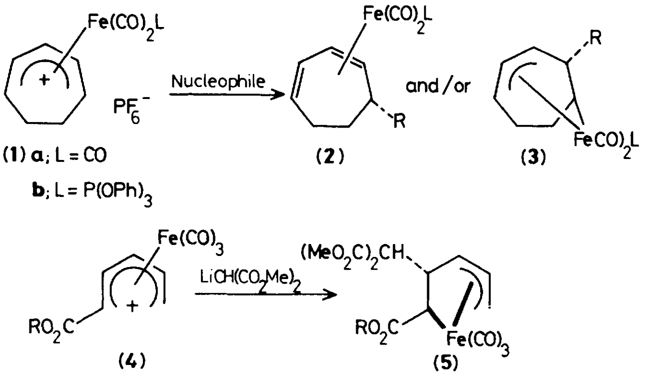
Preparation and Reactions of Methoxycarbonyl-substituted Cycloheptadienyliron Tricarbonyl Cations: Unusual Regiochemistry during the Addition of Stabilized Enolate Nucleophiles

Anthony J. Pearson* and Marco P. Burello

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

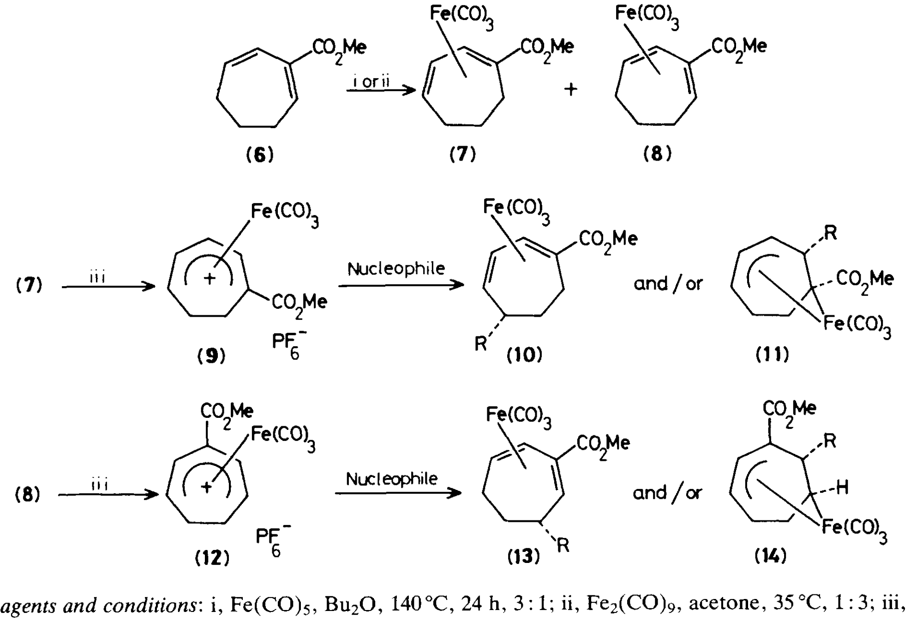
Tricarbonyl(1-methoxycarbonylcycloheptadienyl)iron hexafluorophosphate (**9**) and tricarbonyl(3-methoxycarbonylcycloheptadienyl)iron hexafluorophosphate (**12**) were prepared and their reactions with a range of nucleophiles were examined. Cyanide, borohydride, and malonate enolate all added exclusively to C-2 of (**9**) and predominantly to C-2 of (**12**), while Me_2CuLi, hydroxide, and potassium phthalimide all reacted at C-1 of both complexes. The unusual regioselectivity during additions of $NaCH(CO_2Me)_2$ reflects a considerable perturbation of the dienyl–Fe system by the ester substituent.

We have previously reported[1] on the chemistry and synthetic applications of cationic cycloheptadienyl–$Fe(CO)_2L$ complexes (**1**). Nucleophile addition to these systems generally occurs either at C-1 or C-2 to give adducts of structure (**2**) or (**3**), respectively, depending on the nature of the nucleophile and the ligand L. With complex (**1b**), soft nucleophiles such as the stabilized enolate $NaCH(CO_2Me)_2$, cuprates (R_2CuLi), and thiophenoxide, give exclusively (**2**) [L = $P(OPh)_3$], while 'harder' nucleophiles, such as Grignard reagents, $NaBH_4$, and NaCN give exclusively (**3**) [L = $P(OPh)_3$]. When the tricarbonyliron complex (**1a**) is used, yields are usually low, side products are evident, and mixtures of regioisomers (**2**) and (**3**) are obtained from reactions with, *e.g.*, NaCN and $NaBH_4$. This behaviour appears to be consistent with competing frontier orbital (FMO) *vs.* charge control, since the lowest unoccupied MO (LUMO) of the dienyliron complex has largest coefficients[2] at the terminal carbons C-1 and C-5, while ^{13}C n.m.r. studies[3] and MO calculations[2,4] indicate that C-2 and C-4 carry the greatest amounts of positive charge. Therefore, nucleophiles whose highest occupied molecular orbital (HOMO) is closer in energy to the complex LUMO will react under FMO control (at C-1/C-5) while those having lower energy HOMO will add under charge control (at C-2/C-4).[5] A recent report from Donaldson and Ramaswamy,[6] in which it was observed that $LiCH(CO_2Me)_2$ adds predominantly (>20:1) at C-2 of the acyclic pentadienyl–$Fe(CO)_3$ complex (**4**) (Scheme 1), prompts us to disclose the results of our own studies on the related complexes (**9**) and (**12**).

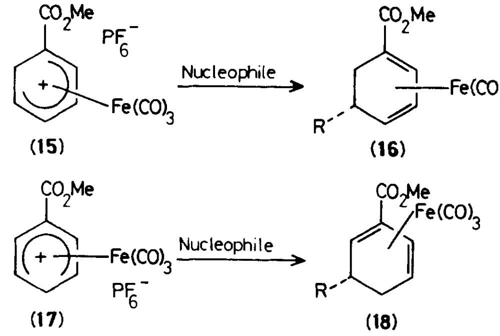


Scheme 1

The cycloheptadiene (**6**) was prepared according to the method of Pawlak and Berchtold.[7] Treatment of (**6**) with pentacarbonyliron in refluxing di-n-butyl ether gave a 3:1 mixture of diene complexes (**7**) and (**8**) in 75% combined yield, while the use of milder reaction conditions [$Fe_2(CO)_9$, acetone, 35 °C] gave a 1:3 mixture of (**7**) and (**8**) (74% yield). These complexes were separated by flash chromatography. Hydride abstraction (Ph_3CPF_6, CH_2Cl_2) proceeded regioselectively, (**7**) giving (**9**) (95% yield) and (**8**) giving (**12**)



Scheme 2. *Reagents and conditions*: i, $Fe(CO)_5$, Bu_2O, 140 °C, 24 h, 3:1; ii, $Fe_2(CO)_9$, acetone, 35 °C, 1:3; iii, Ph_3CPF_6.



Scheme 3

Table 1. Nucleophile additions to complexes (**9**) and (**12**).

Complex	Nucleophile	Product(s) (yield)
(**9**)	PhS^-	(**10**) R = PhS (81%)
(**9**)	Me_2CuLi	(**10**) R = Me (64%)
(**9**)	OH^-	(**10**) R = OH (36%)
(**9**)	K phthalimide	(**10**) R = $N(CO)_2C_6H_4$ (84%)[a]
(**9**)	$NaBH_4$	(**11**) R = H (60%)
(**9**)	NaCN/acetonitrile	(**11**) R = CN (88%)
(**9**)	$NaCH(CO_2Me)_2$	(**11**) R = $CH(CO_2Me)_2$ (82%)
(**12**)	PhS^-	(**13**) R = SPh (88%)
(**12**)	Me_2CuLi	(**13**) R = Me (64%)
(**12**)	OH^-	(**13**) R = OH (63%)
(**12**)	K phthalimide	(**13**) R = $N(CO)_2C_6H_4$ (70%)[a]
(**12**)	$NaBH_4$	(**14**) R = H (60%)
(**12**)	NaCN/acetonitrile	(**14**) R = CN (56%)
(**12**)	$NaCH(CO_2Me)_2$	(**13**) (21%); (**14**) (62%), R = $CH(CO_2Me)_2$

[a] The phthalimide adducts are unstable and could not be fully purified by chromatography. These yields are approximate.

(67% yield). The reactions of (**9**) and (**12**) with a series of simple nucleophiles were examined (Scheme 2), and the results are summarized in Table 1.[8]

There are two noteworthy features of these results. Firstly, the yields obtained during nucleophile additions to (**9**) and (**12**) are generally better than those from complex (**1a**), fewer by-products being formed. Secondly, the regioselectivity during these reactions is more pronounced than for (**1a**), particularly with borohydride and cyanide, which lead to mixtures of (**2**) and (**3**) on reaction with (**1a**), but which give single products on reaction with (**9**) or (**12**). The most noteworthy observation is that the reaction of dimethyl sodiomalonate with (**9**) gives exclusively the C-2 adduct (**11**), and with (**12**) gives a 3 : 1 mixture in favour of the C-2 adduct (**14**). This agrees with Donaldson's results for the acyclic pentadienyl complex (**4**), but is in stark contrast to those for (**1a**) or (**1b**), both of which give exclusively C-1 adducts (**2**) [R = $CH(CO_2Me)_2$]. Furthermore, the analogous cyclohexadienyl-Fe(CO)$_3$ complexes (**15**) and (**17**) only give terminal addition products (**16**) and (**18**) on reaction with all nucleophiles studied[9] (Scheme 3).

The differences in behaviour between six-membered ring dienyl-Fe(CO)$_3$ complexes and their cycloheptadienyl and acyclic dienyl counterparts has never been fully explained. The results presented here and earlier[1] indicate that significant changes in reactivity occur when the electronic character of the cycloheptadienyl ligand is perturbed. In the present case, the introduction of an electron withdrawing group may shift the MO energy levels of the complex in such a way that the LUMO is now higher. This would place it further away from, *e.g.*, the malonate enolate HOMO, thereby leading to a weaker FMO interaction, and resulting in essentially total charge control. While a complete rationalization must await a proper theoretical treatment, it is clear that substituent effects on regioselectivity may be quite dramatic.

We are grateful to the U.S. Public Health Service, National Institutes of Health, for financial support of this research (grant GM 32114).

Received, 15th May 1989; Com. 9/02021G

References

1 A. J. Pearson, S. L. Kole, and T. Ray, *J. Am. Chem. Soc.*, 1984, **106**, 6060, and references cited therein; A. J. Pearson and T. Ray, *Tetrahedron Lett.*, 1986, **27**, 3111; A. J. Pearson and Y. S. Lai, *J. Chem. Soc., Chem. Commun.*, 1988, 442.

2 O. Eisenstein, W. M. Butler, and A. J. Pearson, *Organometallics*, 1984, **3**, 1150; R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, 1976, **98**, 107.

3 A. J. Birch, P. W. Westerman, and A. J. Pearson, *Aust. J. Chem.*, 1976, **29**, 1671; A. I. Rezvukhin, V. N. Piottukh-Peletskii, R. N. Berezina, and V. G. Shubin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, 694.

4 D. W. Clack, M. Monshi, and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, 1976, **107**, C40.

5 G. Klopman, *J. Am. Chem. Soc.*, 1968, **90**, 223; L. Salem, *J. Am. Chem. Soc.*, 1968, **90**, 543 and 553. For an excellent discussion of charge *vs.* orbital control during nucleophile additions to organic substrates, see: I. Fleming 'Frontier Orbitals and Organic Chemical Reactions,' John Wiley & Sons, Chichester, 1976, pp. 37—47.

6 W. A. Donaldson and M. Ramaswamy, *Tetrahedron Lett.*, 1989, **30**, 1339 and 1343.

7 J. L. Pawlak and G. A. Berchtold, *J. Org. Chem.*, 1988, **53**, 4063.

8 New compounds were fully characterized by 200 MHz ^1H n.m.r., high resolution mass, and i.r. spectroscopy, and purity was established by combustion analysis.

9 A. J. Pearson and M. W. Zettler, *J. Am. Chem. Soc.*, 1989, **111**, 3908; A. J. Birch and D. H. Williamson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1892; B. M. R. Bandara, A. J. Birch, and L. F. Kelly, *J. Org. Chem.*, 1984, **49**, 2496; A. J. Birch, L. F. Kelly, and D. V. Weerasuria, *J. Org. Chem.*, 1988, **53**, 278.