fascinATEing complexes

Helpful resources.

[GM Literature seminar, T. Mashiko (2007)]

Ate complexes are salts formed from the stoichiometric reaction of a Lewis base and Lewis acid, wherein the acidic moiety formally increases its valence and becomes anionic.

(Very) brief history.
- first alkali-metal ate complex, NaZnEt₃, synthesized in Wanklyn (1858)
- the term "ate" coined by Wittig (1951); first synthesis of magnesiate

Structure and reactivity.
Two standard reaction pathways:

Non-oxidative charge neutralization (ligand transfer)

Oxidative charge neutralization (non-ligand transfer)

"Much of this synthetic and structural chemistry has a synergic element to it, in the sense that compounds with a heterobimetallic (ate) combination of an alkali metal (usually Li, Na, or K) and magnesium or zinc or aluminum, can effect (often surprising) reactions which cannot be replicated by the corresponding homometallic (non-ate) alkali-metal, magnesium, zinc, or aluminium compounds." (Mulvey, 2007)

- enhanced solubility in organic solvents is a reliable indicator of ate formation
- two types: contact-ion pair (CIP) and solvent-separated ion pair (SSIP)
- lower-order: (AM)MR₃, higher-order: (AM)₂MR₄

Weiss motifs.

Molecular architecture construction is a two-stage process:
- anchoring bonds: stronger, more covalent (metal–R interactions)
- ancillary bonds: more ionic, enable lithium ions to affix to framework (CIPs)

Extraordinary" structure.

Reactions of diethylmagnesium–ethyl lithium solutions with pyridine.

Deprotonation of furans using lithium magnesates.

*can be trapped with E or engaged in a Pd-cat. cross-coupling event with 2-bromopyridine

Deprotonation of thiophenes using lithium magnesates.

Deprotonation of 2-bromopyridine using lithium magnesates.


Preparation of azulenylium and magnesium reagents utilizing halogen–metal exchange reaction of several iodoazulenes with organolithium or magnesium ate complex. Ito. *Tet. Lett.* 2004, 45, 2891.


Although...,(n-Bu)(α-Bu)Mg (DCM) was not suitable as the sole initiator to polymerize butadiene and sytrene, its "ate" complex with... (sec-BuLi)... could initiate the polymerization of both. Disperisty of 1.06 obtained in all cases; indicative of a "living" anionic polymerization.


**Polymers**


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**Zincates.**


All reactions were performed using THF, −85 to 0 °C.

R1R2H (86%)

R1R2H (68%)

R1R2H (72%)

R1R2H (66%)


All attempts to cross-couple aryl-zincate (sic)... were unsuccessful, generally giving no reaction."

"We believe the complete lack of reactivity... is due to the electron-withdrawing effects of the aryl substituents."


Fragment 1
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1. TsOH, MeOH; K$_2$CO$_3$

2. Cp$_2$ZrHCl; I$_2$

Fragment 2

H$_2$C\(\text{OEt}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)\(\text{EtO}\)

PMBO\(\text{O}\)\(\text{OTBS}\)

N$_3$\(\text{CO}\)\(\text{N}^3\)

\(\text{ZnMe}_2\text{Li}\)

AcOH, H$_2$O, Me$_2$CO

PMBO\(\text{O}\)\(\text{OTBS}\)

Fragment 3

O\(\text{O}\)

1. BnOH\(\text{tBuOK}\) cat.

2. ClCO$_2$Me\(\text{Et}_3\text{N}\)

1. Dess-Martin

2. (Ph$_3$PCH$_2$)I, NaHMDS

Chelation-controlled addition of 1 and 2

\(\text{OMe}\)

\(\text{MeZn}\)

Boronates.

Asymmetric addition of chiral boron-ate complexes to cyclic iminium ions.


Total synthesis of roseophilin.


- shielding exerted by rigid ansa-chain provides facial guidance in Michael add’n
- forces protonation of enolate to occur from the same side
- corresponding cuprate proved ineffective

possible pathway to undesired
fascinATEing complexes


Improper use of nomenclature?

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MIDA boronates are hydrolysed fast and slow by two different mechanisms. Cheong, Burke, and Lloyd-Jones. Nat. Chem. 2016, 8, 1067.

Two distinct mechanisms.
1. Base-mediated: 3 orders of magnitude faster, RLS = attack by hydroxide at MIDA carbonyl C
2. Neutral: No exogenous acid or base, RLS = B–N cleavage by a small water cluster, (H2O)n

Total synthesis of synechoxanthin through iterative cross-coupling.

MIDA Boronates. (see M. Farmer, "Boron" GM 2014)

- "indefinitely" bench-top stable under air
- chromatography compatible
- unreactive under standard anhydrous cross-coupling using either mild base
- rate of hydrolysis is (mostly) unaffected by substrate; can be controlled by reaction conditions


MIDA deGruyter

Justine MIDA - Burke.

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Cuprates.
Copper-mediated aerobic oxidative trifluoromethylation of terminal alkynes with Me$_3$SiCF$_3$.
The role of ate complexes in the copper-mediated trifluoromethylation of alkynes.

Oxidative trifluoromethylation and trifluoromethylthiolation reactions using (trifluoromethyl)trimethylsilane as a nucleophilic CF$_3$ source.

Practical methods for the synthesis of trifluoromethylated alkynes: Oxidative trifluoromethylation of copper acetylides and alkynes.

Total synthesis of auripyrone B using a non-aldol–cuprate opening process.

Practical methods for the synthesis of trifluoromethylated alkynes: Oxidative trifluoromethylation of copper acetylides and alkynes.
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Aluminum ates.

Molybdenum or tungsten alkylidyne ates.

Tin ates.