# Anion-induced migration reaction of acetylide from iron to cyclopentadienyl in (cyclopentadienyl)irondicarbonyl(acetylide) complexes

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The anion-induced migration reaction of acetylide in $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2(C\equiv CPh)$ 1 was observed in a sequential treatment of lithium diisopropylamide then MeI or MeC(O)Cl resulting in $(\eta^5\text{-}C_5H_4C\equiv CPh)Fe(CO)_2Me$ 2 or $(\eta^5\text{-}C_5H_4C\equiv CPh)Fe(CO)_2$-$C(O)Me$ 3, respectively, the structure of 3 being confirmed by a single-crystal X-ray study.

The anion-induced migration reaction of a ligand from a metal atom to a neighboring cyclopentadienyl carbon atom has been known for about 20 years.[1] Such a reaction is characterized by its *intramolecular* nature and is generally initiated by a *deprotonation of the cyclopentadienyl ring* causing a group to migrate from a metal to a cyclopentadienyl ring, followed by quenching of the anion produced. The known examples include acyl,[2,3] ester,[3] hydride,[4] and heteroatom-containing (Si,[5] Ge,[6] Sn[6] and P[7]) groups, in conjunction with Group 6 to Group 8 transition-metal elements. In this communication, the migrating group is extended to carbon-containing functions; the first observation of an acetylide migration from iron to cyclopentadienyl is detailed.

To a solution of the iron–acetylide complex $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2(C\equiv CPh)$ 1[8] at $-78\,^\circ$C was added dropwise lithium diisopropylamide (LDA, 1.5 equivalents) and this was stirred for a short time before an excess of MeI was added to give a yellow compound $(\eta^5\text{-}C_5H_4C\equiv CPh)Fe(CO)_2Me$ 2 (60%).† Compound 2 revealed in the $^1$H NMR spectrum resonances at $\delta$ 4.95 (t, $J = 2.1$, 2 H), 4.76 (t, $J = 2.1$ Hz, 2 H) for $C_5H_4$ protons, clearly indicating a monosubstitution of the cyclopentadienyl ring. The Me resonance at $\delta$ 0.38 (s, 3 H) was in agreement with that in $(\eta^5\text{-}C_5H_4R)Fe(CO)_2Me$ ranging from $\delta$ 0.35 to 0.38 for R = SiMe$_3$, SiMe$_2$N(Pr$^i$)$_2$, SiMe$_2$NMe$_2$.[9] The Me resonance at $\delta$ $-18.7$ in the $^{13}$C NMR spectrum also indicated the presence of Fe–Me bonding, not $C_5H_4$–*Me* [cf. the $^{13}$C NMR signal of $C_5H_4$–*Me* in $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2CH_2SiMe_3$ at $\delta$ 12.7, whereas that of Fe–Me in $(\eta^5\text{-}C_5H_4SiMe_2CH_2SiMe_3)Fe(CO)_2$-Me is at $\delta$ $-22.6$[10]]. During the process, an anionic intermediate 1′ was present whose IR $\nu(CO)$ bands were red-shifted from those of 1 by 170 cm$^{-1}$. The anionic intermediate 1′ possibly has its negative charge residing on Fe, *i.e.*, after the acetylide relocation stage.[4,5,6,10,11] The migration of the phenylacetylide group may be viewed as a 1,2-shift with the carbanion generated on the cyclopentadienyl ring attacking the neighboring acetylide (Scheme 1).
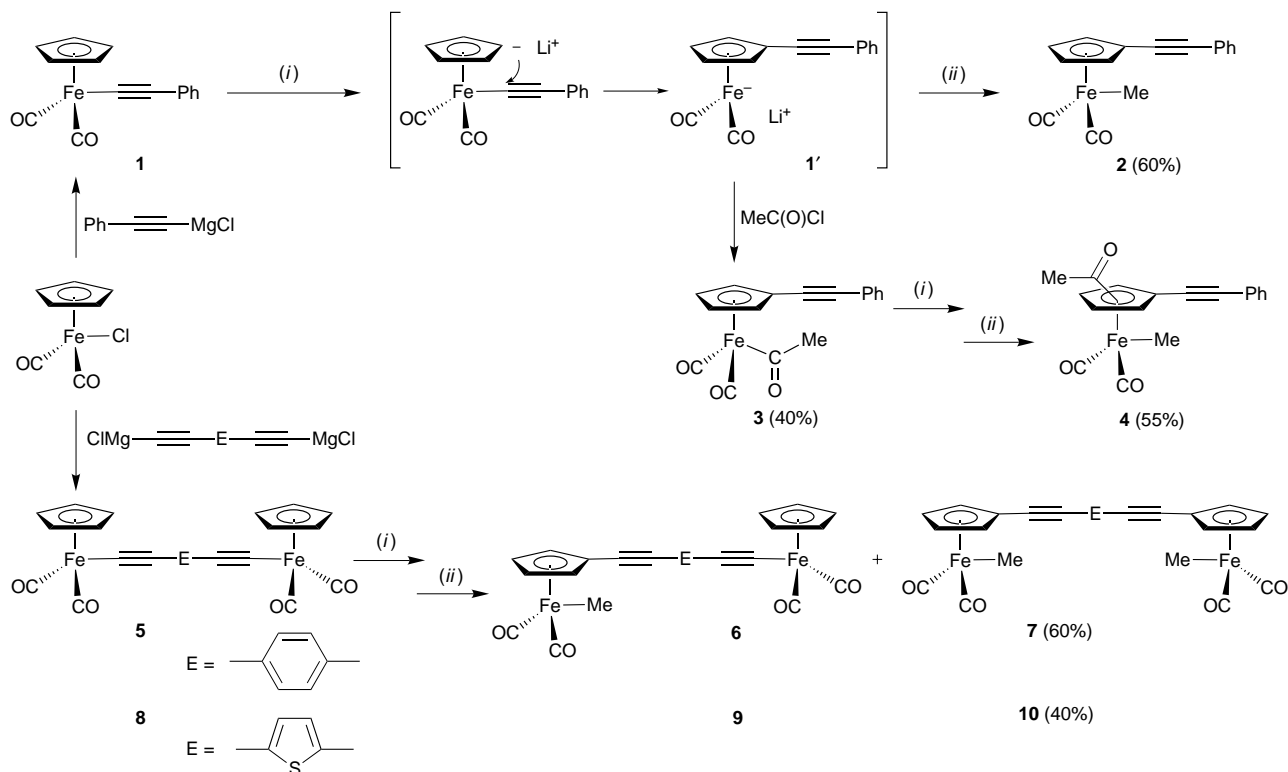
A similar anion-induced migration reaction of acetylide, yet quenching with MeC(O)Cl instead of MeI, resulted in $(\eta^5\text{-}C_5H_4C\equiv CPh)Fe(CO)_2[C(O)Me]$ 3 (40%), whose molecular structure was deduced on the basis of spectroscopic data and confirmed by an X-ray structure determination,‡ revealing the correct molecular connectivity (Fig. 1): The acetylide group is

indeed connected to the cyclopentadienyl ring instead of Fe. With further treatment of LDA then MeI, compound 3 pro-
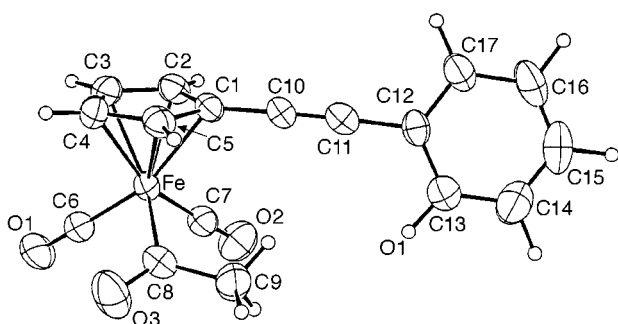
**Scheme 1** (*i*) LDA, −78 °C; (*ii*) MeI



**Fig. 1** An ORTEP[12] plot of complex **3**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Selected bond lengths (Å) and angles (°): Fe–C6 1.765(3), Fe–C7 1.764(4), Fe–C8 1.984(3), C8–O3 1.201(4), C8–C9 1.501(4), C1–C10 1.432(4), C10–C11 1.184(4), C11–C12 1.436(4); Fe–C6–O1 178.1(3), Fe–C7–O2 178.2(3), Fe–C8–O3 122.71(23), Fe–C8–C9 118.41(21), O3–C8–C9 118.8(3), C1–C10–C11 177.1(3), C10–C11–C12 177.4(3)

ceeded with an acetyl migration to give {η⁵-C₅H₃(C≡Ph)-[C(O)Me]}Fe(CO)₂Me **4** (55% total) with two regio-isomers in *ca.* 3:2 ratio based on ¹H NMR peak intensity integration, the 1,2-isomer being preferred to the 1,3.

In view of the recent surge of investigations on highly ethynylated organometallic structures that are of relevant interest in materials science,[13] a variety of mono- and bis-(transitional metal) σ-acetylide complexes have been reported in the literature.[14] The present anion-induced acetylide migration reaction would deliver an extra degree of freedom in positioning an ethynylated chromophore on a cyclopentadienyl ring. The anion-induced acetylide migration reaction was extended to the diiron–diacetylide complex (η⁵-C₅H₅)Fe(CO)₂[C≡C(1,4-C₆H₄)-C≡CFe(CO)₂(η⁵-C₅H₅)] **5**, which was prepared similarly to **1**.[8] Accordingly, to a solution of **5** at −78 °C was added dropwise LDA (3 equivalents), followed by quenching with an excess of MeI, resulting in a yellow powder consisting of the double-end acetylide migration product Fe(CO)₂Me[(η⁵-C₅H₄)C≡C(1,4-C₆H₄)C≡C(η⁵-C₅H₄)]Fe(CO)₂Me **7** (60%) that had very similar spectroscopic data to **2**. The dianionic intermediate should have

two singly negative charges residing on the two Fe centers which are independent. The single-end acetylide migration product (η⁵-C₅H₅)Fe(CO)₂[C≡C(1,4-C₆H₄)C≡C(η⁵-C₅H₄)]Fe(CO)₂Me **6** could be separated from **7** when a smaller amount of LDA was employed. Spectroscopically **6** seemed to possess a combination of those properties of **5** and **7**. No attempt was made to maximize the yield of **6** however. The anion-induced acetylide migration of (η⁵-C₅H₅)Fe(CO)₂[C≡C(2,5-C₄H₂S)C≡C]Fe(CO)₂-(η⁵-C₅H₅) **8**[15] gave double-end acetylide migration product Fe(CO)₂Me[(η⁵-C₅H₄)C≡C(2,5-C₄H₂S)C≡C(η⁵-C₅H₄)]Fe-(CO)₂Me **10** (40%). The single-end acetylide migration product (η⁵-C₅H₅)Fe(CO)₂[C≡C(2,5-C₄H₂S)C≡C(η⁵-C₅H₄)]Fe(CO)₂Me **9** was similarly obtained using smaller amounts of LDA. Although the transformations of **1** to **2**, of **1** to **3** then to **4**, of **5** to **7**, and of **8** to **10** were 100% on the basis of IR ν(CO) monitoring, the isolated yields of migration products by column chromatography were only *ca.* 40–60%, reflecting a loss during purification. With a wide area to improve and to explore, the acetylide migration reaction is expected to be of use in the preparation of polyethynylated organometallic materials.

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