

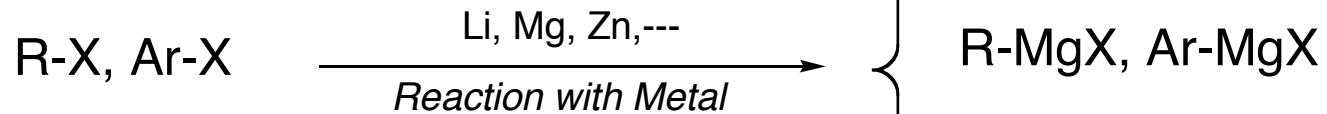
有機リチウム化合物の合成法

有機基質	Li反応剤	反応式	反応形式
RX (ArX)	Li	$\text{RX} + 2\text{Li} \rightarrow \text{RLi} + \text{LiX}$	有機ハロゲン化物と金属リチウムの直接反応
	$\text{Ar}^- \text{Li}^+$ (lithium arenide)	$\text{RX} + 2 \text{Ar}^- \text{Li}^+ \rightarrow \text{RLi} + \text{LiX} + 2 \text{Ar}$	有機ハロゲン化物とリチウムアレニドの反応
	R'Li	$\text{RX} + \text{R}'\text{Li} \rightarrow \text{RLi} + \text{R}'\text{X}$	ハロゲンとリチウムの交換反応
RH (ArH)	Li	$\text{RH} + \text{Li} \rightarrow \text{RLi} + 1/2 \text{H}_2$	炭化水素と金属リチウムの直接反応
	R'Li (R'₂NLi etc.)	$\text{RH} + \text{R}'\text{Li} \rightarrow \text{RLi} + \text{R}'\text{H}$	水素とリチウムの交換反応
C=C, C≡C	R'Li	$\text{C}=\text{C} \text{ or } \text{C}\equiv\text{C} + \text{R}'\text{Li} \rightarrow \begin{array}{c} \text{R}' \\ \\ \text{C}-\text{C}-\text{Li} \end{array} \text{ or } \begin{array}{c} \text{R}' \\ \\ \text{C}=\text{C}-\text{Li} \end{array}$	カルボリチオ化反応
RY, Y=Met (Sn, Hg)	Li, R'Li	$\text{RY} + 2\text{Li} \rightarrow \text{RLi} + \text{LiY}$ $\text{RY} + \text{R}'\text{Li} \rightarrow \text{RLi} + \text{R}'\text{Y}$	他の金属とリチウムの交換反応
RY, Y=chalcogen (O, S, Se, Te)	$\text{Li}, \text{Ar}^- \text{Li}^+$ (lithium arenide)	$\text{RY} + 2 \text{Ar}^- \text{Li}^+ \rightarrow \text{RLi} + \text{LiY} + 2 \text{Ar}$	有機カルコゲン化物とリチウムアレニドの反応
	R'Li	$\text{R}'\text{Li} + \text{R}'-\text{CH}(\text{NHSO}_2\text{Ar})-\text{N}(\text{R}'')-\text{H} \rightarrow \text{R}'-\text{CH}(\text{Li})-\text{NHSO}_2\text{Ar} + \text{N}_2 + \text{ArSO}_2\text{Li} + 2\text{R}'\text{H}$	Shapiro反応
		$\text{R}'\text{Li} + \text{R}-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{R}' \rightarrow \text{R}-\text{CH}(\text{Li})-\text{CH}(\text{Br})-\text{R}' + \text{R}'\text{H} + \text{LiBr} + \text{R}'\text{Br}$	Fritsch-Buttenberg-Wiechell型転位
その他			

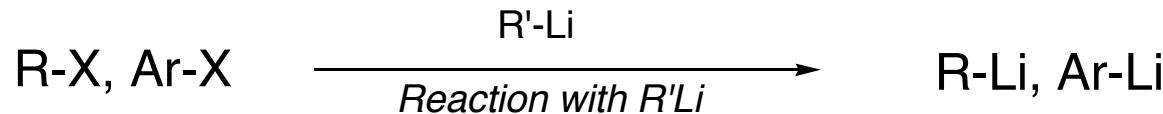
Preparation of R-Li, R-MgX, RZnX, etc. (1)

From R-X, Ar-X

- **Halide–Metal Direct Reaction (Oxidative Addition)**

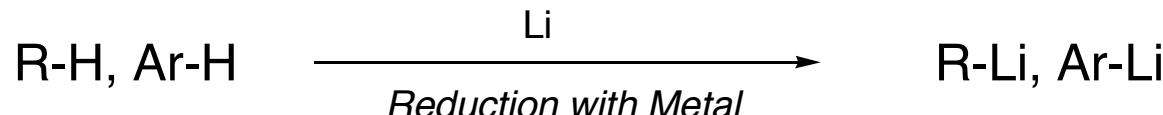


- **Halogen–Metal Exchange**

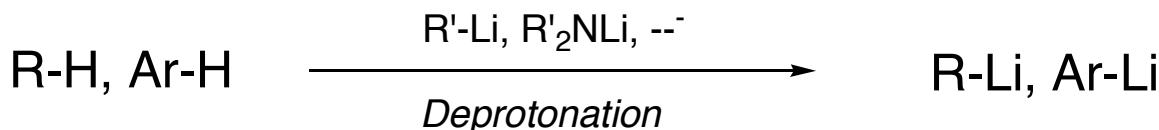


From R-H, Ar-H

- **Hydrocarbon–Metal Direct Reaction**



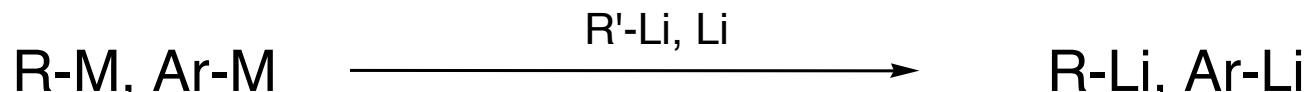
- **Hydrogen–Metal Exchange**



Preparation of R-Li, R-MgX, RZnX, etc. (2)

From R-Met., Ar-Met.

- Metal-Metal Exchange

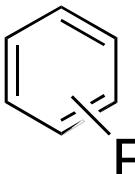


M = Sn, Hg, Se, --

From C=C, C≡C

- Insertion (Hydrometalation, Carbometalation, ---)



From  , Ar-C≡C-Ar

- Unsaturated Hydrocarbon–Metal Direct Reaction

RLiの安定性（化学的，熱的）

主としてエーテル系溶媒と反応することで分解



RLi	solvent	temp.	t _{1/2}
MeLi	Et ₂ O	rt	several month
EtLi	Et ₂ O	rt	54 h
n-BuLi	Et ₂ O	rt	153 h
n-BuLi	THF	rt	2 h
s-BuLi	THF	0 °C	0.5 h
t-BuLi	Et ₂ O	rt	vigorously react.
t-BuLi	THF	0 °C	vigorously react.
PhLi	Et ₂ O	reflux	12 h
vinyl Li	Et ₂ O	rt	<7 h