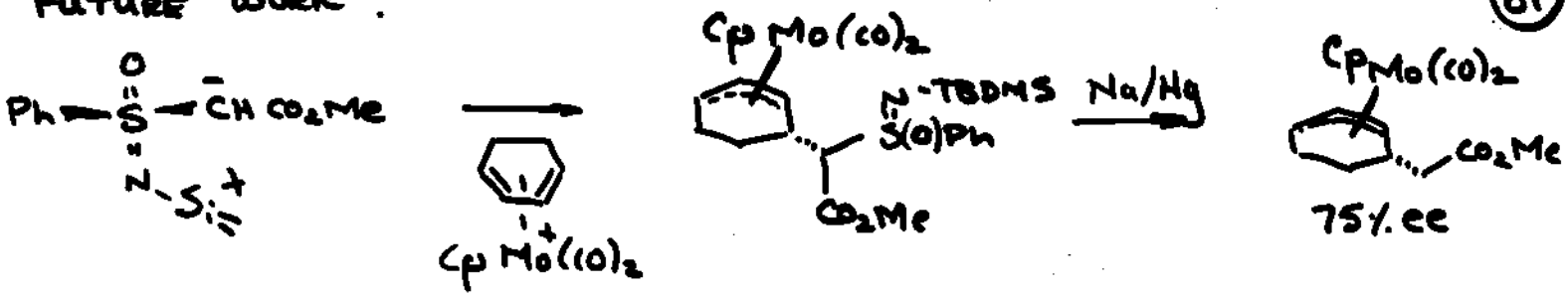
FUTURE WORK?



PEARSON, A.J. ET AL TETRAHEDRON LETT. 1987, 28, 2459.

c) WILL NOT DISCUSS THIS IN DETAIL, BUT THE FOLLOWING IS KNOWN

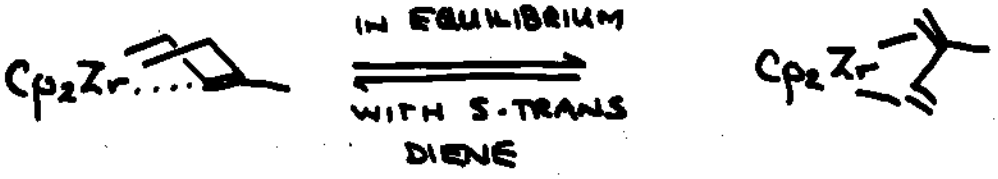
Nu⁻ USUALLY R_2N^- OR AcO^-
OXIDANT USUALLY BENZOQUINONE
SOME CASES OF C-C BOND FORMATION

} SEE BÄCKVALL REVIEW.

5. η^4-DIENE COMPLEXES AS NUCLEOPHILES.

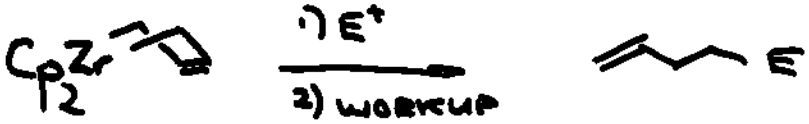
a) - EARLY TRANSITION METAL DIENE COMPLEXES DON'T REALLY BEHAVE LIKE DIENES

- DOMINATED BY Cp_2Zr COMPLEXES



BEHAVES LIKE

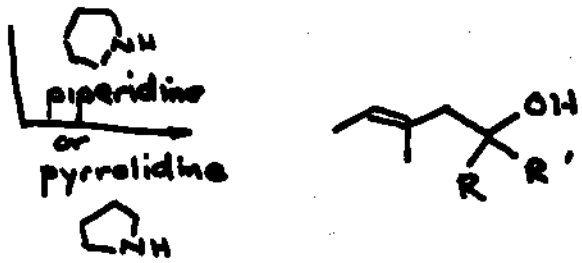
RELATIVE REACTIVE AS NUCLEOPHILE, PARTICULARLY WITH OXYGEN CONTAINING ELECTROPHILES



REGIOCHEMISTRY :

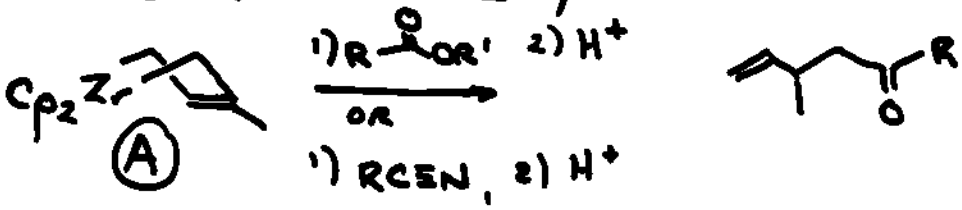
- IF A SUBSTITUTUENT IS AT THE 2-POSITION OF THE DIENE, RXN IS AT MORE SUBSTITUTED END.

BASE CLEAVAGE OF PRODUCT GIVES DOUBLE BOND ISOMER.



OTHER OXYGEN BEARING E^+'S.

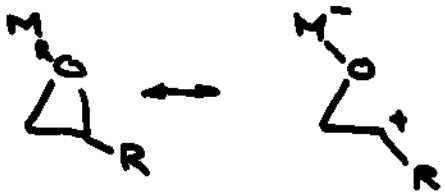
ESTERS (OR NITRILES)



EPOXIDES

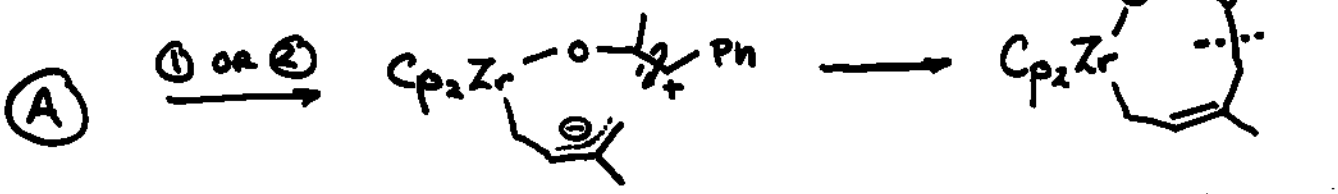
R = ARYL, VINYL

REACTION IS AT MORE SUBSTITUTED END OF EPOXIDE (NOTE R)



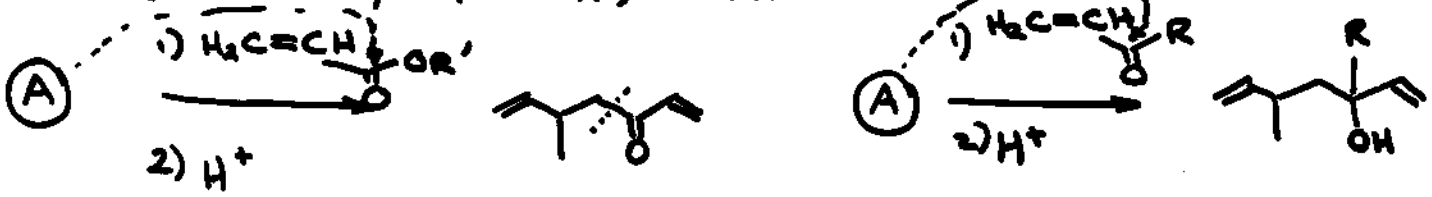
PROOF OF THIS S_N1-LIKE REACTIVITY

REACT TO GIVE SAME PRODUCT



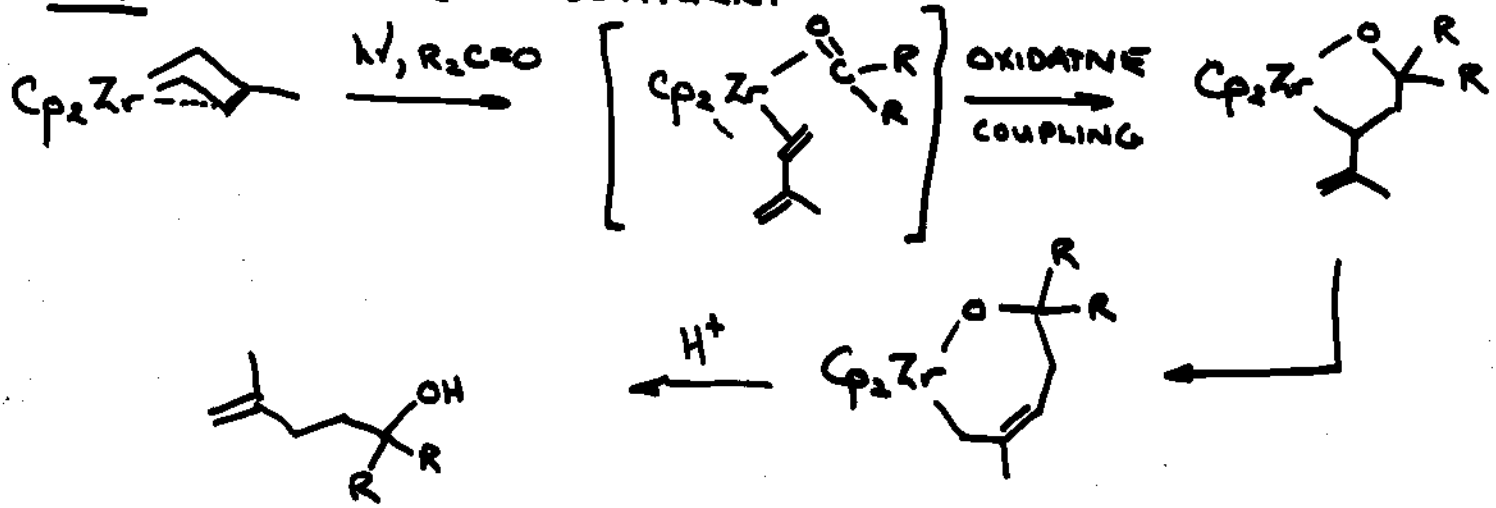
α, β- UNSATURATED CARBONYLS

- GIVE HIGH 1,2- (>95%) ADDITION

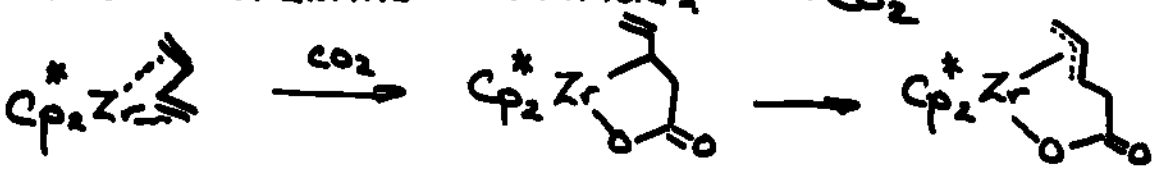


- PHOTOCHEMICAL REACTIONS
  - WITH CARBONYL COMPOUNDS, A PHOTOCHEMICAL REACTION OCCURS AT MUCH LOWER T (-70°)

- THE BIGGEST DIFFERENCE IS THAT THE REACTION NOW <u>OCCURS AWAY</u> FROM A 2- SUBSTITUENT



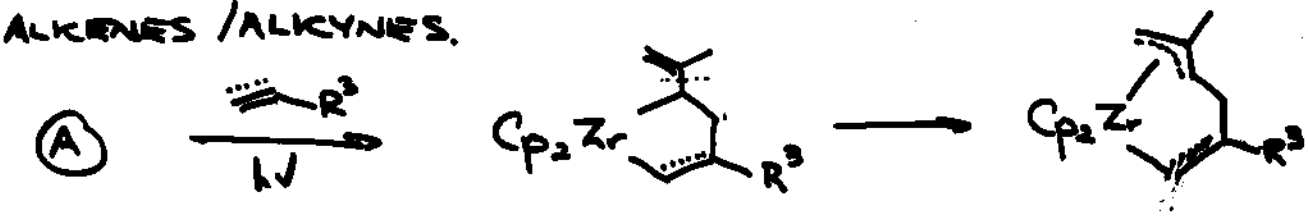
BACK TO THERMAL REACTIONS — CO_2



- BUT IN MANY CASES, CAN'T STOP FURTHER REACTION

ISOCYANATES.

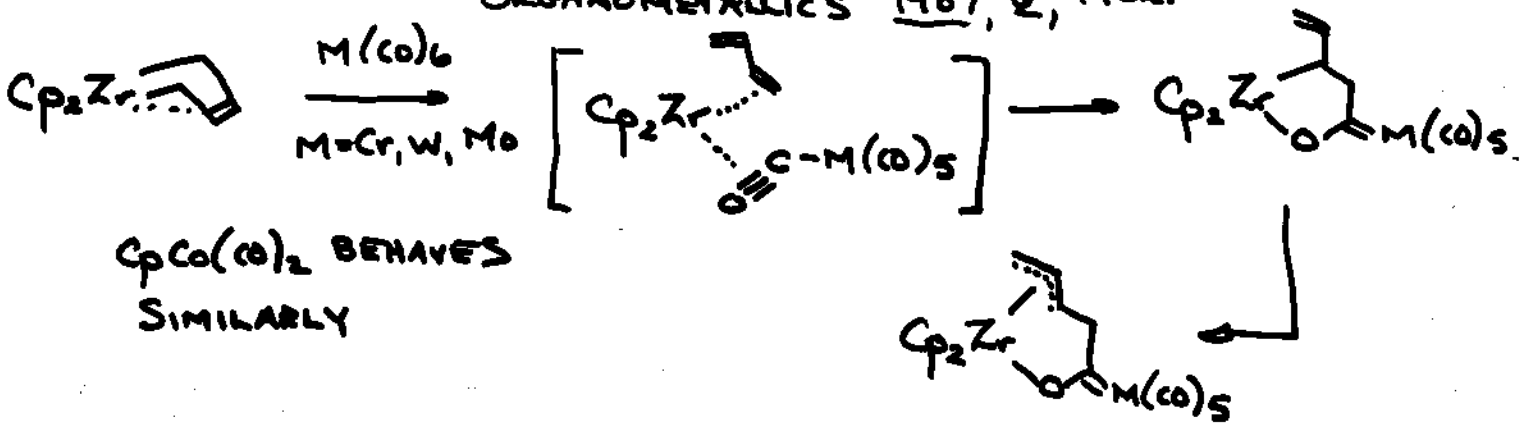
ALKENES / ALKYNES.



NOTE AGAIN, REGIOCHEM FLIP.

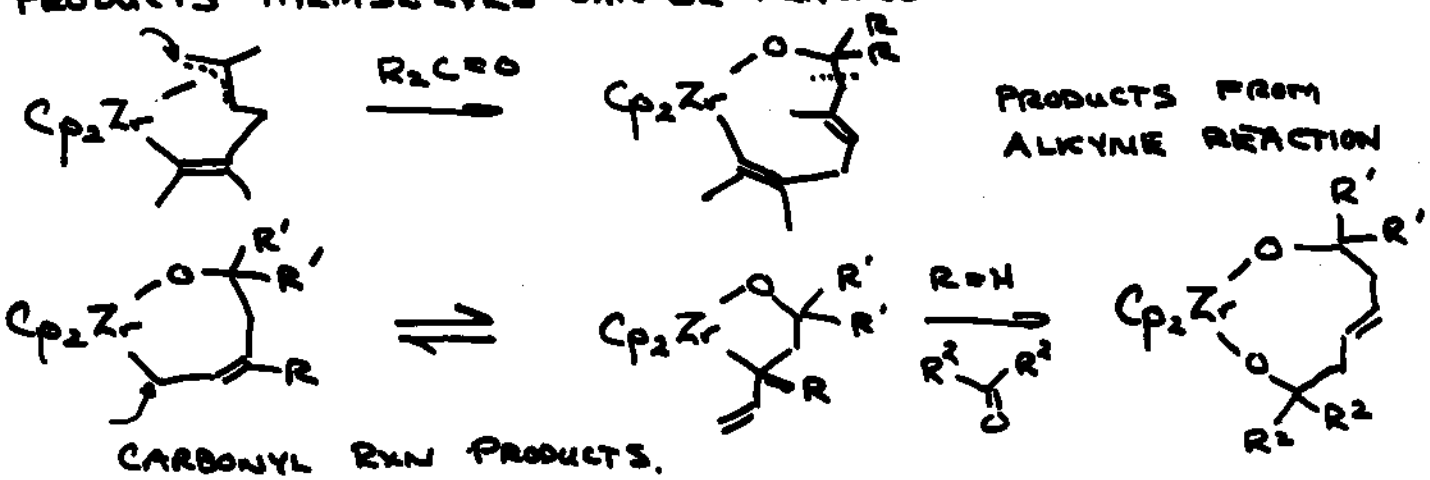
METAL CARBONYLS

- SEE ERKER, G. POLYHEDRON 1988, 7, 2451
ORGANOMETALLICS 1987, 6, 1962.

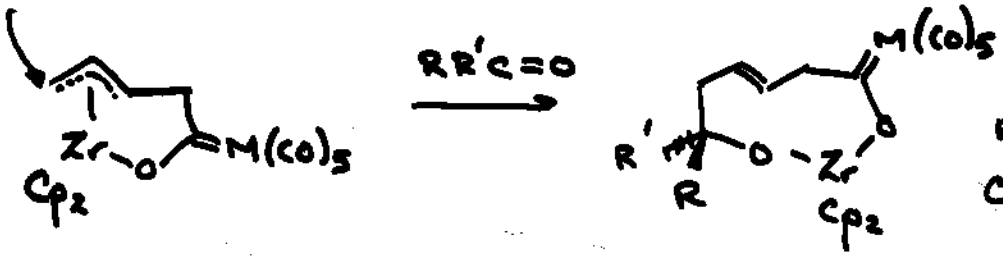


$CpCo(CO)_2$ BEHAVES SIMILARLY

AND FINALLY, AT LEAST FOR SOME PRODUCTS, THE ALLYL-Zr PRODUCTS THEMSELVES CAN BE REACTED FURTHER WITH CARBONYLS



CARBONYL RXN PRODUCTS.



METAL CARBONYL PROBS.

ERKER, G. ET AL
ORGANOMETALLICS 1989, 8, 450.

- IN ALL CASES, GET 9-MEMB. RING W/ TRANS C=C

NOTE: $Cp_2Hf(diene)$; $Cl_2Cp^*Ta(diene)$; $CpTa(diene)_2$; $CpNb(diene)_2$

- CAPABLE OF SIMILAR RXNS - GROUP V LESS REACTIVE.

- SEE YASUDA, H.; NAKAMURA, H. ANGEW. CHEM. INT. ED. ENGL, 1987, 26, 723 (R)

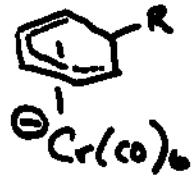
Fe-diene COMPLEXES - ALSO SEE GRÉE, R. SYNTHESIS 1989, 342 (R)

ACYLATIONS - FRANCK-NEUMAN, M. NOUV. J. CHEM. (NEW) 1990, 14, 471.

η^5- DIENE COMPLEXES.

DOMINATED BY

AND TO A LESSER EXTENT BY



WILL COVER UNDER η^6- COMPLEXES

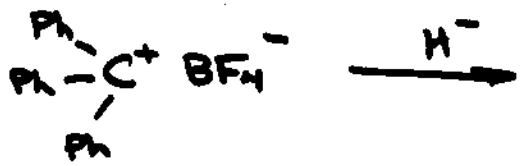
AUTHORS DOMINATED BY A.J. BIRCH

NOW BY A.J. PEARSON (CASE WESTERN)

ACYCLICS. W.A. DONALDSON (MARQUETTE)

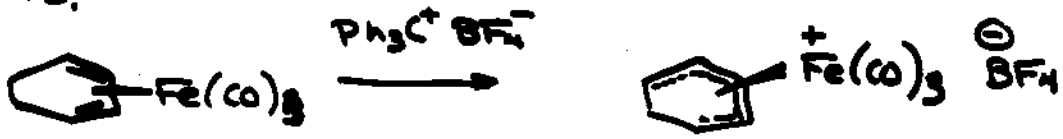
GENERATION OF η^5- CATIONIC COMPLEXES

- HYDRIDE ABSTRACTION FROM DIENE COMPLEXES.
  - NORMALLY BY



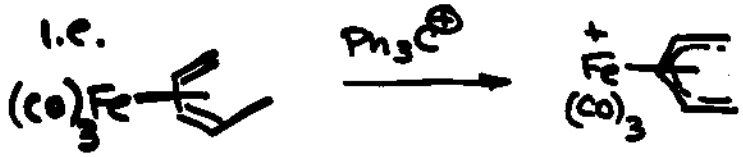
TRIPHENYLMETHYL (TRITYL) CATION

THUS,

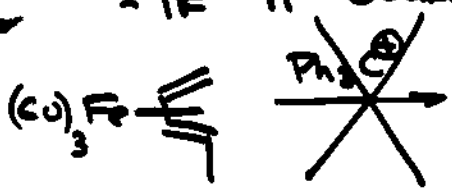


- GOOD WITH CYCLIC DIENES, AS ADJACENT SUBSTITUENT MUST BE <u>CIS</u>.
- WITH ACYCLIC DIENES, CAN ABSTRACT $H^{\ominus}$ IF SOURCE IS <u>CIS</u>

i.e.



- IF "H^- SOURCE" IS TRANS, THOUGH, RXN USUALLY FAILS.

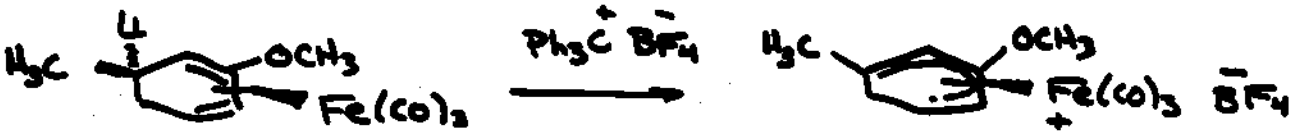


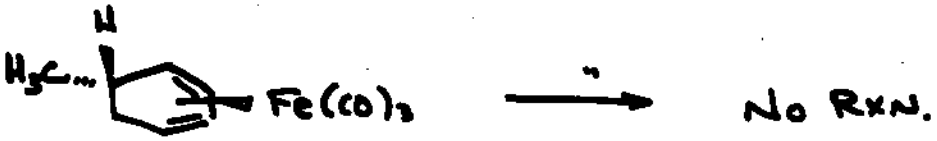
NO RXN.

MAHLER, J.E.; PETTIT, R. J. AM. CHEM. SOC. 1963, 85, 3955

STEREOCHEMISTRY

- HYDRIDE ABSTRACTION OCCURS FROM THE FACE EXO- FROM (OPPOSITE TO) THE METAL.

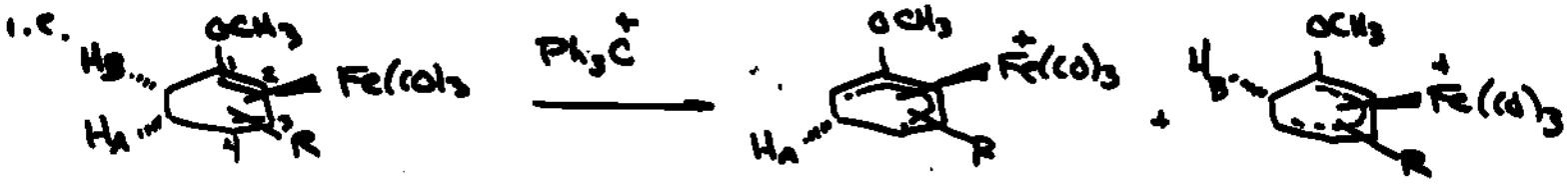




- REGIOCHEMISTRY

- ABSTRACTION IS USUALLY PRETTY SELECTIVE, BUT NOT READILY PREDICTABLE. IT DOES NOT CORRESPOND TO THE MOST STABLE CATION

- PEARSON HAS MADE AN ORBITAL INTERACTION EXPLANATION..., SEE PEARSON, A.J. ET AL ORGANOMETALLICS 1984, 3, 1150.



R	H_B ABSTR	H_A ABSTR.
H	20	80
3-CH_3	0	100
4-CH_3	90	10
3-OCH_3	56	44
4-	100	0

R	H_A ABSTR.	H_B ABSTR.
H	90	10
1-CO_2Me	100	0
4-CO_2Me	0	100
4-CH_3	0	100
4-OCH_3	56	44

- REACTIONS OF DIENYL ALCOHOL COMPLEXES WITH STRONG ACID.
  - MOST COMMON METHOD FOR ACYCLIC PENTADIENYL-IRON COMPLEXES

H^+ = HBF_4, HPF_6

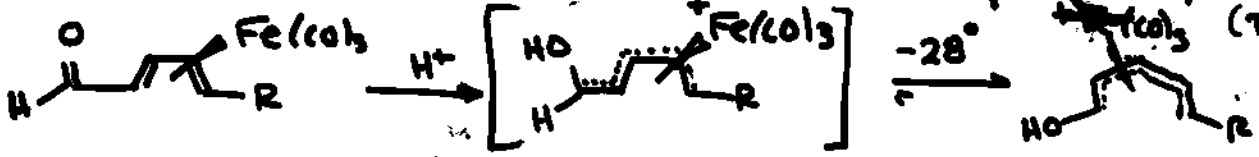
SEE DONALDSON, W.A. ALDRICHIM. ACTA 1997, 30, 17. (R)

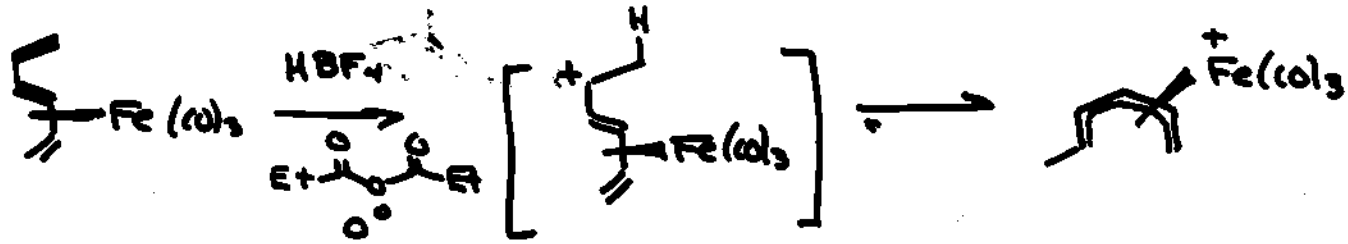
ALSO DONALDSON, W.A.; RAMASWAMY, M. SYNTH. REACT. INORG. MET.-ORG. CHEM. 1987, 17, 49.

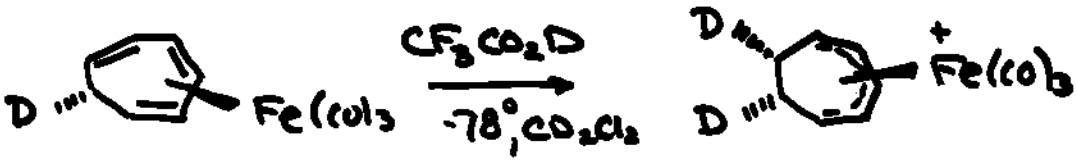
MAGYAR, R.S. ET AL INORG. CHEM. 1978, 17, 1775.

BIEHL, E.R. ET AL J. ORGANOMET. CHEM. 1979, 174, 297.

RELATED METHODS OF PREPARATION FROM CARBONYLS, ALKENES. (TRIENES)



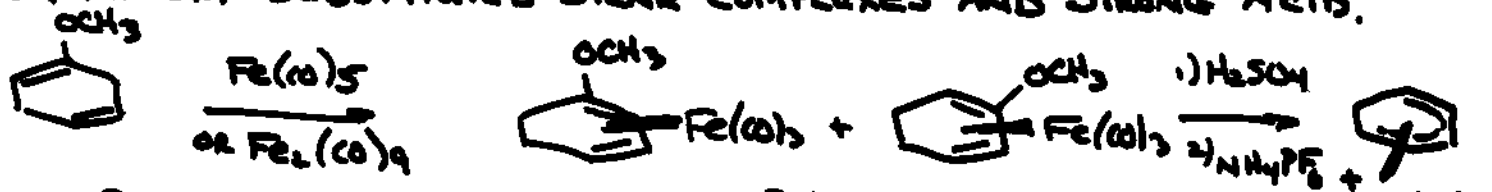




NOTICE FACE OF ATTACK

J. C. S. DALT. TRANS. 1977, 794 + 2340.

FROM ALKOXY-SUBSTITUTED DIENE COMPLEXES AND STRONG ACID.

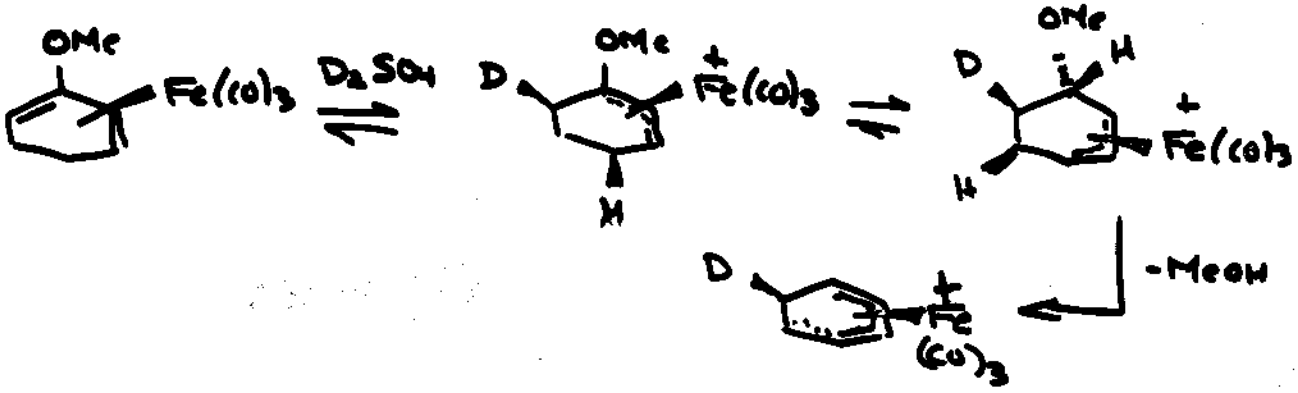


BIRCH REDN.

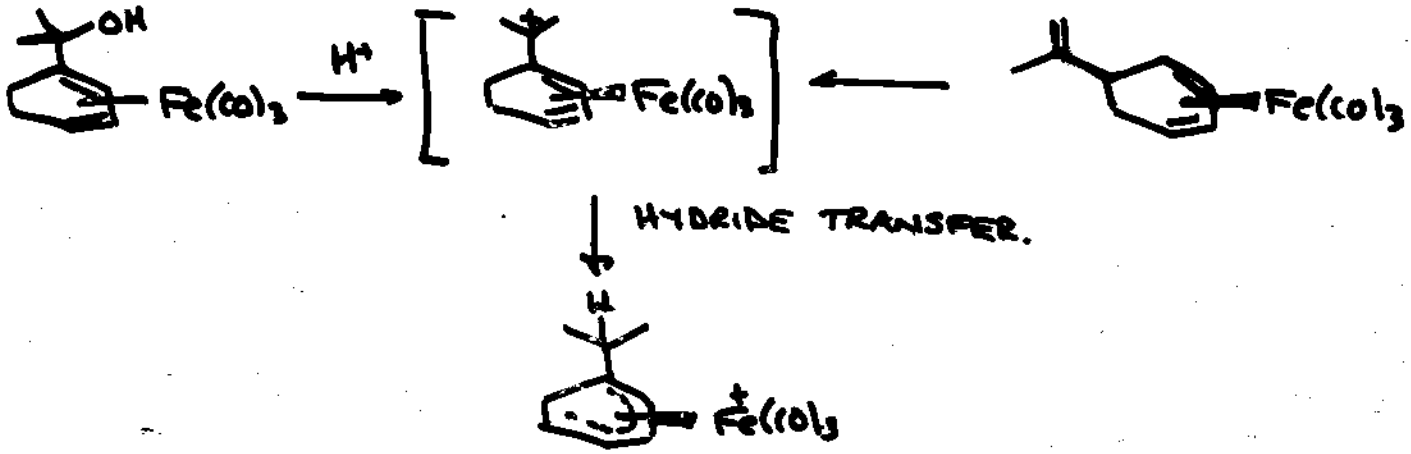
2 : 1

GOES VIA

- OR SOMETHING CLOSELY RELATED.



BY CATION REARRANGEMENT



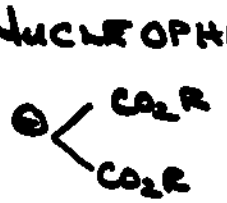
REACTIONS AS ELECTROPHILES:

NUCLEOPHILIC ATTACK ON η^5-COMPLEXES

- THESE CATIONS (NORMALLY) READILY REACT WITH NUCLEOPHILES TO GIVE C-C OR C-HETEROATOM BOND FORMATION

- ATTACK IS FROM THE <u>EXO</u>-FACE (STEREOSELECTIVE)
- 'NORMAL' MODE OF ATTACK IS AT C-1 TERMINUS

NUCLEOPHILES



STABILIZED ENOLATES

SILYL ENOL ETHERS
SILYL KETENE ACETALS

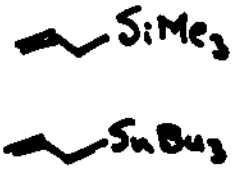
TETRAHEDRON LETT 1988 29, 869
TETRAHEDRON 1982, 38, 1813.

ENOLATES ONLY WORK SOMETIMES

ENAMINES.

RLi, RMgBr USUALLY FAIL

R_2Cd, R_2Zn, R_2CuLi, $RCu(CN)ZnI$
→ USUALLY BETTER



ALLYL SILANE (TINS)

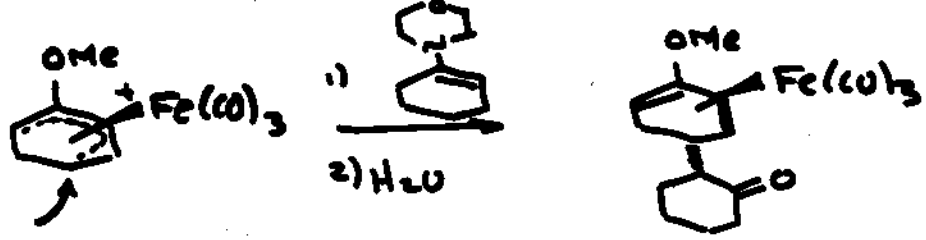
—X BONDS

R_2NH (AMINES), H_2O, MeO^-, R_3P (PHOSPHINES)
$(RO)_3P$ (PHOSPHITES)
R_3As (ARSINES).

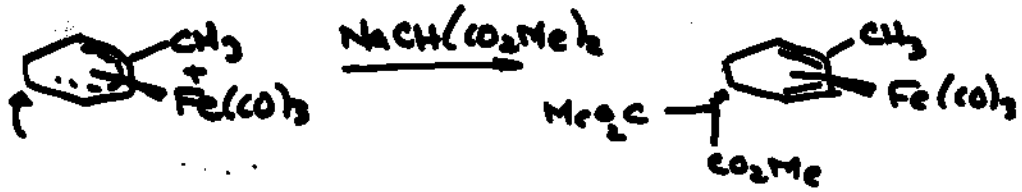
$NaBH_4$, Et_3SiH, $NaBH_3CN$ (HYDRIDE SOURCE)

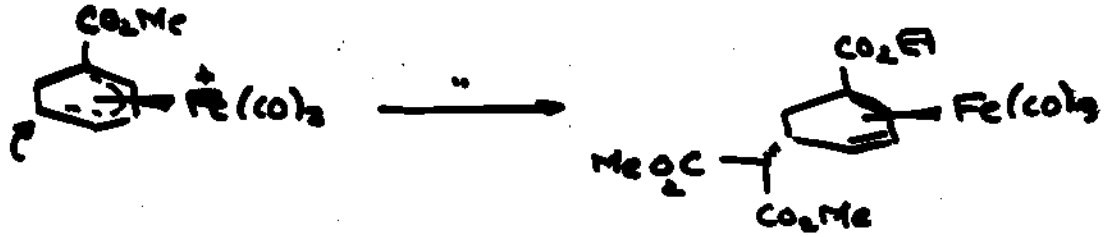
REGIOCHEMISTRY, PART II

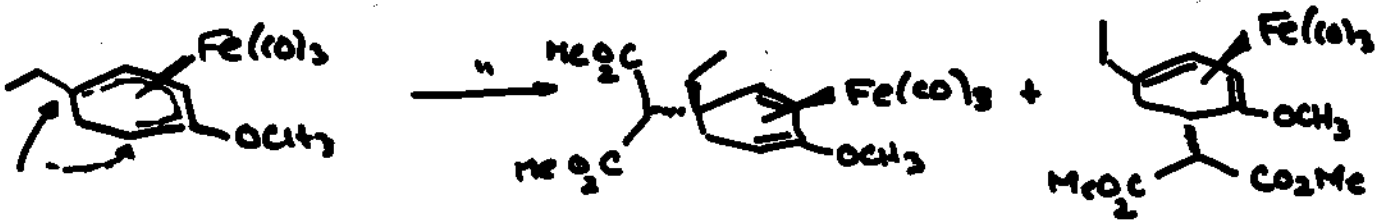
- ATTACK OF NUCLEOPHILES IS AT LESS SUBSTITUTED TERMINUS
- MeO AS A SUBSTITUENT IS UNUSUALLY POWERFUL IN THIS RESPECT.



- ENAMINE
- REGIOCHEM
- STEREOCHEM. (EXO).

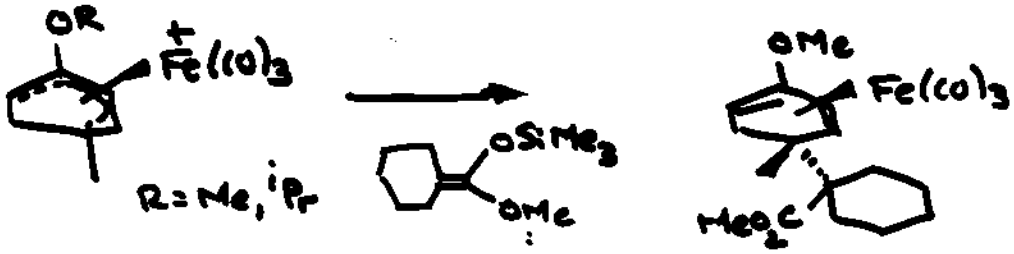






82 : 18

COUNTERION DEPENDENT



SEE

PEARSON, A.J. IN COMPREHENSIVE ORGANOMETALLIC CHEMISTRY Vol. 8, p 939–1011 (R)

IN COMPREHENSIVE ORGANIC SYNTHESIS, 1991 Vol. 4, p 663–694 (R)

IRON COMPOUNDS IN ORGANIC SYNTHESIS 1994, CH 5. (R)

ADV. MET. ORG. CHEM. 1989, 1, 1. (R)

HARRINGTON, P.J. "TRANSITION METALS IN TOTAL SYNTHESIS, CH. 4 (R)