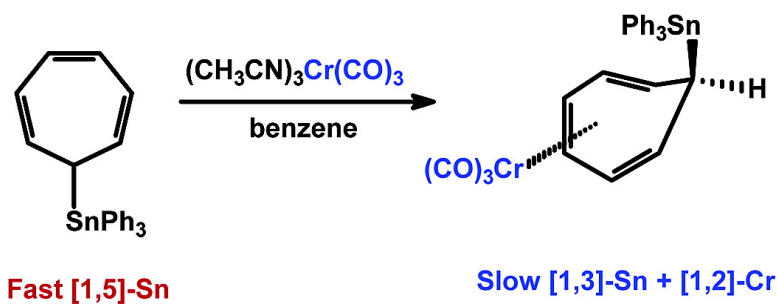
Communication

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“Electronic Lock” in Chromiumtricarbonyl Complex of Cycloheptatrienyln

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Metallotropic rearrangements are useful for probing our understanding of reactivity and selectivity in chemistry. The minimized importance of the solvent effects and any other intermolecular interactions simplifies the overall experimental outcome, making possible more clear-cut conclusions on the reaction mechanism compared to the solvent-assisted multicomponent transformations. We report here a new phenomenon of locking the fast [1,5]-Sn migrations in cycloheptatrienyl(triphenyl)tin (**1**) by involving the π -electrons of cycloheptatrienyl ring into the coordination with the chromiumtricarbonyl group (in complex **2**).

Organometallic derivatives of cycloheptatriene exhibit various types of intramolecular dynamics. A η^1 -bonded organometallic substituent can migrate around the seven-membered ring by the mechanism of a [1,*j*] sigmatropic rearrangement.¹ On the other hand, η^x ($x > 1$)-bonded organometallic groups often undergo haptotropic shifts around the π -system of cycloheptatriene.² The most interesting situation emerges when a cycloheptatriene moiety bears several organometallic groups, since such molecules provoke an interesting problem of simultaneous intramolecular shift of both substituents (diatropic migrations), which has been scarcely studied thus far.

In their pioneering work,³ Cotton and Reich analyzed in detail the temperature-dependent ¹H NMR spectra of the bimetallic μ - η^3 : η^4 -Cp(CO)₂Mo(C₇H₇)Fe(CO)₃ complex and concluded that the most probable mechanism of the observed fluxionality is the simultaneous [1,2] shift of both metals with the probable admixture of the [1,3] shift mechanism.³ Later, a series of cycloheptatrienyl-bridged homo- and heterobimetallic complexes with two η^x ($x > 1$)-bonded organometallic groups was studied.^{2a,4–7} All syn-bridged complexes exhibit ring whizzing of the cycloheptatrienyl moiety,^{4–7} which in most cases is too rapid to be frozen in the NMR experiments.⁴ Some of these compounds were reported to give low-temperature-limiting ¹H and ¹³C spectra at 190–200 K;^{5–7} however, no mechanistic studies have been made thus far.

In (η^1 : η^4) complexes Me₃XC₇H₇Fe(CO)₃ (X = Si, Ge), relatively facile [1,3]-Fe haptotropic shifts have been characterized, whereas sigmatropic migrations of Me₃X groups were not detected.⁸ In contrast, in Pr₂B(C₇H₇)Fe(CO)₃ a diatropic rearrangement involving simultaneous [1,7]-B and [1,2]-Fe migrations is significantly faster than the [1,3]-Fe haptotropic shift and [1,3]-B sigmatropic migration.⁹

Several examples of (η^1 : η^6) complexes of cycloheptatriene have been recently described.¹⁰ The results of a ¹³C spin saturation transfer (SST) experiment for the [Mo(CO)₃(μ - η^6 : σ^1 -C₇H₇)Ru(CO)₂-Cp] were interpreted in favor of the 1,2-shift process, whereas the observations of the line shape changes in the ¹H NMR spectra of other compounds could not be satisfactorily accounted for. Here we report the synthesis of a new cycloheptatriene (η^1 : η^6) complex,

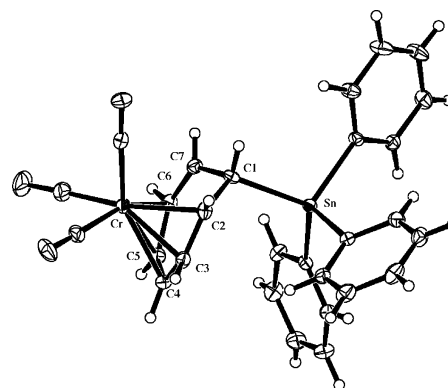
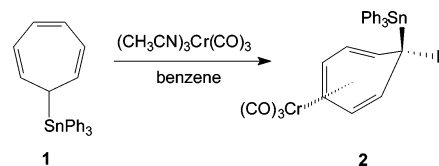


Figure 1. Molecular structure (30% thermal ellipsoids) of complex **2**. Selected bond lengths: C(1)–C(2) = 1.494(4), C(1)–C(7) = 1.496(5), C(2)–C(3) = 1.382(4), C(3)–C(4) = 1.416(6), C(4)–C(5) = 1.393(5), C(5)–C(6) = 1.416(4), and C(6)–C(7) = 1.375(4) Å. A slight bond alternation is observed in the cycloheptatriene ring. The atoms C(2)–C(3)–C(4)–C(5)–C(6)–C(7) are almost planar (within 0.0453 Å), and the C(1)–C(2)–C(7) plane is inclined by 45.63° from the ring.

Ph₃Sn(C₇H₇)Cr(CO)₃ **2**, and the mechanism of diatropic rearrangement in this compound.

Synthesis and Stereochemistry of Complex 2. Reaction of cycloheptatrienyl(triphenyl)tin (**1**) with (CH₃CN)₃Cr(CO)₃ in boiling benzene occurred rapidly and according to NMR control resulted in complete transformation of **1** to **2** in 20 min (Scheme 1).

Scheme 1



Recrystallization of the raw material from ether yielded complex **2** as a purple solid in 65% yield. At ambient temperature, the ¹H NMR spectrum of **2** is well resolved and shows the presence of a (η^1 : η^6)-bonded cycloheptatriene unit. The 8.6 Hz coupling between H⁴ and H¹ attests for the exo configuration of **2**.¹¹ This was explicitly proved by X-ray structure of **2** shown in Figure 1.

Dynamic Behavior of Complex 2. A facile [1,5]-Sn sigmatropic shift occurs in triphenyl(cycloheptatrienyl)tin **1**.^{1a–d} Activation barrier of this dynamic process ($\Delta G^\ddagger_{300} = 15.4 \pm 0.1$ kcal mol⁻¹)^{1d} is low enough to cause an extensive broadening of the resonances in the ¹H NMR spectrum of **1** at 348 K (Figure 2). On the other hand, the line shape in the ¹H NMR spectrum of complex **2** at the same temperature is only slightly affected by the dynamic effects. SST experiments on protons suggest that the 1,3-diatropic rearrangement occurs (Figure 3).

Thus, the diatropic migrations in (η^1 : η^6) complex **2** proceed much slower and by different topology compared to the 1,5-Sn shift in

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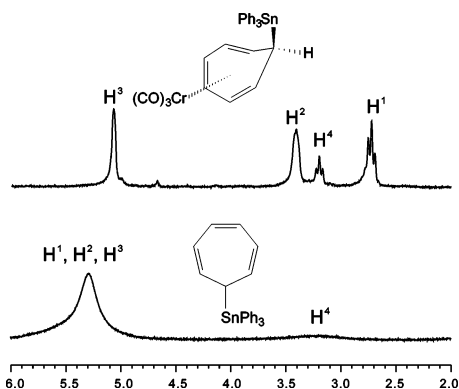


Figure 2. “Electronic lock”: Comparison of the ^1H NMR spectra (300 MHz, benzene- d_6 , 348 K) of cycloheptatrienyl(triphenyl)tin **1** (below) and its chromiumtricarbonyl complex **2** (above).

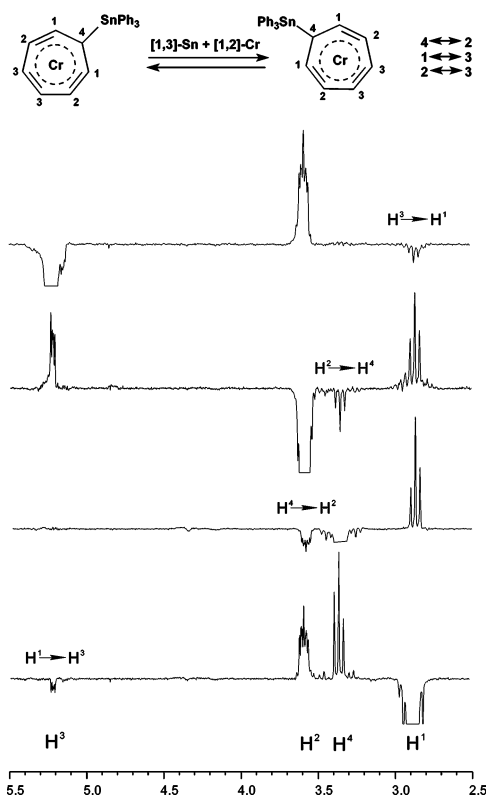


Figure 3. Difference SST spectra of complex **2** (300 MHz, benzene- d_6 , 298 K) confirming the topology of the diatropic rearrangement. The exchange between H^2 and H^3 is obscured by the NOEs with adjacent protons.

the η^1 -stannane **1**. This observation is in contrast to the relatively facile diatropic [1,7]-B + [1,2]-Fe shift in $\text{Pr}_2\text{B}(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3$,⁹ which has the same topology and proceeds faster than the [1,7]-B migration in $\text{Pr}_2\text{B}(\text{C}_7\text{H}_7)$.^{1b} Therefore, the particular cooperative effects in diatropic migrations may vary depending on the nature of the organometallic groups involved.

A sigmatropic shift of the Ph_3Sn group in **2** would induce only slight (if any) movement of the $\text{Cr}(\text{CO})_3$ moiety, and the motion

of the Ph_3Sn group is exactly the same as in the compound **1**. Therefore, the reason for the significantly slower sigmatropic migrations of tin in **2** must be purely electronic. Any diatropic rearrangement in **2** requires a reorganization of the π -system of the cycloheptatriene ring and, therefore, significant perturbations of the π -donative bonds between the cycloheptatrienyl ring and the chromium atom. We conclude that this is the reason for the significantly decreased mobility of the triphenylstannyl group. This corresponds to the topology of the observed rearrangements, since the [1,3] migration requires the reorganization of a single double bond compared to two double bonds in the case of the [1,5]-Sn migration or three in the case of the [1,7]-Sn shift.

In conclusion, we have shown that the chromiumtricarbonyl group acts as a selective “electronic lock” upon coordination to cycloheptatrienyltin, efficiently blocking the [1,5]-Sn migrations but participating in a slower [1,3]-Sn + [1,2]-Cr rearrangement. Further work on diatropic rearrangements in cyclic organometallic systems is in progress.

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Supporting Information Available: Experimental details (PDF) and crystallographic analysis of **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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