Tetrahedron Letters No. 15, pp 1229 - 1232, 1976. Pergamon Press. Printed in Great Britain.

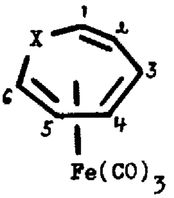
THE CYCLOADDITION REACTION OF TROPONEIRONTRICARBONYL AND TETRACYANOETHYLENE

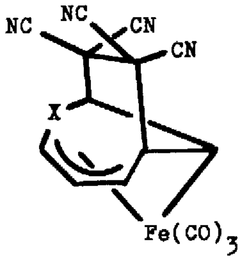
Zeev Goldschmidt* and Y. Bakal

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

(Received in UK 3 February 1976; accepted for publication 1 March 1976)

The ability of transition metals to alter the reactivity of coordinated olefins toward cycloaddition reactions is a current topic of interest. The elegant studies by Green[1] and subsequently by Paquette[2] have revealed that tricarbonyliron complexes of cycloheptatriene (1) and cyclooctatetraene (2) undergo a facile 1,3-exo-cycloaddition reaction with uniparticulate electrophiles,[3] e.g tetracyanoethylene (TCNE), forming the novel σ,π-iron complexes 3 and 4 respectively.





1 X = CH_2 3

2 X = CH=CH 4

We wish to report that the reaction of troponeirontricarbonyl (5) with TCNE yields a new σ,π-iron bonded adduct 6, arising from the yet unobserved 1,5-exo-cycloaddition. We also wish to disclose some mechanistic features concerning the initial site of attack by the electrophile on the coordinated ligand.

Stirring an equimolar CH_2Cl_2 solution of troponeirontricarbonyl[4] and freshly sublimed TCNE at room temperature (4 hr.) gave a 90% yield of the 1:1 adduct 6 as a yellow precipitate[5] which was recrystallized from acetone-pentane, mp. 148-150° (dec.). The structural assignment of 6 was established from its spectroscopic data m/e (70 eV) 246 (M-TCNE), 218, 190, 162, 106 (246-$Fe(CO)_3$), ir (nujol) 2010, 2020, 2100 (coordinated CO), 1665 (carbonyl CO) cm^{-1}. The nmr spectrum (in$(CD_3)_2CO$) is particularly instructive, displaying signals at δ 2.26 (H_6,dd, J = 9, 2), 3.92 (H_1,dd,8.5,2), 4.19 (H_5,dd,9,7.5), 4.53 (H_4,dt,7.5,6,2), 5.27 (H_2,dt,8.5,7,2), 5.64 (H_3,bt,7,6)[6] The close resemblance to an analogous complex 7 previously prepared by Eisenstadt[7] via a different route is noteworthy.

As noted earlier by Green[1] and Paquette[2], initial electrophilic attack on complexed cyclic polyolefins may *a priori* occur on either a coordinated or free double bond, *exo* to the iron, forming a dipolar transient 8, which collapses to product by nucleophilic attack of the carbanion on position 3 of the pentadienyl moiety with formation of an Fe-C_2 σ bond. Accordingly, an analogous dipolar transient 9 would represent the first step in the reaction of the tropone complex and TCNE. In this case however, the carbanion prefers to attack at C_5 rather than at C_3 with formation of an Fe-C_6 σ bond.

This reversed selectivity could suggest the dominant intervention of electronic factors in stabilizing, by carbonyl conjugation, the transition state leading to the 1,5-adduct over the otherwise prefered transition state for the 1,3-cycloaddition.[8]

Finally, to further elucidate the mechanistic details of this intriguing cycloaddition, a study aimed at revealing the initial position of electrophilic attack was undertaken by selectively labeling one of the two possible reaction sites.

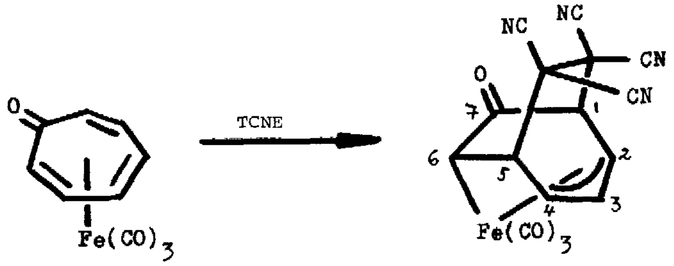
1-d-Troponeirontricarbonyl (10) (32% deuterium by nmr)[9] was prepared according to Eisenstadt[10] and Hunt[4] by treating 5 with D_2SO_4-CH_2Cl_2 at 0° for 5 hr., quenching with CH_3OH-K_2CO_3 and treating the crude 1,2-adduct with HBF_4 in Ac_2O. The isolated fluoborate salt wad decomposed with Et_3N-CH_2Cl_2 to give 10.

Clearly, the fate of the deuterium in the TCNE adduct should distinguish between the two alternative pathways, labeling C_1 if the free bond is electrophilicly attacked and C_6 if the coordinated carbon is attacked first Nmr analysis of the resulting adduct shows unambiguously that all the deuterium is found exclusively at position 1 (11). Thus we conclude that the cycloaddition reactions of TCNE and complexed cyclic polyolefins involve initial electrophilic addition to a noncoordinated double bond.

Further studies concerning the effect of electronic and other factors on the cycloaddition are in progress

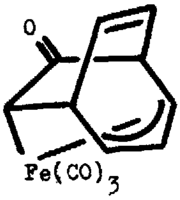
Acknowledgement:

We gratefully acknowledge helpful discussion with Dr. S. Hoz. The partial support of this research by the Bar-Ilan Research Committee under Grant No 161-84-15-8 is also gratefully acknowledged.

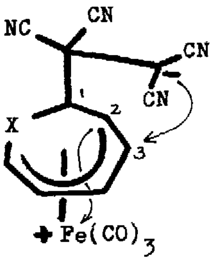

O
TCNE
Fe(CO)$_3$
NC
NC
CN
CN
O
7
1
2
6
5
3
4
Fe(CO)$_3$

5

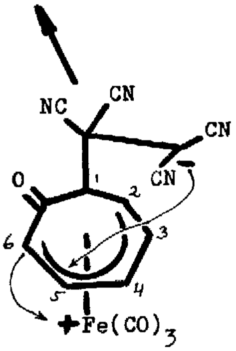
6


O
Fe(CO)$_3$

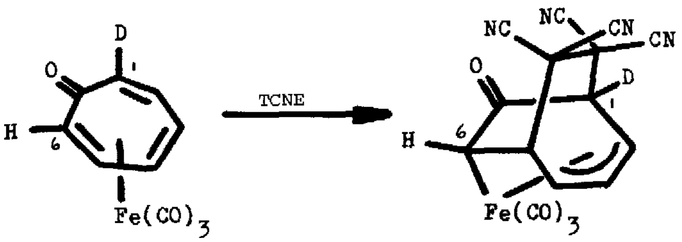
7


NC
CN
CN
CN
1
2
X
3
+Fe(CO)$_3$

8


NC
CN
CN
O
CN
1
2
6
3
5
4
+Fe(CO)$_3$

9


D
O
1
H
6
Fe(CO)$_3$
TCNE
NC
NC
CN
CN
O
D
1
H
6
Fe(CO)$_3$

10

11

References and Footnotes

1) M Green, S. Heathcock and D.C Wood, *J.C.S. Dalton*, 1564 (1973).

2) L A. Paquette, S V Ley, S Maiorana, D.F. Schneider, M.J. Broadhurst and R.A Boggs, *J Amer. Chem. Soc.*, **97**, 4658 (1975).

3) L A. Paquette, G R. Allen and M.J Broadhurst, *ibid.*, **93**, 4503 (1971)

4) D.F. Hunt, G.C Farrant and R.T. Rodheaver, *J Organomet. Chem*, **38**, 349 (1972).

5) Elemental analysis. ($C_{16}H_6FeN_4O_4$) C, H, Fe, N.

6) Nmr assignments were confirmed by decoupling experiments.

7) A. Eisenstadt, *Tetrahedron Letters*, 2005 (1972)

8) The interesting question why a 1,5-cycloaddition is not observed in cycloheptatriene and cyclooctateraene complexes, has not yet been considered. It may be argued that steric effects in the two nonplanar complexes prevent this mode of reaction However, such an argument requires a concerted mechanism or one in which there will not be a full development of the planar pentadienyl transient **8**.

9) Deuteration at the C_6 position was less than 10%

10) A Eisenstadt, J.M. Guss and R Mason, *J. Organomet. Chem.*, **80**, 245 (1973).