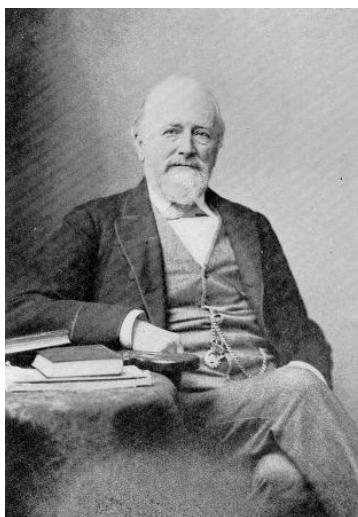


## 5.3: Organometallic Chemistry of Zinc

The first dialkyl zinc derivatives,  $\text{Me}_2\text{Zn}$  and  $\text{Et}_2\text{Zn}$ , were prepared in 1848 by Edward Franklin. He also prepared the monoalkyl derivatives,  $\text{RZnX}$ .



British chemist Sir Edward Franklin FRS (1825–1899).

Initially alkyl zinc compounds were used in organic synthesis, however, their use diminished significantly once Grignard reagents had been discovered. Little further was investigated of their chemistry until their use in the growth of electronic materials developed in the 1980's.

### RZnX

The monoalkyl derivatives are not widely used, but were historically the first to be prepared (Equation 5.3.1).



While the iodide derivatives can be isolated as unsolvated derivatives, the chloride and bromides need to be prepared in the presence of dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Alternative methods of synthesis involve the reaction with a Grignard reagent, (Equation 5.3.2), or electrochemical synthesis with a zinc electrode.



In the solid state  $\text{RZnI}$  exists as cage oligomers or polymeric chain structures. These structures are broken by the addition of strong Lewis bases to form Lewis acid-base complexes. In solution there exists a Schlenk equilibrium (equation 5.3.3) whose presence has been determined by IR and Raman spectroscopy (Table 5.3.1).

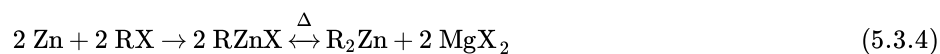


Stretch	IR ( $\text{cm}^{-1}$ )	Raman ( $\text{cm}^{-1}$ )
symmetric C-Zn-C	Not observed	477
asymmetric C-Zn-C	551	Not observed
C-Zn-I	510	510

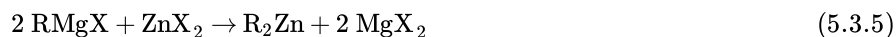
**Table 5.3.1:** IR and Raman spectroscopic characterization of the components of the Schlenk equilibrium,

### $\text{R}_2\text{Zn}$

Dialkyl zinc compounds are prepared via the monoalkyl derivatives (Equation 5.3.4). The Schlenk equilibrium is shifted at high temperatures by the distillation of the volatile  $\text{R}_2\text{Zn}$  derivative. The zinc is usually alloyed with copper (10%) to improve the reaction rate.



Alternative preparation methods include the reaction of  $\text{ZnX}_2$  with a Grignard (Equation 5.3.5) or by metal-metal exchange (Equation 5.3.6).



## Bibliography

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- J. J. Habeeb, A. Osman, and D. G. Tuck. *J. Organomet. Chem.*, 1980, **185**, 117

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