Echavarren, :A.M. Chen. Rev. $\frac{2015}{90288}$.
$A_{u}^{\text {I }}$ Catalyzeo addns to Alveynes Cuesia, A.E. "Nem Gomo - Chanarizad Rxis AnT APPICATIONS in Tita Statitesis of Alkaloids, CH.I spaingiar 2013

- in simplest for, many mietal cations Aetivate Amkenkes to nucheophule ATTACE. - VAGUELY SIMILAR NT HECK TYPE RXAS OF Pd (il)
- Include $P+(11), A_{g}(1)$, anis $A_{u}(111)$
- But espmeciany $A_{u}$ (t).
- Priztar complexation ALKKniEs lancenes 7 garbontins But Averues complex is MODE REACTUUN:
- Vary tunable - of tan a Ag(1) added to thre

$$
L A_{8}^{4} x \text { ro }\left[1 A A_{u}\right]^{+} \text {- Assumed RATAER }
$$



LESS ELECTROPHILIC


MORE ELFGROPHILIC

Geniztal Ron Schmies


INTERMOLECURAR ATTACR OF NUCLEOPHILES

- Mamt examples of $0, N$, Ant Somé $C$ Nucleophiles with $\mathrm{H}_{2} \mathrm{O}$, cant ES REPLACED $\mathrm{Hg}^{2+}$ in ADDN TO ALKENAMS IPr a
$120^{\circ}$

$$
\underbrace{\text { meo ore }}
$$

N-

$$
R_{+}^{2}-\text { EwG } \xrightarrow[\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{RT}_{T}]{\mathrm{Ph}_{3} P A_{4} \mathrm{NTf}_{2}++}
$$



M-Of MUSRY moomatic cases, OR ONES W ï DELOCALIZED.
$C-$

$$
N=-2.5-73
$$

$$
\xrightarrow[\mathrm{MeNO}_{2}]{\text { [AuCl } \left.\left(\mathrm{PPh}_{3}\right]_{2}\right], B F_{0} \cdot O E t_{2}}
$$



So far so Stealght forward - Do Have to watch out ror di-addition, taulull

Intramo necular cases.

$$
=-R^{\prime}+R^{2}-\frac{1}{50}
$$

- Therf are many cases where reactivity is cuite Stralgitt forward

0 -

 $x=0, \mathrm{Cl}_{2}$, NTS

N- NOTE: IN YOUR EXPERIENCE, S-EXO ALMAYS WINIS OYER G-ENIDO - BUT WE'RE NOW IN RRIPLE BOAD TERRITORY; I.E. S-EXO-DIG VS CO-ENDOMIG, AND THIS IS A CLOSE COMPETETITIUN OFTE N JUST decided by the substituents.




$\rightarrow R^{2}=H$ muser
SOME R 2 ALLYL

Gond - Cammzed 1,6-Entne CyChizations

- WHEN THE GOING GETS WEIRD. T MANY REARRANGEMENT PRODUCTS
- WHAT YOU WOULD EXPECT IS THE FOLLOWING. SINCE ALL HAS 1 OPEN SITE ONLY.


 - Without a NuCLEORHILE.....






But recall also, the b-ENdo -dig CTCLIzation has also become Possible

- this las Sievirah Possible outcomes, but one is most common


of COURE, if a nUCLEOPHILE IS PRESENT, IT MAY intercept the camomile species AMD Lo dR COnventionp.

IPrAuntfz




THERE ARE RUN MANIFOLD SIMILARLY COMPLEX FOR 1,S-ENYMES AND, T-ENYNES, BUT WEiLL CALL THESE BEYOND THE COURSE'S SCOPE...

Reactions or Propargin Carsorvhates (i.e. Acethtes or honger)

- Propargil ace tates (or bigger esters) Give Ran Results that are initiatip BY EITHER 1,2- OR 1.3-ACYLOXY MIGRATIONS
- these correspond rouqhiy to 5-Ex0-dic ant 6-Endo-dia Attacks OF THE ESTER CARBONYL - ALL IN EQUILIBRIUMI



$$
\iint_{\text {or G EMDO }}^{1,3-\text { Migrationt }}
$$



For ALIENE Co-ordination
1.3-

1,3.


${ }^{2} \mathrm{Bu}^{\circ} \stackrel{0}{\circ} \mathrm{O} \mathrm{OM}$


Alever, Ph
12.


IF No NuChEOPAILE

$$
\begin{aligned}
& x=B r, C_{1}
\end{aligned}
$$

OR IF TWERE'S A WRY OUT OF THE CATION WITHIN THE CARgOXVLATE, THE SYSTEM WILL OFTEN TAKE II



Mourins - MAN Sur, $V$;;
Frmsterbank, h. IsR.J.CHEM 2018, 58,586.

$$
+H^{+},-\left[A_{U} L\right]^{4}
$$

- IF YOU ADD An MLKENE, THE GOND CARBENE OETEN ACTS LIKE A Ranz Chrbenoid, Cychopropanating ite Alkente

- Yes. I did find an intramolecular case, but it rearranges meterwarms

- G. Allenes - $2^{\text {tD }}$ most Rexctive Functionar Groud For Au(i) (orAu(ini)) ACTVATION - No TIME, BYT SELE

Yamg. w. ; Hasmi,AS.k. Chem. Suc. ReV. 2014, 43, 2941.

