DALTON
COMMUNICATION

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

Ling-Kang Liu,*[a,b] Kuo-Yang Chang[a,b] and Yuh-Sheng Wen[a]

[a] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Republic of China*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan 10767, Republic of China*

The anion-induced migration reaction of acetylide in (η^5-C_5H_5)Fe(CO)$_2$(C≡CPh) **1** was observed in a sequential treatment of lithium diisopropylamide then MeI or MeC(O)Cl resulting in (η^5-C_5H_4C≡CPh)Fe(CO)$_2$Me **2** or (η^5-C_5H_4C≡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 (η^5-C_5H_5)Fe(CO)$_2$(C≡CPh) **1**[8] at −78 °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 (η^5-C_5H_4C≡CPh)Fe(CO)$_2$Me **2** (60%).† Compound **2** revealed in the ^{1}H NMR spectrum resonances at δ 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 δ 0.38 (s, 3 H) was in agreement with that in (η^5-C_5H_4R)Fe(CO)$_2$Me ranging from δ 0.35 to 0.38 for R = SiMe$_3$, SiMe$_2$N(Pr^i)$_2$, SiMe$_2$NMe$_2$.[9] The Me resonance at δ −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 (η^5-C_5H_4Me)Fe(CO)$_2$CH$_2$SiMe$_3$ at δ 12.7, whereas that of Fe–Me in (η^5-C_5H_4SiMe$_2$CH$_2$SiMe$_3$)Fe(CO)$_2$Me is at δ −22.6[10]]. During the process, an anionic intermediate **1′** was present whose IR ν(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).

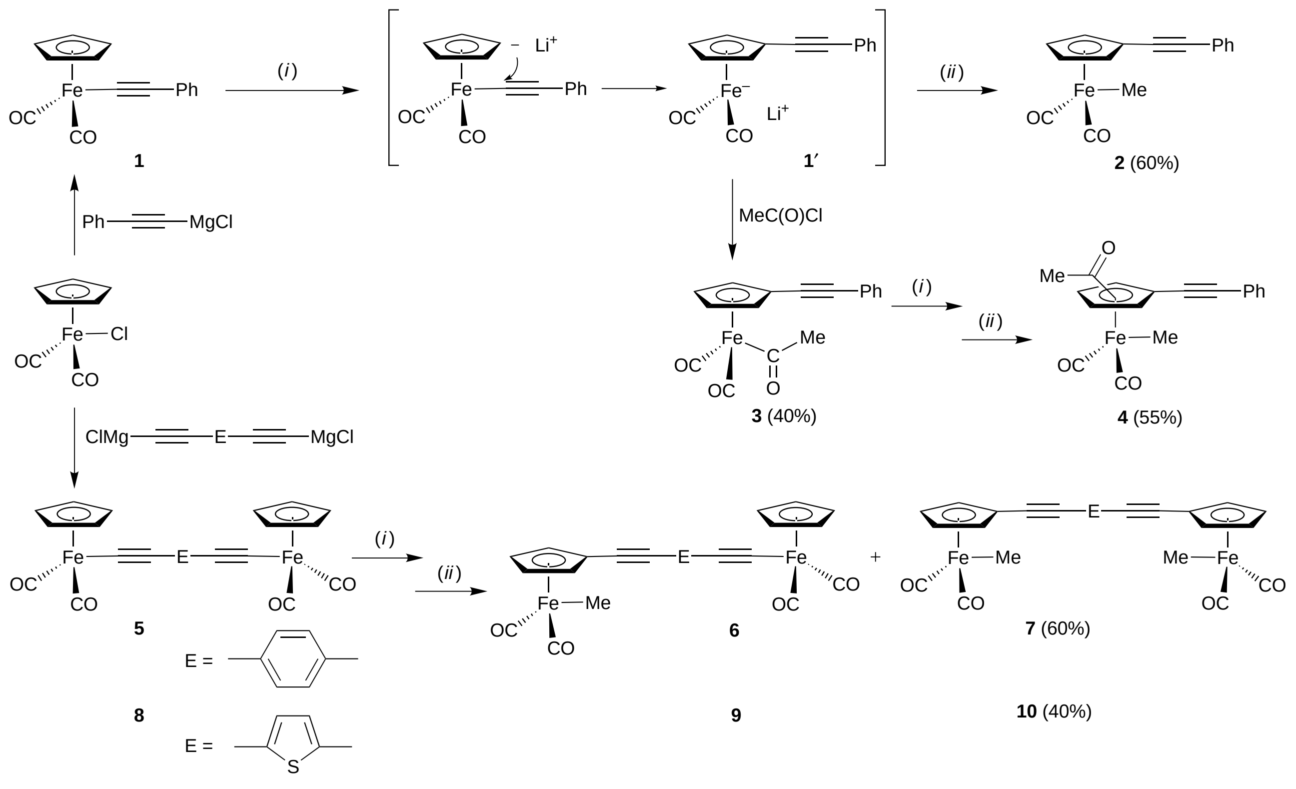
A similar anion-induced migration reaction of acetylide, yet quenching with MeC(O)Cl instead of MeI, resulted in (η^5-C_5H_4C≡CPh)Fe(CO)$_2$[C(O)Me] **3** (40%), whose molecular structure was deduced on the basis of spectroscopic data and confirmed by an X-ray structure determination,‡ revealing the 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-

---

* E-Mail: liuu@chem.sinica.edu.tw

† Typical anion-induced acetylide migration reaction. To a solution of compound **1** (1.0 mmol) in THF (50 mL) at −78 °C was added dropwise LDA (1.5 mmol in 1.0 mL of THF). The solution changed from tan yellow to dark red. The IR bands at 2108w cm^{-1} ν(C≡C), 2040s, 1993s cm^{-1} ν(CO) disappeared as two new bands showed up at 1870s, 1758s cm^{-1}. After being stirred for 30 min, an excess of MeI was added and the solution returned to tan yellow. The IR ν(CO) bands changed position to 2008s, 1952s cm^{-1}. A work-up by SiO$_2$ column chromatography (eluent 4:1 *n*-hexane–CH$_2$Cl$_2$) resulted in a yellow compound **2** (0.60 mmol, 60%). All compounds gave satisfactory elemental analyses. Selected spectroscopic data. For compound **1**. IR (CH$_2$Cl$_2$): ν(C≡C) 2108w; ν(CO) 2040s, 1993s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.30–7.06 (5 H, m, Ph), 5.04 (5 H, s, C_5H_5). ^{13}C NMR (CDCl$_3$): δ 212.3 (CO), 131.4, 127.8, 127.7 (*ipso* C), 125.3 (*p*-C), 116.5 (C_α), 88.2 (C_β), 85.2 (C_5H_5). For compound **2**. IR (CH$_2$Cl$_2$): ν(CO) 2008s, 1952s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.50–7.31 (5 H, m, Ph), 4.95 (2 H, t, $J = 2.1$, C_5H_4), 4.76 (2 H, t, $J = 2.1$ Hz, C_5H_4), 0.38 (3 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 216.4 (CO), 131.7, 128.6 (*p*-C), 128.3, 122.6 (*ipso* C), 89.4, 89.1, 84.4, 83.2, 82.2, −18.7 (Fe–Me). For compound **3**. IR (CH$_2$Cl$_2$): ν(CO) 2022s, 1964s; ν(C=O) 1639w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–7.30 (5 H, m, Ph), 5.11 (2 H, t, $J = 2.1$, C_5H_4), 4.84 (2 H, t, $J = 2.1$ Hz, C_5H_4), 2.67 (3 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 254.4 (C=O), 213.4 (CO), 131.6, 128.8 (*p*-C), 128.4, 122.2 (*ipso* C), 90.0, 89.7, 85.7, 83.9, 81.5, 51.2 [C(O)*C*H$_3$]. For compound **4**. IR (CH$_2$Cl$_2$): ν(CO) 2018s, 1970s; ν(C=O) 1682w cm^{-1}. ^{1}H NMR (1,2-isomer, CDCl$_3$): δ 7.48–7.30 (5 H, m, Ph), 5.46 (1 H), 5.12 (1 H), 4.91 (1 H), 2.52 [3 H, s, C(O)Me], 0.43 (3 H, s, Fe–Me). ^{1}H NMR (1,3-isomer, CDCl$_3$): δ 7.48–7.30 (5 H, m, Ph), 5.54 (1 H), 5.36 (1 H), 5.07 (1 H), 2.33 [3 H, s, C(O)Me], 0.43 (3 H, s, Fe–Me). For compound **5**. IR (CH$_2$Cl$_2$): ν(C≡C) 2104w; ν(CO) 2042s, 1995s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.11 (4 H, s, C_6H_4), 5.03 (10 H, s, C_5H_5). For compound **6**. IR (CH$_2$Cl$_2$): ν(C≡C) 2106w; ν(CO) 2041s, 2008sh, 1995s, 1953m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.43–7.12 (4 H, m, C_6H_4), 5.05 (5 H, s, C_5H_5), 4.91 (2 H, t, $J = 2.2$, C_5H_4), 4.74 (2 H, t, $J = 2.2$ Hz, C_5H_4), 0.35 (3 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 216.5, 212.1 (CO), 131.3, 128.1 (*ipso* C), 118.9 (*ipso* C), 116.6, 93.4, 89.9, 88.9, 85.3 (C_5H_5), 84.9 (*ipso* C), 83.1, 82.6, −18.8 (Fe–Me). For compound **7**. IR (CH$_2$Cl$_2$): ν(CO) 2010s, 1954s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.42 (4 H, s, C_6H_4), 4.95 (4 H, t, $J = 2.1$, C_5H_4), 4.77 (4 H, t, $J = 2.1$ Hz, C_5H_4), 0.36 (6 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 216.3 (CO), 131.6, 122.7 (*ipso* C), 89.3, 88.9, 84.3, 83.7, 83.3, −18.9 (Fe–Me). For compound **8**. IR (CH$_2$Cl$_2$): ν(C≡C) 2096w; ν(CO) 2042s, 1996s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.59 (2 H, s, C_4H_2S), 5.02 (10 H, s, C_5H_5). For compound **9**. IR (CH$_2$Cl$_2$): ν(C≡C) 2095w; ν(CO) 2043m, 2008s, 1998sh, 1954s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.97 (1 H, d, $J = 3.8$, C_4H_2S), 6.71 (1 H, d, $J = 3.8$, C_4H_2S), 5.05 (5 H, s, C_5H_5), 4.91 (2 H, t, $J = 2.1$, C_5H_4), 4.74 (2 H, t, $J = 2.1$ Hz, C_5H_4), 0.34 (3 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 216.4 (CO), 211.7 (CO), 132.1, 130.6, 128.2, 118.7, 107.7, 100.5, 89.4, 88.9, 85.4 (C_5H_5), 84.7, 83.4, 83.2, −18.8 (Fe–Me). For compound **10**. IR (CH$_2$Cl$_2$): ν(CO) 2008s, 1954s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.08 (2 H, s, C_4H_2S), 4.96 (4 H, t, C_5H_4), 4.78 (4 H, t, C_5H_4), 0.36 (6 H, s, Me). ^{13}C NMR (CDCl$_3$): δ 216.1 (CO), 132.3 (C_4H_2S), 124.2 (C_4H_2S *ipso* C), 89.4, 87.4, 83.4, 83.1, 81.8, −19.0 (Fe–Me).

‡ Crystal data for compound **3**. $C_{17}H_{12}FeO_3$, $M = 320.13$, triclinic, $P\bar{1}$, $a = 7.0582(6)$, $b = 9.4461(11)$, $c = 11.8836(9)$ Å, $\alpha = 70.379(7)$, $\beta = 76.162(7)$, $\gamma = 80.945(8)°$, $U = 722.07(12)$ Å^3, $Z = 2$, $F(000) = 328$, $D_c = 1.47$ g cm^{-3}, $T = 298$ K, $\lambda = 0.710\ 69$ Å, $2\theta(\text{max}) = 45.0°$, $\mu = 1.05$ mm^{-1}, transmission factors 0.894–0.998. $R = 0.029$, $R' = 0.051$, $S = 3.73$, for 33 atoms, 190 parameters and 1808 out of 1893 reflections ($I > 2.5\sigma_I$). CCDC reference number 186/873.



Scheme 1 (*i*) LDA, −78 °C; (*ii*) MeI

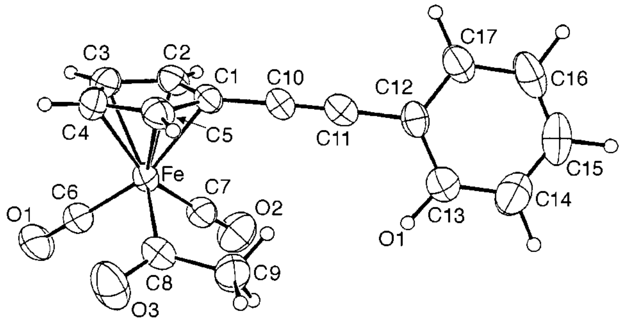


Fig. 1 An ORTEP[12] plot of complex **3**. The thermal ellipsoids for non-H atoms are plotted at the 50% probability level. Selected bond lengths (Å) and angles (°): Fe–C6 1.765(3), Fe–C7 1.764(4), Fe–C8 1.984(3), C8–O3 1.201(4), C8–C9 1.501(4), C1–C10 1.432(4), C10–C11 1.184(4), C11–C12 1.436(4); Fe–C6–O1 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 {η^5-C_5H_3(C≡Ph)-[C(O)Me]}Fe$(CO)_2$Me **4** (55% total) with two regio-isomers in *ca.* 3 : 2 ratio based on ^{1}H 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 (η^5-C_5H_5)Fe$(CO)_2$[C≡C(1,4-C_6H_4)-C≡CFe$(CO)_2$(η^5-C_5H_5)] **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$(CO)_2$Me[(η^5-C_5H_4)C≡C(1,4-C_6H_4)C≡C(η^5-C_5H_4)]Fe$(CO)_2$Me **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 (η^5-C_5H_5)Fe$(CO)_2$[C≡C(1,4-C_6H_4)C≡C(η^5-C_5H_4)]Fe$(CO)_2$Me **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 (η^5-C_5H_5)Fe$(CO)_2$[C≡C(2,5-C_4H_2S)C≡C]Fe$(CO)_2$-(η^5-C_5H_5) **8**[15] gave double-end acetylide migration product Fe$(CO)_2$Me[(η^5-C_5H_4)C≡C(2,5-C_4H_2S)C≡C(η^5-C_5H_4)]Fe-$(CO)_2$Me **10** (40%). The single-end acetylide migration product (η^5-C_5H_5)Fe$(CO)_2$[C≡C(2,5-C_4H_2S)C≡C(η^5-C_5H_4)]Fe$(CO)_2$Me **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.

Acknowledgements

The authors are indebted to Academia Sinica and the National Science Council, Republic of China for kind financial support.

References

1 W. K. Dean and W. A. G. Graham, *Inorg. Chem.*, 1977, **16**, 1061.
2 P. C. Heah and J. A. Gladysz, *J. Am. Chem. Soc.*, 1984, **106**, 7636; M. Akita and A. Kondoh, *J. Organomet. Chem.*, 1986, **299**, 369; P. C. Heah, A. T. Patton and J. A. Gladysz, *J. Am. Chem. Soc.*, 1986, **108**, 1185.
3 S. Abbot, G. L. Baird, S. G. Davies, I. M. Dordor-Hedgecock, T. R. Maberly, J. C. Walker and P. Warner, *J. Organomet. Chem.*, 1985, **289**, C13.
4 G. L. Crocco and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 6110.
5 S. R. Berryhill and B. Sharenow, *J. Organomet. Chem.*, 1981, **221**, 143; S. R. Berryhill, G. L. Clevenger and F. Y. Burdurlu, *Organometallics*, 1985, **4**, 1509.

6 J. Cervantes, S. P. Vincenti, R. N. Kapoor and K. H. Pannell, *Organometallics*, 1989, **8**, 744.
7 H. Nakazawa, M. Sone and K. Miyoshi, *Organometallics*, 1989, **8**, 1564.
8 M. L. H. Green and T. Mole, *J. Organomet. Chem.*, 1968, **12**, 404.
9 W. Malisch, G. Thum, W. Ries and D. Greissinger, *J. Organomet. Chem.*, 1983, **252**, C67.
10 K. H. Pannell, S. P. Vincenti and R. C. Scott, III, *Organometallics*, 1987, **6**, 1593.
11 M. Nitay and M. Rosenblum, *J. Organomet. Chem.*, 1977, **136**, C23; K. H. Pannell, S. Sharma, J. Cervantes, J. L. Mata-Mata, M. Brun and F. Cervantes-Lee, *Organometallics*, 1995, **14**, 4269.
12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
13 Y. Sun, N. J. Taylor and A. J. Carty, *Organometallics*, 1992, **11**, 4293; D. L. Lichtenberger, S. K. Renshaw, A. Wong and C. Tagge, *Organometallics*, 1993, **12**, 3522; W. Beck, B. Niemer and M. Wieser, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 923; H. Lang, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 547; U. H. F. Bunz, V. Enkelmann and F. Beer, *Organometallics*, 1995, **14**, 2490; J. E. C. Wiegelmann-Kreiter and U. H. F. Bunz, *Organometallics*, 1995, **14**, 4449; T. Bartik, B. Bartik, M. Brady, R. Dembinsky and J. A. Gladysz, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 414; U. H. F. Bunz, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 969.
14 A. Wong, P. C. W. Kang, C. D. Tagge and D. R. Leon, *Organometallics*, 1990, **9**, 1992; E. Viola, C. L. Sterzo, R. Crescenzi and G. Frachey, *J. Organomet. Chem.*, 1995, **493**, 55; M. I. Bruce, M. Ke and P. Low, *Chem. Commun.*, 1996, 2405; O. Lavastre, M. Even and P. H. Dixneuf, *Organometallics*, 1996, **15**, 1530.
15 E. Viola, C. L. Sterzo, R. Crescenzi and G. Frachey, *J. Organomet. Chem.*, 1995, **493**, C9; E. Viola, C. L. Sterzo and F. Trezzi, *Organometallics*, 1996, **15**, 4352.

Received 19*th December* 1997; *Communication* 7/09100A