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REACTION OF ORGANOLITHIUM REAGENTS WITH η^5-PENTADIENYL IRON COMPLEXES: FORMATION OF σ,η^3-IRON COMPLEXES

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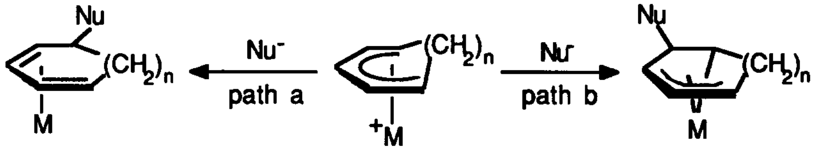
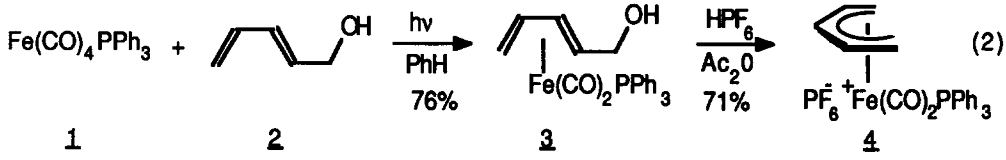
Summary: Reaction of organolithium reagents with η^5-pentadienyl iron complex 4 occurs at the C2/C4 position of the π-system, generating σ,η^3-iron complexes 5. Air oxidation of these σ,η^3-iron complexes generates cyclohexenones. Reaction of the slightly more electron-poor η^5-pentadienyl iron complex 11 gives nucleophilic attack at both the C2/C4 and the C1/C5 position.

The regioselective reaction of nucleophiles at the terminus of the π-system of cationic (η^5-cyclohexadienyl)iron tricarbonyl complexes to produce η^4-cyclohexadiene iron complexes (Eq. 1, path a, M=Fe(CO)$_3$, n=1) has been intensely studied and utilized in organic synthesis.[1,2] The literature, however, also contains scattered reports of nucleophilic attack at the C2 position of cationic η^5-dienyl transition metal complexes, especially with acyclic η^5-pentadienyl and η^5-cycloheptadienyl complexes, generating σ,η^3-complexes[3,4] (Eq. 1, path b). Although few detailed studies have been reported,[5] it appears that the regioselectivity of this reaction depends on a variety of factors, including the nature of the nucleophile, the electronic characteristics of the metal and its ligands, and the substituents on the η^5-dienyl system. Our interest in the chemistry of σ,η^3-transition metal complexes led us to investigate the reaction of nucleophiles with η^5-pentadienyl iron complexes as a general route to σ,η^3-iron complexes.



(1)

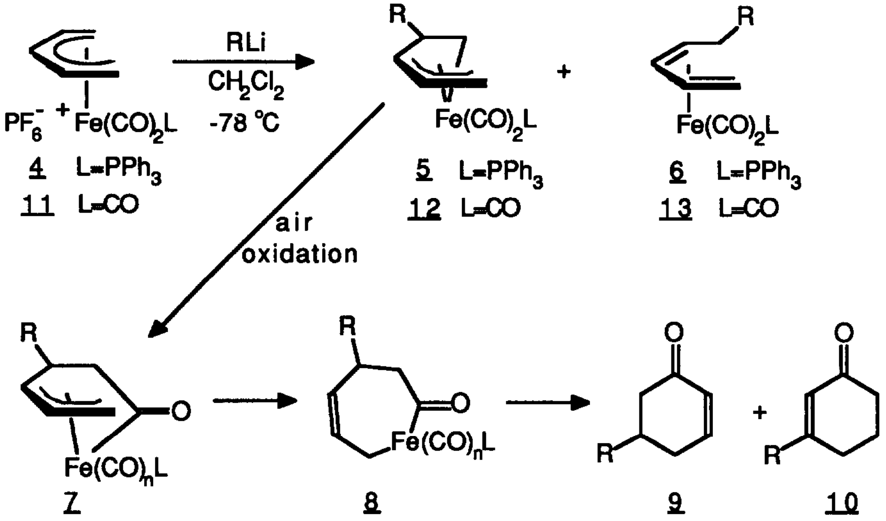
Since it appeared from the literature that nucleophilic attack at the C2 position of η^5-pentadienyl iron complexes would be enhanced by the use of electron donating spectator ligands,[3a,b,c] a study of the reactivity of η^5-pentadienyl iron complex 4 was initiated. Irradiation of Fe(CO)$_4$PPh$_3$ (1)[6] in benzene in the presence of 2,4-pentadien-1-ol (2)[7] provided iron diene complex 3 in 76% yield.[8,9] Reaction of 3 with hexafluorophosphoric acid generated cationic η^5-pentadienyl iron complex 4 in 71% yield[10] (Eq. 2). Complex 4 is a yellow crystalline solid which can be stored at room temperature in the air for at least six months without decomposition.



(2)

Since Pearson has reported that the reaction of organolithium reagents with cationic η^5-cycloheptadienyl iron dicarbonyl triphenylphosphine complexes takes place mainly at the C2 position of the π-system,[3c] the reaction of 4 with several lithium reagents was explored. Thus, reaction of methyllithium, n-butyllithium, or phenyllithium with 4 at -78°C in dichloromethane generates σ,η^3-iron complex 5 in near quantitative yield, along with very small amounts of iron diene complex 6 (Scheme 1). Although 5 decomposes readily in air (vide infra), ^{1}H NMR and IR data[11] confirm formation of the desired σ,η^3-iron complex resulting from attack at the C2/C4 position of the η^5-pentadienyl complex. The large upfield shift (to -0.62 ppm) of the H_{1anti} proton is especially indicative of a metal-carbon σ-bonded species.[3a,d]

The instability of σ,η^3-iron complexes 5 in air apparently is the result of an oxidatively-induced reductive coupling of iron acyl complex 7, formed by a facile insertion of carbon monoxide into the metal-carbon σ-bond of σ,η^3-complex 5 (Scheme 1). This reductive coupling takes place upon stirring a solution of 5 in dichloromethane in air for 12-24 hours *without the addition of carbon monoxide*, producing cyclohexenones 9 and 10 (Table 1) in moderate yield.[12,13] It should be noted that the σ,η^3-cycloheptenediyl iron complex produced by the reaction of nucleophiles with η^5-cycloheptadienyliron cations fails to undergo this transformation unless subjected to high pressures of carbon monoxide and high temperatures or strongly oxidizing conditions.[14]



Scheme 1

In order to determine if the triphenylphosphine ligand is necessary for this reaction to occur, η^5-pentadienyliron complex 11[15] was reacted with organolithium reagents under the same conditions used for reactions of complex 4. This reaction, after air oxidation, also produces cyclohexenones 9 and 10, the result of nucleophilic attack at the internal position of the π-system, along with considerable amounts of η^4-diene complex 13 (Scheme 1, Table 1). It appears, therefore, that replacing a carbonyl ligand with a phosphine in this system does promote nucleophilic attack at the internal position, as expected. This result follows the predictions of Davies, Green, and Mingos[15] that nucleophilic attack on open odd π-systems with electron-rich metal centers should take place at the even numbered carbons.

Table 1. Yields of 2-cyclohexenones vs. iron diene complexes: Comparison of attack at C2/C4 to attack at C1/C5

R	L	9	10	6/13	C2/C4:C1/C5
Me	PPh_3	15%	21%	<1%	>36:1
"	CO	25%	10%	30%	1.2:1
nBu	PPh_3	35%	31%	<1%	>66:1
"	CO	10%	8%	25%	1:1.4
Ph	PPh_3	31%	36%	<1%	>67:1
"	CO	10%	8%	12%	1.5:1

From these results it is apparent that, in contrast to the reaction of η^5-cyclohexadienyl iron complexes, where internal attack has not been reported, the reaction of nucleophiles at the two position of both η^5-pentadienyl and η^5-cycloheptadienyl iron complexes is favored over reaction at the terminus of the π-system in some cases. Also, the transformation of the resulting σ,η^3-iron complex into 2-cyclohexenones under mild conditions demonstrates the potential reactivity of such systems. Current studies include the examination of different spectator ligand combinations on the reactivity of the η^5-iron complex, the range of suitable nucleophiles, and the effect of substitution in the pentadienyl system. Further transformations of the σ,η^3-iron complex are also under investigation.

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References and Notes

1. a) Birch, A.J., *J. Organomet. Chem.* **1985,** *285,* 267. b) Pearson, A.J.; Kole, S.J.; Yoon, J. *Organometallics* **1985,** *5,* 2075. c) Pearson, A.J.; Ray, T. *Tetrahedron* **1985,** *41,* 5765. d) Ghazy, T.; Kane-Maguire, L.A.P. *J. Organomet. Chem.* **1988,** *338,* 47. e) Howard, P.W.; Stephenson, G.R.; Taylor, S.C. *J. Organomet. Chem.* **1988,** *339,* C5. f) Howell, J.A.S.; Tivengadum, M.-C.; Walton, G. *J. Organomet. Chem.* **1988,** *338,* 217.

2. The chemistry of η^5-cyclohexadienyl manganese complexes has also been investigated in detail. a) Chung, Y.K.; Choi, H.S.; Sweigart, D.A.; Connelly, N.G. *J. Amer. Chem. Soc.* **1982,** *104,* 4245. b) Chung, Y.K.; Sweigart, D.A. *J. Organomet. Chem.* **1986,** *308* , 223.

3. a) Bleeke, J.R.; Hays, M.K. *Organometallics* **1987,** *6,* 1367. b) Bleeke, J.R.; Rauscher, J.J.; *J. Amer. Chem. Soc.* **1989,** *111,* 8972. c) Pearson, A.J.; Kole, S.L.; Ray, T. *J. Amer. Chem. Soc.* **1984,** *106,* 6060. d) Donaldson, W.A.; Ramaswamy, M. *Tet. Lett.* **1989,** *30,* 1343. e) Edwards, R.; Howell, J.A.S.; Johnson, B.F.G.; Lewis, J. *J. Chem. Soc. Dalton Trans.* **1974,** 2105.

f) Cotton, F.A.; Deeming, A.J.; Josty, P.L.; Ullah, S.S.; Domingos, A.J.P.; Johnson, B.F.G.; Lewis, J. *J. Amer. Chem. Soc.* **1971**, *93*, 4624. g) Evans, J.; Johnson, B.F.J.; Lewis, J. *J. Chem. Soc. Dalton Trans.* **1972**, 2668. h) Domingos, A.J.P.; Johnson, B.F.G.; Lewis, J. *J. Chem. Soc. Dalt. Trans.* **1975**, 2288. i) Sosinsky, B.A.; Knox, S.A.R.; Stone, F.G.A. *J. Chem. Soc. Dalt. Trans.* **1975**, 1633.

4. The literature apparently contains only one example of nucleophilic attack at the C2 position of an η^5–cyclohexadienyl transition metal complex (osmium). See Burrows, A.L.; Johnson, B.F.G.; Lewis, J.; Parker, D.G. *J. Organomet. Chem.* **1980**, *194*, C11.

5. See, however, reference 3c for an in-depth study of the reactivity of η^5-cycloheptadienyl iron complexes.

6. Albers, M.L.; Coville, N.J.; Singleton, E. *J. Chem. Soc., Chem. Comm.* **1982**, 96.

7. Schneider, M.D.; Goldbach, M. *J. Amer. Chem. Soc.* **1980**, *102*, 6114.

8. Irradiation of iron carbonyl complexes in the presence of conjugated dienes has been used previously to prepare iron diene complexes. See, for example, Howell, J.A.S.; Thomas, M.J. *J. Chem. Soc. Dalton Trans.* **1983**, 1401.

9. 3: ^{1}H NMR ($CDCl_3$,90 MHz) δ 7.39 (s, 15H, ArH), 5.19 (dd, J=7, 4.5 Hz, 1H, H_4), 4.55 (m, 1H, H_3), 3.72 (d, J=6.3 Hz, 2H, $-CH_2-$), 1.52 (bs, 1H, -OH), 0.80 (m, 2H, H_2,H_{5syn}), 0.032 (bt, J=6.3 Hz, 1H, H_{5anti}). ^{13}C NMR ($CDCl_3$ 100 MHz) δ 220.6, 215.1, 135.5 (d, J_{P-C}=40.1 Hz), 133.1 (d, J_{P-C}=12.2 Hz), 129.8, 128.2 (d, J_{P-C}=9.2 Hz), 84.2, 84.1, 65.8, 56.4, 44.3. Characteristic IR peaks (neat) 1972, 1910 cm^{-1}. Anal. Calcd for $C_{25}H_{23}FeO_3P$: C, 65.52; H, 5.06. Found: C, 65.36; H, 5.10.

10. 4: ^{1}H NMR (CD_3NO_2, 90 MHz) δ 7.60 (bs, 15H, ArH), 6.81 (t, J=6.8 Hz, 1H, H_3), 5.54 (bs, 2H, H_2), 2.91 (bs, 2H, H_{1syn}). 1.71 (d, J=12.2 Hz, 2H, H_{1anti}). ^{13}C NMR (CD_3NO_2 100 MHz) 133.7 (d, J=9.5 Hz), 132.9 (d, J-3.0 Hz), 131.9 (d, J-44.2 Hz), 130, 4 (d, J-10.3 Hz), 103.27, 98.73, 64.07 ($C\equiv O$ not observed). Characteristic IR peaks (CH_2Cl_2) 2052, 2009, 838 cm^{-1}, Anal. Calcd for $C_{25}H_{22}F_6FeO_2P_2$: C, 51.22; H, 3.78. Found: C, 51.45; H, 3.85.

11. 5(R=Ph): ^{1}H NMR ($CDCl_3$, 90MHz) δ 7.3 (m, 20H, ArH), 4.3-4.0 (m, 3H, H_2, H_3, H_4), 2.55 (bs, 1H, H_{5syn}), 2.02 (m, 1H, H_{5anti}), 1.04 (m, 1H, H_{1syn}), -0.62(bt, J=8 Hz, 1H, H_{1anti}). Characteristic IR peaks (neat) 1979, 1920 cm^{-1}).

12. Formation of cyclohexenones from σ,η^3-iron complexes has been noted previously. See a) Aumann, R. *J. Amer. Chem. Soc.* **1974**, *96*, 2631. b) Victor, R.; Ben-Shoshan, R.; Sarel, S. *Tet. Lett.* **1970**, 4253.

13. All compounds have been characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectroscopy. All new compounds gave acceptable combustion or HRMS analysis.

14. Eilbracht, P.; Jelitte, R.; Trabold, P. *Chem. Ber.* **1986**, *119*, 169.

15. Mahler, J.E.; Pettit, R. *J. Amer. Chem. Soc.* **1963**, *85*, 3955.

16. Davies, S.G.: Green, M.L.H.: Mingos, D.M.P. *Tetrahedron* **1978**, *34*, 3047.

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