Nucleophilic additions of methanolate and the acetylenes PhC=C^— and t-BuC=C^— to the cationic complex [CpFe(η^5-Cot)]^+(1^+)(Cot = cyclooctatetraene) exclusively occur on the Cot ring in high yield. However, the new products are not stable with respect to molecular fluxionalities. To establish the mechanism of the fluxional processes, different NMR techniques were applied on CpFe(η^5-C5H5) (3) and CpFe(η^5-C5H5D) (3-di). The monodeuterated complex 3-di has been obtained in two ways: (i) by nucleophilic addition of D^- from Li[B(Et4)2] to 1^+ and (ii) by deprotonation of 3 with Lin-Bu at —30 °C, forming the anionic complex [CpFeCot]^- (4), and successive deuteration with MeOD. The addition of D^+ to 4, as well as the addition of D^- to 1^+, initially yielded CpFe(η^5-C5H5-1-exo-D), although the deuterium is later distributed over all positions of the cyclo-C5 ligand with the exception of the endo-position. Various NMR studies demonstrate two different exchange processes: a slow 1,3-metal shift, as shown by spin saturation transfer (SST) experiments, which leads to an enantiotopomerization of 3, and a 1,4-hydrogen shift as an even slower process.

Introduction

The C—C bond formation reactions of coordinated cyclooctatetraene (Cot) have become the focus of some attention.1 Recently, we were able to show that nucleophilic addition to coordinated Cot in the cationic complex [CpFe(η^5-Cot)]^+(1^+)2,3 is a new complementary way4 in which to introduce special functionalities to Cot in a highly stereo- and regioselective manner. The nucleophilic addition products from malonate nucleophiles represent a different intramolecular rearrangement1 of Cot—like species.4,5 Further to our previous findings, we report herein new processes with activation barriers dependent on the substituent of the cyclo-C5 ligand.

Results and Discussion

Since we were interested in acetylenic and methoxy substitution of the Cot ligand, we have chosen two representative acetylenes and methanolate as nucleophiles in reactions with 1^+. As mentioned earlier, the reactions (eq 1) occur almost quantitatively.

\[
\text{CpFe}\text{Cot} + \text{Nu}^\ominus \overset{\text{THF}}{\longrightarrow} \text{CpFeNu}^\ominus
\]

If the reaction products are isolated within 1 h, it is possible to obtain the ^1H-NMR spectra of 2a and 2c, which show the formation of only one product. The ^1H-NMR spectra are in very good agreement with those described recently for Nu = CH(CO2R)2 (R = Me, Et) and NMe2.6 The two proton resonance signals between 5.1 and 5.6 ppm correspond to the olefinic protons belonging to the uncoordinated double bond of the cyclo-C5 ligand. After three days, however, the ^1H-NMR spectrum of 2a changes dramatically, showing at least four different products, which can be identified by four Cp and t-Bu signals at ca. 4 and 1.2 ppm, respectively. Warming up the NMR tube to 60 °C for 16 h

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simplifies the 1H-NMR spectrum to a set of signals indicating two different products with the ratio 2:1. However, these products could not be isolated separately by either fractional crystallization or column chromatography. A similar fluxional behavior, within a shorter period of time, is observed for 2e (Nu = OMe). The phenylethylnyl derivative 2b is even more labile, and in contrast to 2a, the number of different products caused by the fluxionality is even larger for 2b and 2c.

The molecular transformation in 2a–2e is at variance with our former results,1d and we have thus been forced to investigate this behavior more thoroughly. We decided therefore to study the stereochemistry in the monodeuterated cyclooctatrienyl complex CpFe(η⁵-C₈H₅D) (3-d₁), which can be obtained from deuteride addition to 1⁺ similar to the synthesis of CpFe(η⁵-C₈H₉) (3)1d (eq 2).

Providing that the addition of D⁻ to the cyclooctatetraene ligand in 1⁺ occurs stereo- and regioselectively, as with normal nucleophilic additions to coordinated olefinic ligands, only one signal should be observed in a 2H-NMR spectrum. In the case of molecular transformations in 3-d₁, for each isomer, one singlet is to be expected.

A monodeuterated derivative of 3 can also be prepared by the deprotonation of 3 with Lin-Bu and subsequent protolysis with MeOD (eq 3).

When the first 1H-NMR spectra of 3-d₁ were obtained from both synthetic routes (recorded within a few hours after the reaction had been performed), a doublet of multiplets of very low intensity at δ = 1.78 ppm was observed. This corresponds to a negligible number of exo-protons of the C₈-ring ligand, as it is this position that is occupied by the deuterium (Figure 1A). The endo-proton only shows a broad multiplet, which gradually sharpens to reveal a doublet of multiplets. Meanwhile, the intensity of the signal belonging to the exo-proton increases until it is eventually equal to that of the endo-proton (Figure 1B–D).

Since no significant alteration of the other cyclo-C₈ proton signals could be observed, with the exception of some changes in the splitting pattern, time-dependent 2H-NMR experiments were used to obtain a deeper understanding of the mechanism of this molecular rearrangement (Figure 2). As expected from 1H-NMR spectra, the signal of the exo-position can be recognized immediately (Figure 2A), confirming the regioselective addition of the proton (or deuteron) to the metallated complex 4. After 24 h two peaks corresponding to positions 4 and 6 appear with similar intensities (Figure 2B). Furthermore, weak signals originating from positions 3 and 7 can be observed, which become stronger after another day (Figure 2C). In spectrum D of Figure 2, the signals of positions 2 and 8 can be distinguished and the intensity of the signal of position 5 at last increases. Finally, the 2H-NMR spectrum of 3-d₁ shows signals for all of the cyclo-C₈ positions, though not for the endo-position, which indicates an even distribution of the deuterium atom over all cyclooctatrienyl positions with the exception of the endo-position (Figure 2E). The lack of any Cp signal in spectrum E proves that the rearrangement strictly occurs within the C₈ ligand.

The most surprising result that emerges from the 2H-NMR spectra is the successive population in pairs of the positions 4 and 6, 3 and 7, and 2 and 8, respectively, by deuteron; this can best be explained by two different molecular transformations occurring at different rates. One dynamic process is an energetically degenerate 1,3-metal shift (Scheme 1a) as indicated by spin saturation transfer (SST) experiments. In an SST experiment, a proton is irradiated, and as a result, this proton will transfer its spin information to the interchanging position b. Consequently, the population difference between the ground state and the excited state will be diminished for b, revealing a reduced intensity of the resonance signal of proton b, too. Hence, after subtracting a normal 1H-NMR spectrum, used as a reference (Figure 3A), from the SST spectrum, a difference 1H-NMR spectrum is thus obtained. This shows a strong negative signal for the irradiated proton a and a smaller negative one for proton b, whereas all other signal intensities have to be zero. Compared to the SST spectra of 3, however, some signals are left with positive intensities as in Figure 3.

These are caused by nuclear Overhauser effects (NOEs) which stem from dipolar interactions between
vicinal protons, thereby giving rise to positive resonance signals. Hence, the irradiation of proton 7, for example, reveals a negative signal for the interchanging proton 3 in the difference spectrum caused by SST (Figure 3, spectrum B), whereas protons 6 and 8 show positive signals caused by NOEs. The chosen timing of the experiment does not allow one to observe the NOE effects on the "new" position, however, because it has still not built up in any reasonable amount. Comparable intensity alterations can be seen for the other irradiation experiments depicted in Figure 3. For every difference spectrum, the SST and NOE interactions are depicted in the ideograms of Figure 3 as well as the signs (+) of the signals. From these spectra the interconversion of protons 2 and 8, 3 and 7, and 4 and 6, respectively, can be clearly deduced, yielding the enantiomer of 3 by means of a 1,3-metal shift. Since this enantiomerization is slow, with respect to the NMR time scale, it becomes obvious that no indication of this process has been observed before. However, a 1,3-metal shift is not uncommon for \( \eta^5 \)-cyclooctatrienyl and \( \eta^5 \)-cycloheptatrienyl complexes,\(^7\) although for 3 a complete circulation of the metal center is hindered by the interruption of the conjugation of the cyclo-C\(_6\) ligand in position 1. Hence, a "twitching" motion will only occur in 3, the activation barrier of which has to be considerably higher (\( AG^\ddagger > 71 \text{ kJ/mol} \)) than that for the valence isoelectronic complex Mn(CO)\(_3\)(\( \eta^5 \)-C\(_6\)H\(_6\)) (5) (\( AG^\ddagger = 52.7 \text{ kJ/mol} \)).\(^3\) The higher activation barrier of metallo tropic shifts in the cyclopentadienyl complex 3, compared to the tricarbonyl complex 5, parallels the results obtained

for the cyclooctatetraene compounds Cr(CO)$_3$(η$^6$-Cot), CrCp(η$^6$-Cot), and [FeCp(η$^6$-Cot)]$^+$. The second dynamic process in 3 has to be distinctly slower than the 1,3-metal shift; otherwise additional SST and NOE signals would have to have been recorded. The slower dynamic process is assumed to be a metal-mediated 1,4-shift of the endo-proton (Scheme 1) similar to the 1,5-shift discussed for (η$^6$-cycloheptatriene)-(tricarbonyl)chromium. In analogy to other hydrogen shifts in organometallic complexes, the 1,4-hydrogen migration may be initiated by the dechelation of the terminal double bond, which is in conjugation with the free double bond of the η$^5$-cyclooctatrienyl unit, to generate an unsaturated 16 valence electron (ve) η$^3$-cyclooctatrienyl complex (Scheme 1b). Then C–H activation takes place on C1 to form the 18 ve hydride intermediate (Scheme 1c), which is able to transfer the hydride either to position 1 to reveal the starting complex or to position 4 to create the 4-D derivative (Scheme 1d). A subsequent 1,3-shift places the deuterium atom in position 6 (Scheme 2, equilibrium c). From the 6-D derivative, the 7-D compound is formed by the metal-mediated 1,4-shift of the endo-proton (Scheme 2, equilibrium d), with the ensuing degenerate 1,3-shift revealing the 3-D product (Scheme 2, equilibrium e). After this procedure, all of the positions of the cyclooctatrienyl ligand are deuterated in the sequence which was elucidated from the $^2$H-NMR spectra (see Scheme 2, equilibria f–i). From these intramolecular rearrangements it is clear
that, in principle, eight different isomers can be formed upon nucleophilic addition to 1+. The absence or inclusion of the 2a, in order to confirm that the rearrangements discussed above are the reason for their formation. The strict intramolecular 1,4-hydrogen shift in 3 is in accordance with the proposed hydrogen shift in CpV-(η⁵-C₅H₅);¹¹ however, it disagrees with CpZrC₅H₅-d₁ wherein a complete (statistical) distribution of the deuterium atom is found over all cyclo-C₅ positions including the endo- and exo-positions.¹⁶

Experimental Section

All manipulations were performed under nitrogen with thoroughly dried solvents. Standard ¹H-NMR spectra were recorded on a VARIAN Gemini 200 BB spectrometer, while the ²H-NMR spectra were recorded in 10-mm tubes with the broad-band equipment of a BRUKER-AM-360 spectrometer. The initial assignment of the ²H-NMR signals has been performed by means of chemical arguments: the addition of nucleophiles to coordinated -ene and -eny1 ligands (e.g., D⁻ from Li[BEt₃D]; see eq 1) exclusively occurs in exo-position with respect to the metal center. Therefore, the signal of the exo-proton is easily found by comparison of the spectra of 3 and 3-di, when the NMR sample of 3-di has freshly been prepared. The assignment of the remaining ⁴H-resonance signals via standard ¹H-COSY is straightforward. The SST experiments are performed on the AM-360 using the standard NOE-difference procedure with relaxation delay and mixing times of 0.5 s. Differences were calculated to reference spectra with an irradiation frequency close to the on-resonance frequencies. All spectra were recorded at room temperature.

Preparation of CpFe(η⁵-C₅H₅-C₆H₅-C₆H₅) (2a). Twenty-five milliliters of a THF solution containing 0.07 mmol of LiC=C-Bu are added dropwise to a cooled, stirred suspension (T = -78 °C) of 1.07 g (2.8 mmol) of 1 in 40 mL of THF. The orange-colored suspension immediately changes to a clear solution, which is allowed to warm up to room temperature. After 45 min of stirring, the reaction mixture is evaporated to dryness and the residue is extracted with pentane. The pentane extract is reduced in volume until precipitation occurs. Storage at -30 °C for 3 days yields 0.23 g (93%) of 3-di. ¹H-NMR: see Figure 1 and reference ¹. El-MS: m/e 586 (18) [M⁺], 223 (4) [M⁺ - Me₂], 222 (20) [M⁺ - Me₃], 199 (7), 186 (25) [C₆H₅Fe⁺], 160 (12), 152 (30), 134 (17), 121 (75) [C₆H₅Fe⁺], 104 (52), 91 (100), 78 (68), 65 (79), 56 (86). IR (KBr, nujol): 1650 ν (uncoordinated C—C bond of the C₆-ring), 1511 m (C—O—Me). ²H-NMR (C₆D₆, TMS, 200 MHz): δ 5.4 (dd, 1H, uncoordinated C=C of the Cp-ring), 3.9 (m, 2H, Cs-ring), 3.78 and 3.9 (s, 5H, Cp ligand), 2.7–2.9 (m, 1H, Cp-ring). Anal. Calcd for C₁₅H₁₉FeO (M = 256.11): C, 65.65; H, 6.25. Found: C, 65.0; H, 6.3.

Preparation of CpFe(η⁵-C₅H₅-C₆H₅-C₆H₅) (3-di). (a) Via Nucleophilic Addition. The reaction is performed in strict analogy to the synthesis of 3-di Li[BEt₃D] (1.5 mL; 1.0 M in THF) is added to a cooled, stirred suspension (T = -78 °C) of 0.52 g (1.4 mmol) of 1 in 10 mL of THF. The mixture is allowed to warm to room temperature. After 45 min of stirring, the reaction mixture is evaporated to dryness and the residue is extracted with pentane. The pentane extract is reduced in volume until precipitation occurs. Storage at -30 °C for 3 days yields 0.23 g (71%) of 3-di, as orange-red crystals.

(b) Via Deprotonation and Addition of D⁺. Lin-Bu (0.4 mL, 1.6 in hexane) is added to a cooled solution (T = 0 °C) of 0.14 g (0.6 mmol) of CpFe(η⁵-C₅H₅) (3) in 10 mL of THF. The color of the solution immediately changes from orange-red to deep green. After 15 min of stirring, 25 mL of the MeOD is added, yielding an orange-red solution. The reaction mixture is then evaporated to dryness, and the residue is extracted with hexane. The hexane is removed to yield 0.15 g (93%) of 3-di. ¹H-NMR: see Figure 1 and reference ¹. El-MS: m/e (50%) of 3-di (50%) of 3 (15) [15, 15], 175 (10), 121 (70) [48], 56 (100) [76].

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