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

Ling-Kang Liu,*a,b Kuo-Yang Chang,c 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

doi: 10.1021/ja00031a003

© 1998 American Chemical Society

The anion-induced migration reaction of acetylide in \((\eta^1-C_5H_5)\-Fe(CO)\(_2\)(C\(_5\)H\(_5\))\) was observed in a sequential treatment of lithium disopropylamide followed by an excess of MeI, giving a yellow compound \((\eta^1-C_5H_5)\-Fe(CO)\(_2\)(C\(_5\)H\(_5\))\). The NMR spectrum of this compound shows signals for \(\delta = 78.0\) ppm, which is consistent with the presence of the Fe-Cr bond. The synthesized compound is diamagnetic, and its molecular weight is consistent with the expected value.

The anion-induced migration reaction of acetylide from a metal atom to a neighboring cyclopentadienyl carbon atom has been known for about 20 years. 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, ester, hydride, and heteroatom-containing \((Si, Ge, Sn, P)\) 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^1-C_5H_5)\-Fe(CO)\(_2\)(C\(_5\)H\(_5\))\) at \(-78°C\), was added dropwise lithium disopropylamide \((\text{LDA}, 1.5 \text{ equivalents})\) and was stirred for a short time before an excess of MeI was added to give a yellow compound \((\eta^1-C_5H_5)\-Fe(CO)\(_2\)(C\(_5\)H\(_5\))Me\). Typical anion-induced acetylide migration reaction. To a solution of compound 1 (1.0 mmol) in THF (50 mL) at \(-78°C\), was added MeI (1.5 mmol in 1.0 mL of THF). The solution changed from tan yellow to dark red. The IR bands at 2108 cm\(^{-1}\) (MeI) disappeared and an new band showed up at 1758 cm\(^{-1}\). After being stirred for 30 min, an excess of MeI was added and the solution returned to tan yellow. The IR w-c bands changed position to 2088, 1525 cm\(^{-1}\).

† 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 2108 cm\(^{-1}\) (MeI) disappeared and an new band showed up at 1758 cm\(^{-1}\). After being stirred for 30 min, an excess of MeI was added and the solution returned to tan yellow. The IR w-c bands changed position to 2088, 1525 cm\(^{-1}\).

† Crystal data for compound 3. \(C_{12}H_{18}FeO\). M = 330.13, triclinic, \(P\(\bar{1}\), \(a = 7.0582(6)\), \(b = 9.440(1)\), \(c = 11.836(9)\), \(\beta = 76.162(7)\), \(\gamma = 89.054(8)\).\) U = 722.07(12) \(A^3\). Z = 2, \(F(000) = 328, D_c = 1.47 \text{ g cm}^{-3}\). \(T = 298 \text{ K}, \lambda = 0.70169 \text{ Å}, \Delta = 0.005 = 45.0\text{°}, m = 0.15 \text{ mm}^{-1}\). Transmission factors 0.894-0.998. \(R = 0.029, R_p = 0.051, S = 3.73\). E = 15, for 33 atoms, 190 parameters and 1580 of 1893 reflections (\(2 > 2\sigma(I)\)). CCDC reference number 86873.
ceed with an acetyl migration to give \( \text{Fe} \text{Me} \text{Fe} \text{Me} \text{C} \text{Me} \text{Fe} \text{Me} \text{Fe} \text{Me} \) (55%).

The single-end acetylide migration product 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 \( \nu(\text{CO}) \) 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**


Received 19th December 1997; Communication 709100A