η^2 -Olefin/Acetylene Complexes

a) Preparation

i) -most common method - ligand exchange (with CO, CH₃CN, alkenes)

i.e., with Fe° it is almost always as follows



Weiss et al Helv. Chim. Acta. 1963, 46, 288

Note: The departing ligand doesn't need to be CO - some other examples







-volatile alkenes

Jonas, K. et al Angew. Chem. Int. Ed. Engl. <u>1983</u>, 22, 716.



<u>R</u> Sato, F.; Okamoto, S. Adv. Synth. Catal. 2001, 343, 759.

ii) Synthesis by Displacement of Halide

 CI^{-} may be displaced by an alkene, either on its own or with an assisting Lewis acid (S_N^{-1} like reactivity)



Schultz, R. G. *J. Organomet. Chem.* <u>1966</u>, *8*, 435 Davies, S. G. et al *J. Organomet. Chem.* <u>1986</u>, *188*, C41.

iii) -by hydride abstraction (also called σ -bond metathesis)

- this type is common for the preparation of alkene and alkyne early transition metal complexes



Buchwald, S.L.; Nielsen, R. B. *Chem. Rev.* <u>1988</u>, *88*, 1047. see also Sato review

iv) - By intramolecular nucleophilic substitution

-often for alkyne complexes, with a wider variey of metals than hydride abstraction



b) Getting Rid of Them (Decomplexation)

-most organic chemists want the metal removed from the organic 'ligand' at the end of the process

i) Competitive ligand association



ii) oxidation of the metal

-very often, if one oxidizes the metal, it no longer bond very well to the organic ligand, and it simply falls off

-several very common oxidants include.....

 $FeCl_3$, Ce^{+4} ((H_4N)₂ $Ce(NO_3)_6$), others

Me₃N⁺-O⁻ (trimethylamine N-oxide, N-methylmorpholine N-oxide)

Shvo, Y.; Hazum, E. J. Chem. Soc., Chem. Commun. 1974, 336 (for iron diene compelxes)



<u>R</u> Nicholas, K. M. Acc. Chem. Res. <u>1987</u>, 20, 207.

c) Uses of η^2 - Metal Complexes

i) as a protecting group

-recall the intro.....that olefin coordination changes the electron density of 29 that alkene

-can make the alkene more *or* less reactive than the uncomplexes alkene, depending upon the case







-therefore, *very* slightly overall electron donating (essentially the same)

but



charge on complex almost unboubtedly renders $\eta^{2}\text{-complex}$ less electron rich

-as a result, the alkene is less reactive to attack by E⁺, and to hydrogenation
-but(!), the alkene is more reative to attack by Nu⁻

Note:





Alkynes

-many alkyne complexes known



But Co complexes are especially robust



-these are in general very stable complexes

-since p- bonds are used in bonding to metals as well, they are not available to electrophiles, like most other alkynes are



32

<u>R</u> Nicholas, K. M. Acc. Chem. Res. <u>1987</u>, 20, 207.

η²-Complexes as Electrophiles

a) Cationic Complexes (Fp⁺)

-just as the '+' charge, nominally on Fe, ultimately withdraws electron density from the alkene and reduces its reactivity to electrophiles (E⁺)....

-so it by contrast increased reactivity of alkenes to nucleophiles (Nu⁻)



Heteroatom based $R_n NH_{3-n}$; ROH (+Na2CO3); RSH (+Na2CO3); R3P(amines)(alcohols)(thiols)(phosphines)

Stereochemistry of Addition

-The addition of Nu: or Nu⁻ is stereospecifically *trans* to the metal. So.....



Regiochemistry

If you draw various resonance forms of the Fp⁺-alkene cation complex, the nucleophile ends up attacking the carbon atom where the 'traditional' organic cation would be most highly stabilized (i.e., S_N^1 like') reactivity



Note: Unfortunately, with simple alkyl substutuents (like above), the regioselectivity is pretty poor.

However, with strong cation stabilizing or detsabilizing (electron withdrawing) groups, the outcome is much more decisive



35

So what do you do with the products?

-there are very few natural products with covalent Fe-C bonds in them, so it's generally desired to turn these into something 'all organic'

1) -the alkyl-Fp compounds may be transformed into several functional groups, i.e....

Fp-R
$$\xrightarrow{I_2}$$
 R-I **Fp-R** $\xrightarrow{Br_2}$ R-B

-normally, this occurs with *inversion* of configuration at the carbon being attacked.

But.....



2) Oxidation

In the presence of an oxidant, migratory insertion of CO occurs before the metal is lost. The 17 e⁻ species does this very rapidly -common oxidants are Ce^{IV}, Fe^{III}, Cu^{II}, O₂

This is most often done in methanol solvent, so that the final product is a methyl ester.



notice the retention of configuration

This includes Br₂ and Cl₂ as oxidants



3) Elimination

If the is a H atom b- to the iron, which can assume an antiperiplanar conformation, it can be abstracted as H^- , usually by Ph_3C^+



Rules for abstraction:

-if there is a choice between forming a terminal alkene and an internal one, one normally gets the *terminal* alkene - probably a steric accessibility argument



-if internal alkenes must be made, one gets mostly the (Z)- isomer

-no one really knows why....perhaps a greater stability of the complex



References:

R Pearson, A. J. 'Iron Compounds in Organic Synthesis', 1994, Ch.2

<u>R</u> Rosenblum, M. J. Organomet. Chem. <u>1986</u>, 300, 191.

<u>R</u> Rosenblum, M. Pure Appl. Chem. <u>1984</u>, 56, 129.

<u>R</u> Rosenblum, M. Acc. Chem. Res. <u>1974</u>, 7, 122.

R Green, J.R.; Donaldson, W. A. in Encyclopedia of Inorganic Chemistry' 1994, V. 2, p.1735.

Enantiomerically pure versions

Turnbull, M. M.; Foxman, B.M.; Rosenblum, M. *Organometallics* <u>1988</u>, 7, 200. Begum, M. K. et al (Rosenblum) *J. Am. Chem. Soc.* <u>1989</u>, *111*, 5252.

-some similar chemistry is known for the corresponding alkyne complexes, i.e.,

It is not nearly as well explored

R

see Reger, D.L. Organometallics <u>1984</u>, 3, 135 & 1759.



Wong, P. K. (Rosenblum) *J. Am. Chem. Soc.* <u>1977</u>, 99, 2823. Berryhill, S. R. (Rosenblum) *J. Org. Chem.* <u>1980</u>, 45, 1984; <u>1983</u>, 48, 158.



This can be repeated, using other ether function, with modification to get either alkene isomer



40