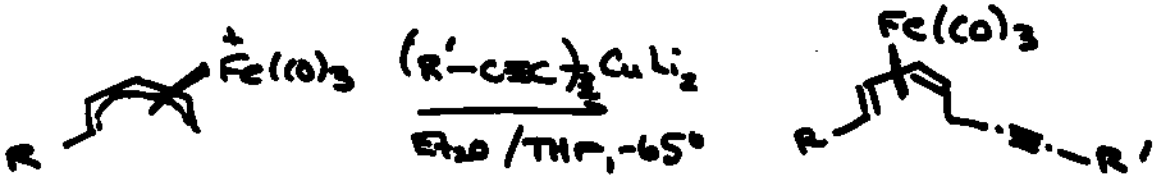
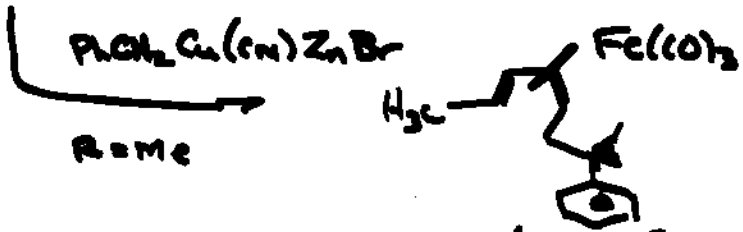
THE ACYCLIC CASES ARE SOMEWHAT LESS WELL STUDIED, BUT...



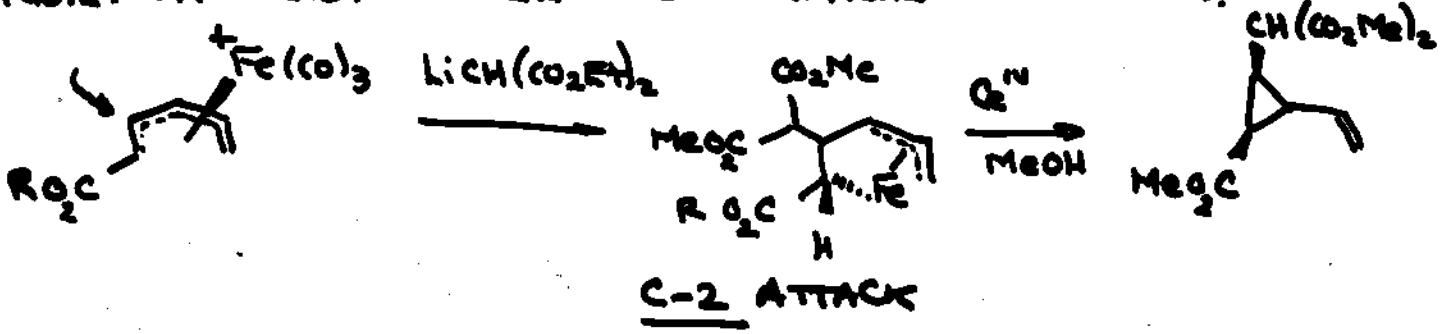


DONALDSON, W.A. ET AL TETRAHEDRON LETT. 1989, 30, 1339.

ALSO RNH_2, H_2O, R_2CdI, R'–≡–$SiMe_3$ + F^-, $NaBH_3CN$,
SILYLENOL ETHERS & ALLYLSILANES (TRANS PRODUCTS!).

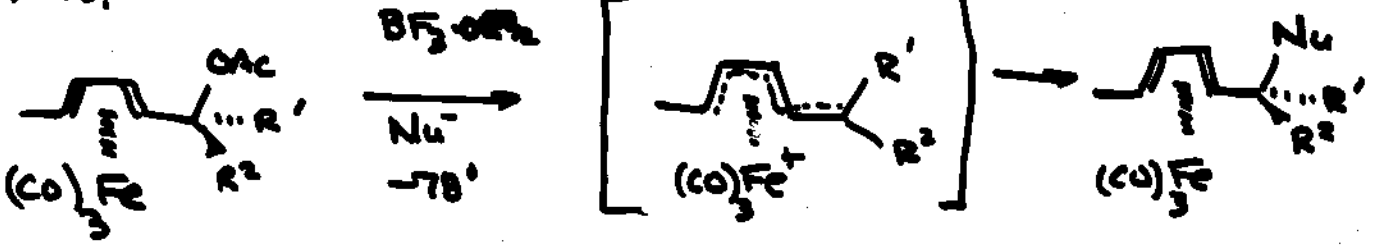
$NaCH(CO_2Et)_2$ IN MANY CASES

NOTE: AT LEAST A FEW REGIOCHEMICAL EXCEPTIONS.



SEE DONALDSON REVIEW.

AND,



- REACTS BEFORE ISOMERIZATION TO 'U' SHAPE OCCURS

UEMURA, M. ET AL TETRAHEDRON LETT. 1987, 28, 641
ROUSH, W.R. ET AL " 1994, 35, 7347, 7351.

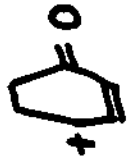
DOESN'T WORK AS WELL

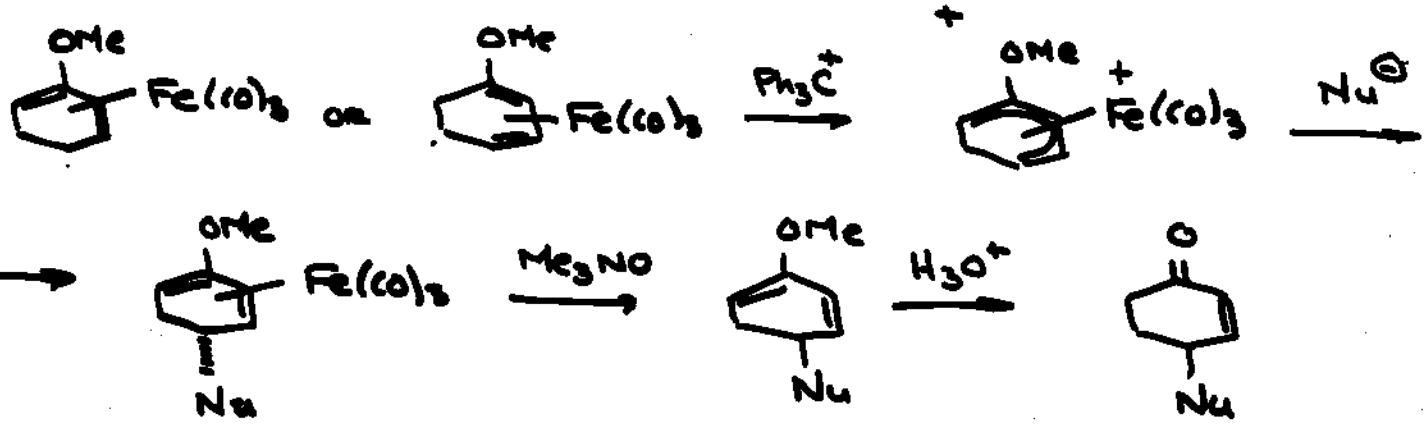
PEARSON'S SOLUTION - SEE BOOK.

Synthetic Uses

- Widely used by Pearson Group, and by Knölker's Group

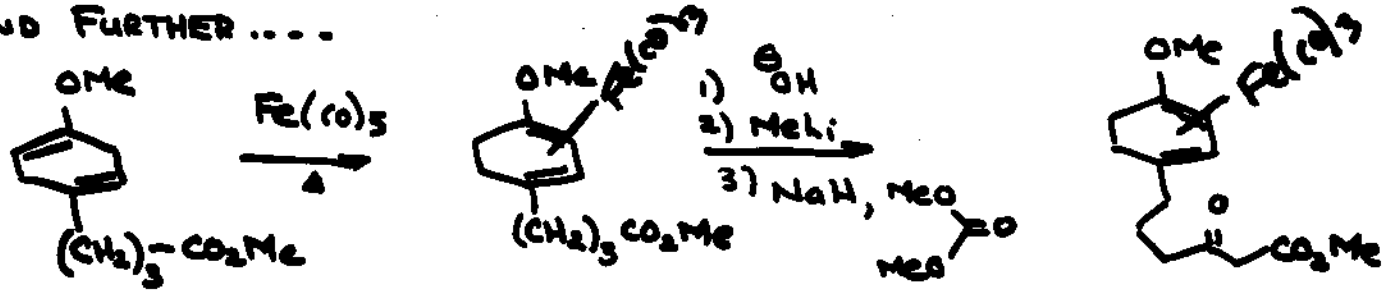
(Review: Synlett 1992, 371)

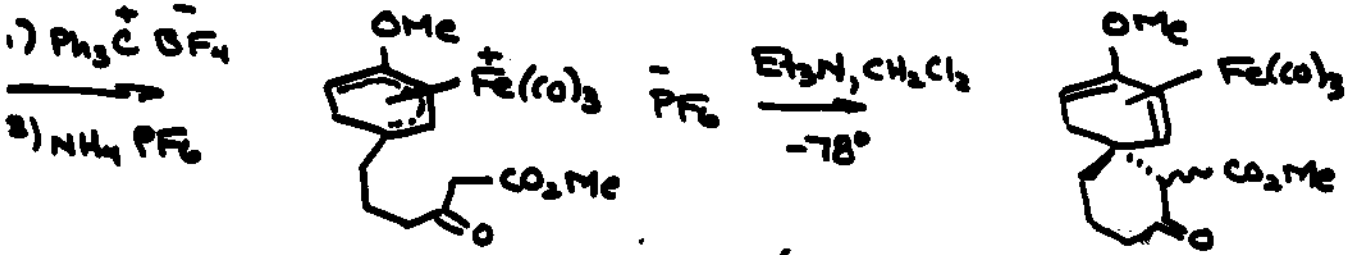
- Examples: as equivalent of  cyclohexenone γ-cation

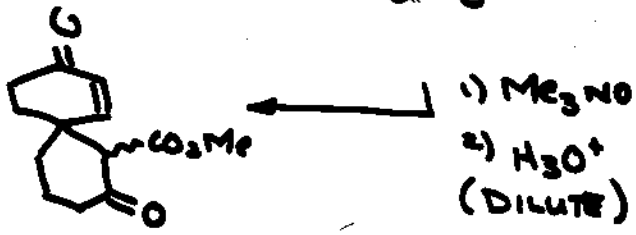


Pearson, A.J. Acc. Chem. Res. 1980, 13, 463.

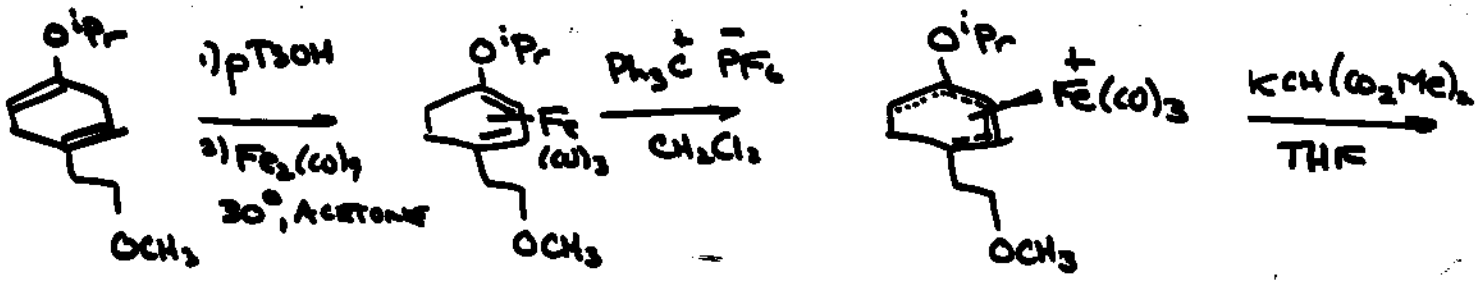
And further....

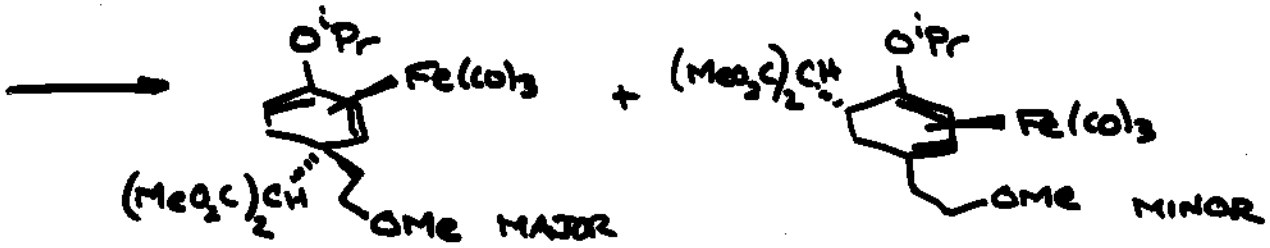


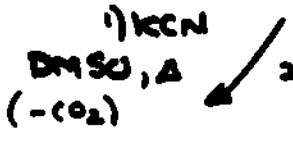


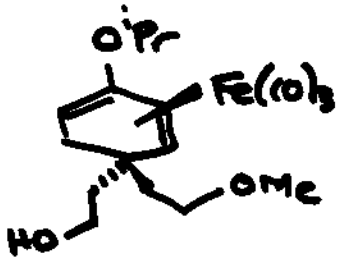


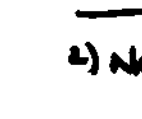
And.

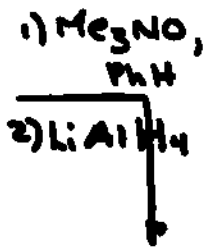


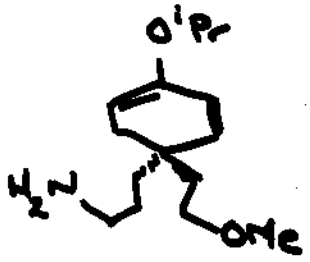


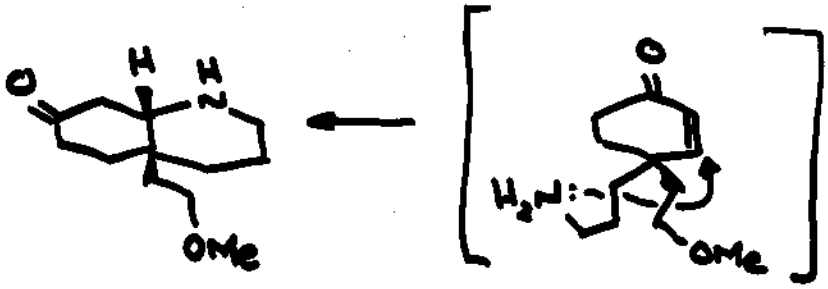


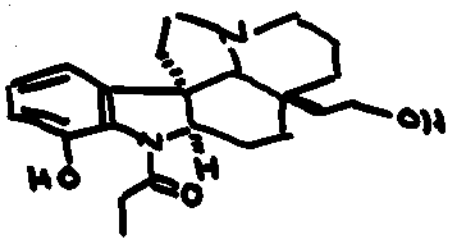












(±) LIMASPERMINE

PEARSON J. C. S. PERKIN I
1982, 489.
1979, 1255.

OTHER PEARSON REVIEWS:

SCIENCE 1984, 223, 895.

PURE APPL. CHEM. 1983, 55, 1767.

CHEM. IND. (LONDON) 1982, 741

KNÖLKER, H.J. CHEM. SOC. REV. 1999, 28, 151.

OTHER METAL PENTADIENYLS, SEE.

ERNST, R.D. CHEM. REV. 1988, 88, 1255.

POWELL, P. ADV. ORGANOMET. CHEM. 1986, 26, 125

ACYCLICS - SYNTHESIS OF 5-HETE METHYL ESTER.

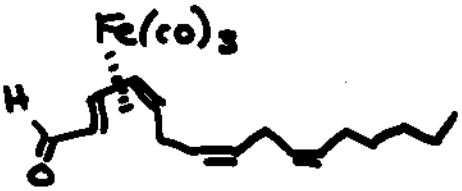
>92% ee

H_nC_5-C≡C-CH_2-C≡C-Li, +CuBr·Me_2S, Et_2O/THF, -45°

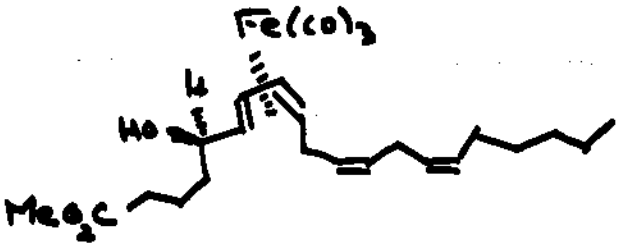
~60%

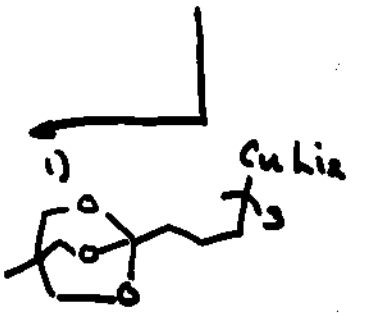
H_2, LINDLAR CAT. ~90%

1) DIBAL 92%
2) MnO_2 ~65%



DIASTEREOMER +





1) CuLi$_2$
2) pTSOH, H_2O/THF
3) MeOH/K_2CO_3

↓ CAN

↓ CAN ~86%

(S)-HETE ESTER ≥98.5% ee.

(R)-HETE METHYL ESTER ≥93% ee.

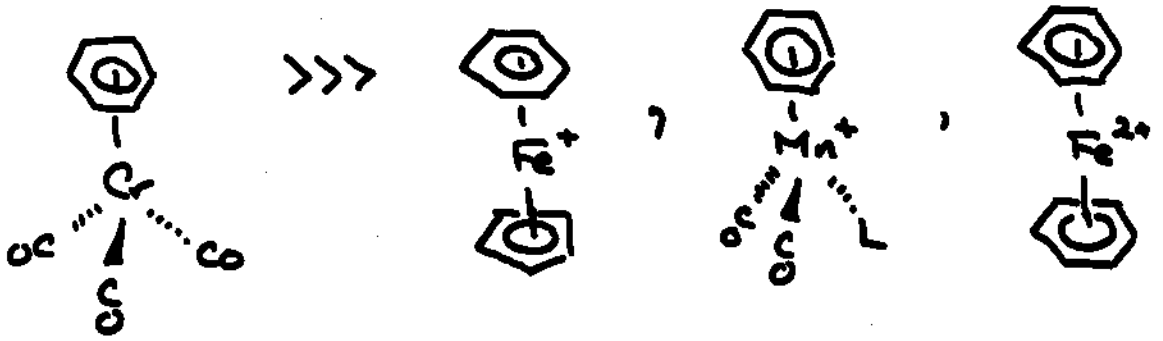
5-HYDROXYEICOSATRIENOIC ACID = 5-HETE

TAO, C.; DONALDSON, W.A. J. ORG. CHEM. 1993, 58, 2134.

η^6-TRIENE METAL COMPLEXES.

- DOMINATED BY η^6-ARENE METAL COMPLEXES
- ONE OF THE MOST WIDELY DEVELOPED AREAS OF SYNTHETIC ORGANOMETALLIC CHEMISTRY
- MANY, MANY COMPLEXES KNOWN.

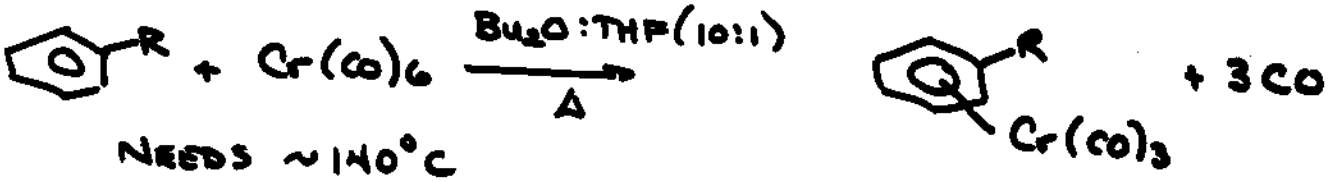
UTILITY



PREPARATION OF COMPLEXES

CHROMIUM

a) STANDARD - ARENE + $Cr(CO)_6$ + Δ



NEEDS ~140°C

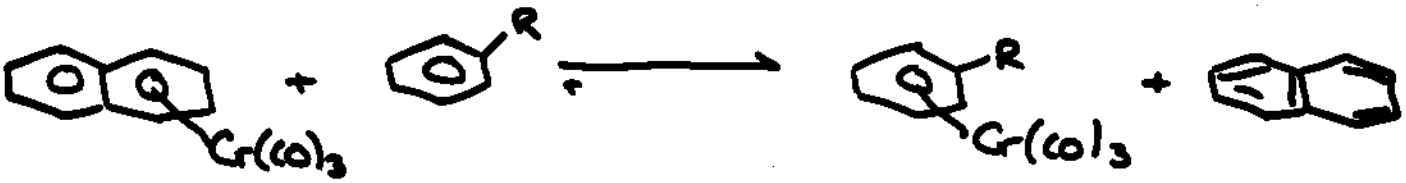
INORG. SYNTH. 1979, 19, 154.

b) MILDER CONDITIONS - ARENE + $L_3Cr(CO)_3$

"L" IS MOST OFTEN ACETONITRILE - REQUIRES ~70°C

c) BY ARENE EXCHANGE

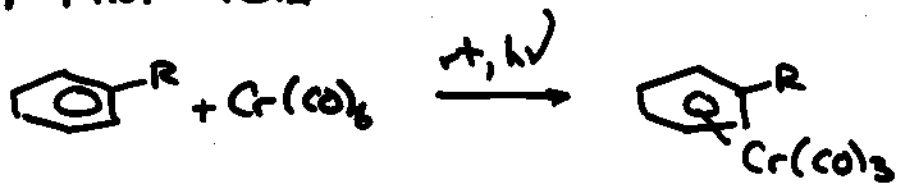
- ONE OF THE MOST WEAKLY BOUND ARENES IS NAPHTHALENE, SO....



EQUILIBRIUM IS WAY TO THE RIGHT, USUALLY.

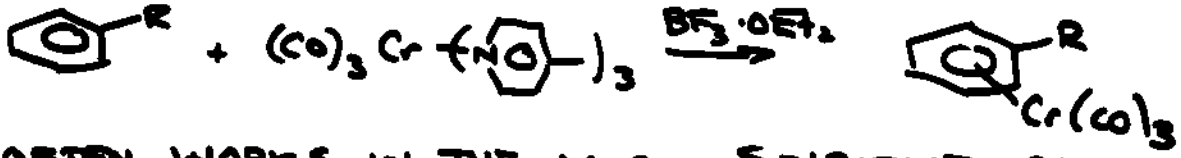
KÜNDIG, E.P. ET AL J. ORGANOMET. CHEM. 1985, 286, 183.

d) PHOTOLYSIS



BICKELHAUPT, F. ET AL J. ORGANOMET. CHEM. 1989, 363, 291.
+ REFS. THEREIN.

e) FROM $(CO)_3Cr-(C_6H_5)_3$ + LEWIS ACID.



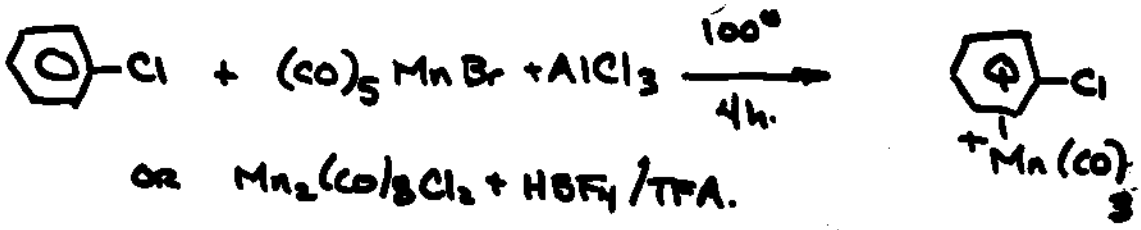
OFTEN WORKS IN THE MOST SENSITIVE CASES.

I.E.  ,  DON'T WORK UNDER NORMAL COND'S. DUE TO OXIDATNE ADDN.

DOES WORK HERE, ALBEIT IN MEDIOCRE YIELDS.

ÖFELE, K. CHEM. BER. 1966, 99, 1732.

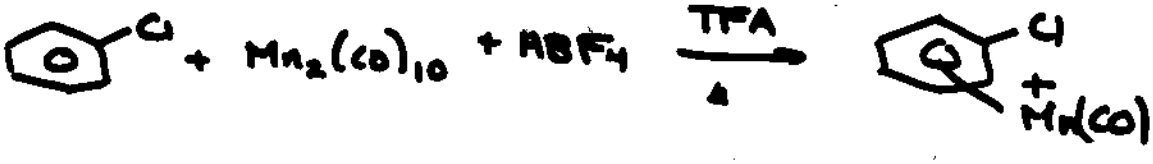
COMPLEXES OF Mn.



PAUSON, P.L.; SEGAL, J.A. J.C.S. DALTON 1975, 1677.

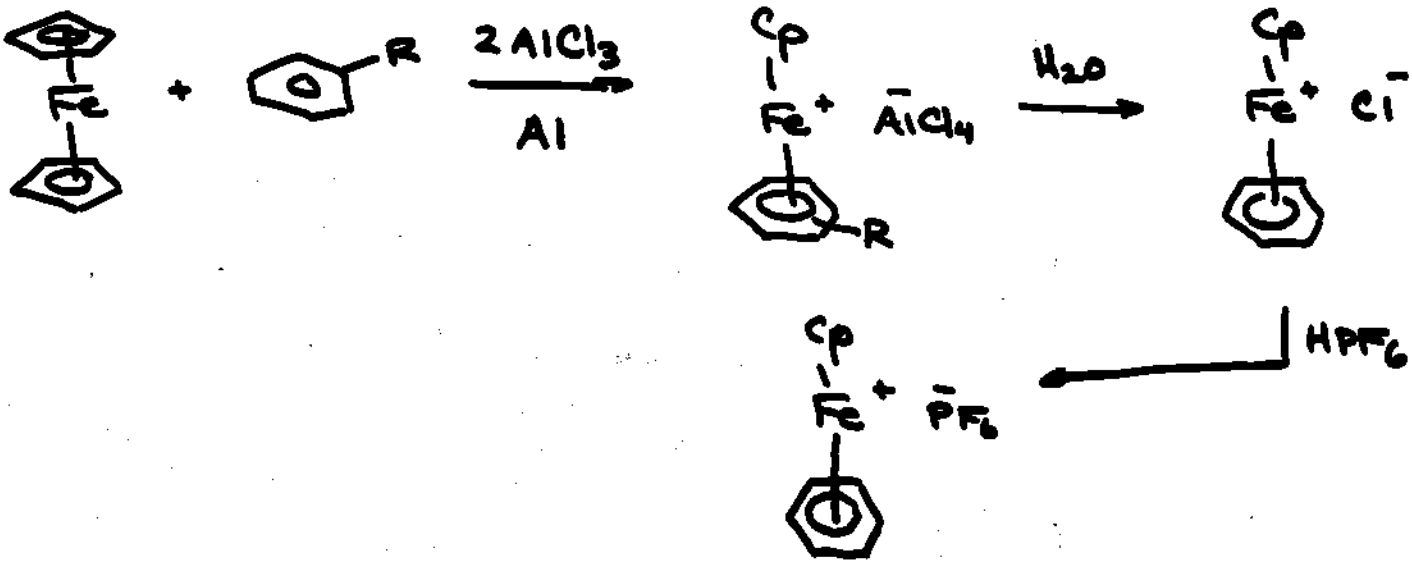
RYBINSKAYA, M.I. ET AL B. ACAD. SCI. USSR, DIV. CHEM. SCI. 1984, 33, 813.

PEARSON, A.J.; SHIN, H. TETRAHEDRON, 1992, 48, 7527 →

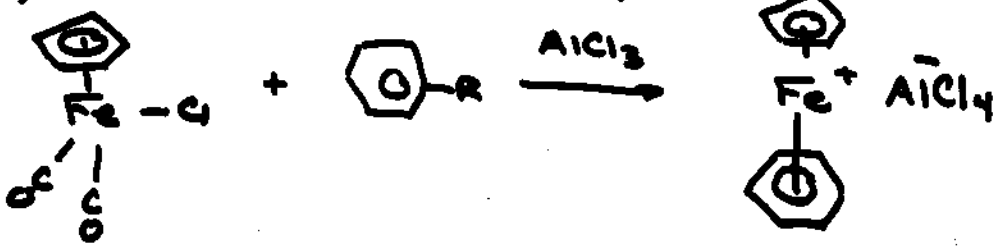


COMPLEXES OF IRON.

a) LIGAND EXCHANGE WITH FERROCENE

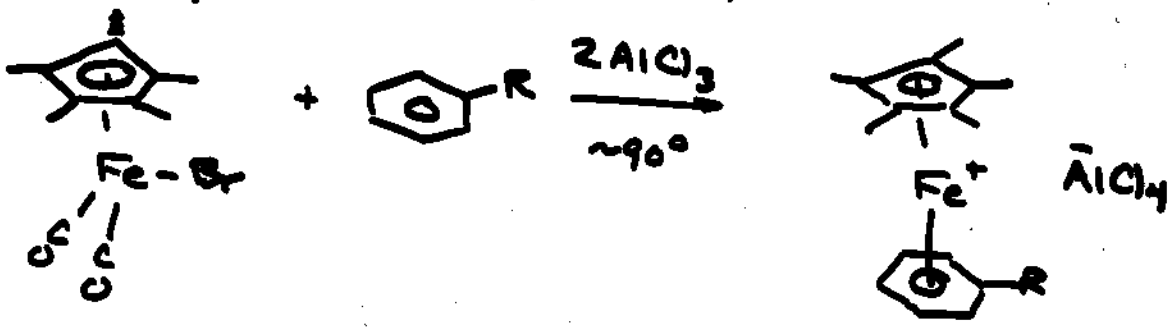


b) USING THE METAL Cp - HALIDES



ORIGINAL PREP, BUT NO LONGER USED

- FOR Cp* COMPLEXES, THOUGH, IT MUST BE

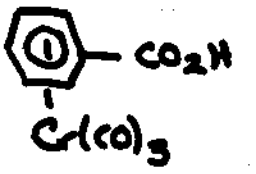
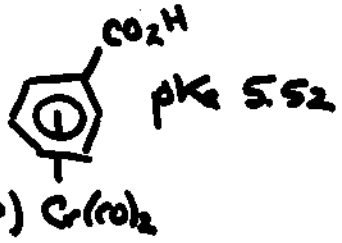
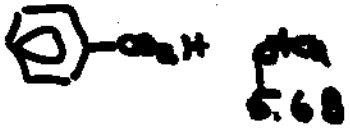


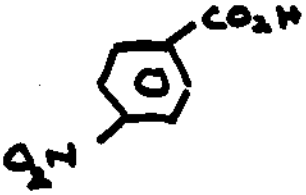
SEE ASTRUC, D. TETRAHEDRON, 1983, 39, 4027.

ELECTRONIC EFFECTS IN η^6 - COMPLEXES

- COMPLEXATION OF ARENE BY $Cr(CO)_3$ CLEARLY NET WITHDRAWER OF "π" - ELECTRON DENSITY.

i.e.  IS WEAKER BASE THAN 

AND  pKa 4.77  pKa 5.52 

CONSIDER  pKa 4.48

∴ OFTEN  CONSIDERED ELECTRONICALLY EQUAL TO 

- THIS INDUCTIVE ELECTRON WITHDRAWING ABILITY, AS WELL AS RESONANCE ELECTRON DONATING AND WITHDRAWING ABILITY, CONTRIBUTES TO THE REACTIONS ARENE-Cr COMPLEXES WILL UNDERGO.

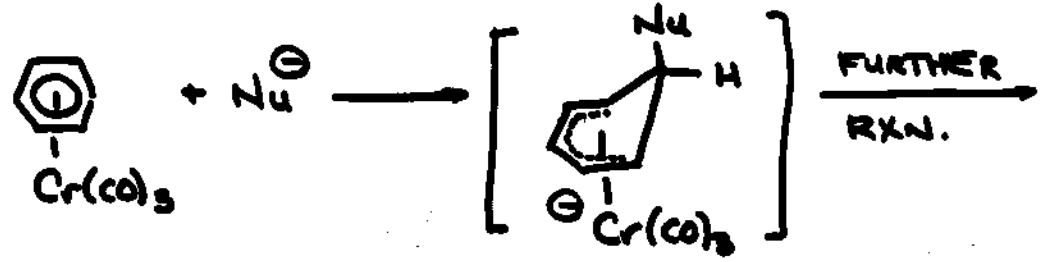
- WILL DISCUSS AS WE ENCOUNTER THEM

NUCLEOPHILIC ADDITIONS TO ARENE-M.

PAPE, A.; KALIAPPAN, K.P.; KÜNDIG, E.P. CHEM. REV. 2000, 100, 2917.

IS NOT NORMALLY A FEASIBLE REACTION, UNLESS THE ARENE HAS SOME STRONGLY ELECTRON WITHDRAWING GROUPS ON IT.

BUT.....

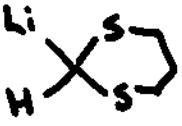


IS VIABLE - A:

- IN 'NORMAL' CASES, NUCLEOPHILES WHICH WORK ARE LIMITED TO ONES WHOSE CONJUGATE ACID (i.e. Nu^+-H) IS pKa > 20

∴ SUCCESSFUL NUCLEOPHILES.

$LiCH_2CO_2R$, $LiCH_2CN$, $KCH_2CO_2{}^tBu$, $LiCHCN(OR)$, $LiCH_2SPh$,



, PhLi, Li—≡—R,  , ${}^tBuLi$

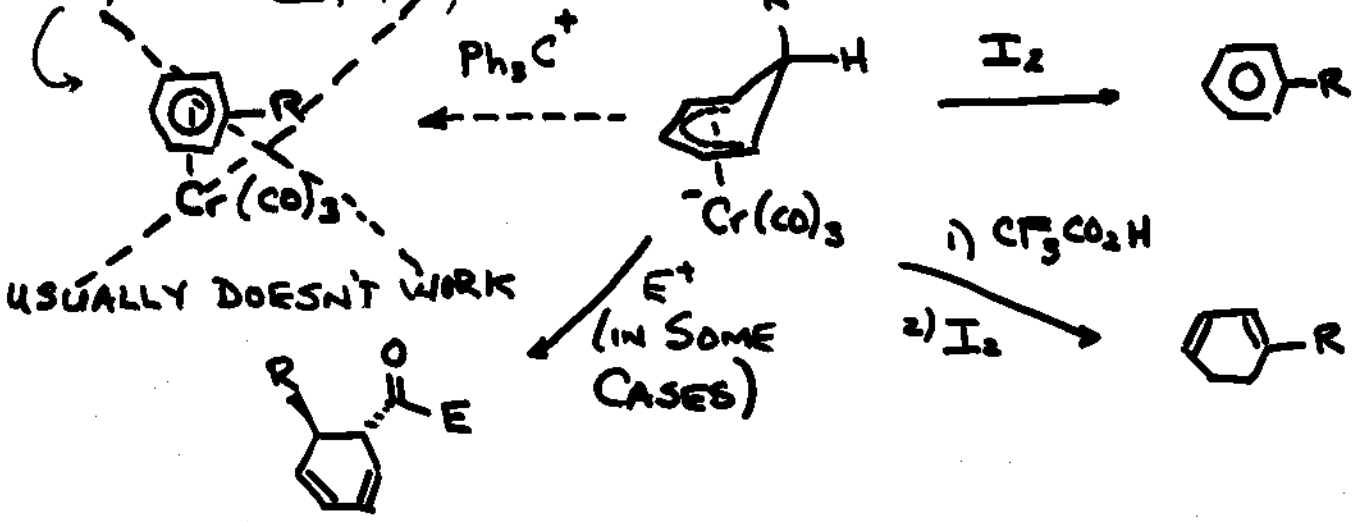
UNSUCCESSFUL

$LiCH(CO_2R)_2$, $Li\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$, GRIGNARDS, Me_2CuLi

NOTE: ${}^nBuLi$, MeLi, ${}^sBuLi$ DO A DIFFERENT REACTION.

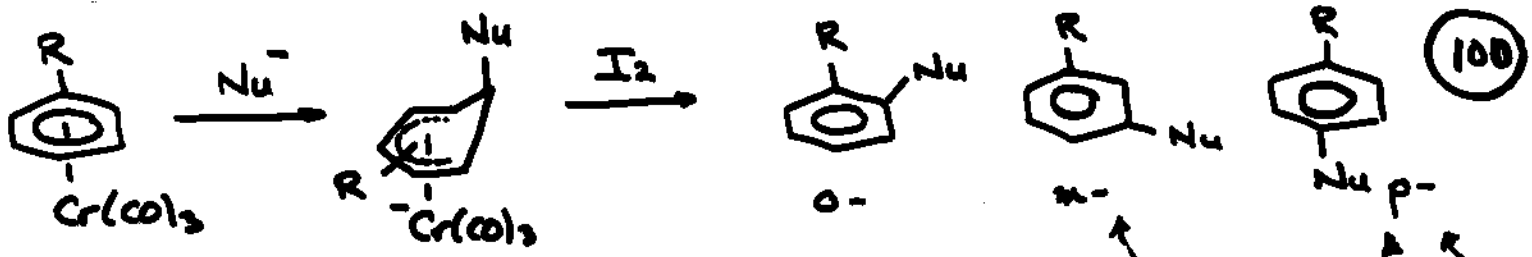
SO WHAT DO YOU DO WITH REACTION INTERMEDIATES (i.e. (A))?

CHEM. EUR. J. 1998, 4, 251; HELV. CHIM. ACTA 1997, 80, 2023



REGIOCHEMISTRY OF NUCLEOPHILIC ATTACK

- IF SUBSTITUTED ARENE-$Cr(CO)_3$ COMPLEXES, THERE ARE MULTIPLE POSSIBILITIES FOR ATTACK



- DO GET MIXTURES UNDER THESE CONDITIONS, BUT THE GENERAL RULES ARE:

R = ELECTRON DONATING ($-OCH_3, -CH_3, -NMe_2$) — META (MAJOR)

R = ELECTRON DONATING AND LARGE ($-SiMe_3, -{}^tBu, -CH({}^tBu)_2$) — PARA (MAJOR)

R = ELECTRON WITHDRAWING (i.e., $-CF_3$) — PARA (MAJOR)

- CONSIDERABLE VARIATION WITH SIZE OF NUCLEOPHILES
  - STERICALLY SMALLER NUCLEOPHILES ( , $^{\ominus}CH_2SPh$)
  - GIVE SUBSTANTIAL ORTHO SUBSTITUTION

THESE ARE KINETIC CONDITIONS (-78°)

REGIOCHEMISTRY - WHY ?

- BEST GUESS - COMBINATION OF CHARGE & ORBITAL CONTROL
- CHARGE CONTROL - CHARGE INDUCED BY PREFERRED M-CEO CONFORMATION
  - ARENE C'S ECLIPSED BY Cr-CO ARE ATTACKED PREFENTIALLY

EDG 

EWG 

BULKY