SEMI-ANIONIC NUCLEOPHILES

Some nucleophiles are added to carbonyls in the form of salts, such as sodium cyanide. In a salt, there is an anion and a cation. The anion can act as a nucleophile, donating a lone pair to the carbonyl. The cation is just a counterion; it is there to balance the charge but doesn't usually play an active role.

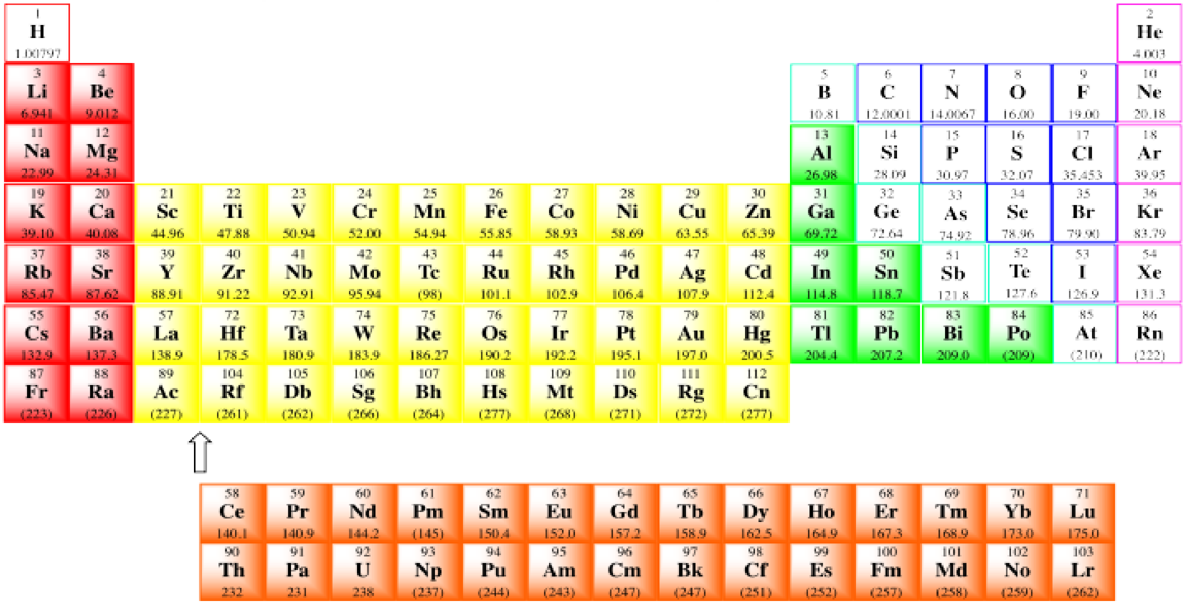
Some anions are too unstable and reactive to be used as salts. This is especially true with a number of carbon nucleophiles. C-H bonds are not usually acidic enough to deprotonate with a strong base. That makes it hard to make a simple salt containing such nucleophiles. There are exceptions, such as acetylide or alkynyl protons like $CH_3CC\mathbf{H}$. In that case, the resulting anion is relatively stable because the lone pair is in a lower-energy orbital with more s character, so it is held more tightly to the nucleus.

Less stable carbon anions can be be stabilized through a covalent bond. If the carbon is covalently attached to a less electronegative atom, the carbon has a partially negative charge. It can still act as though it were an anion. However, the covalent bond stabilizes the would-be "lone pair". Compounds like this can be considered to be "semi-anionic". Frequently, they are described as polar covalent compounds, although that is really a much more general term.

These polar covalent bonds can be found any time a carbon atom is bound to a metal. Remember, the metals are the aroms in the coloured boxes in the periodic table below.

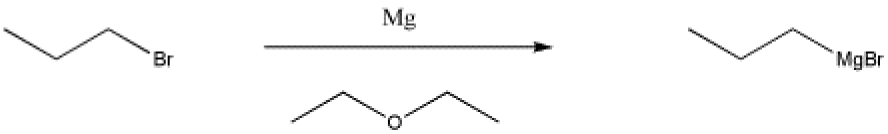
Periodic Table of the Elements

College of Saint Benedict / Saint John's University

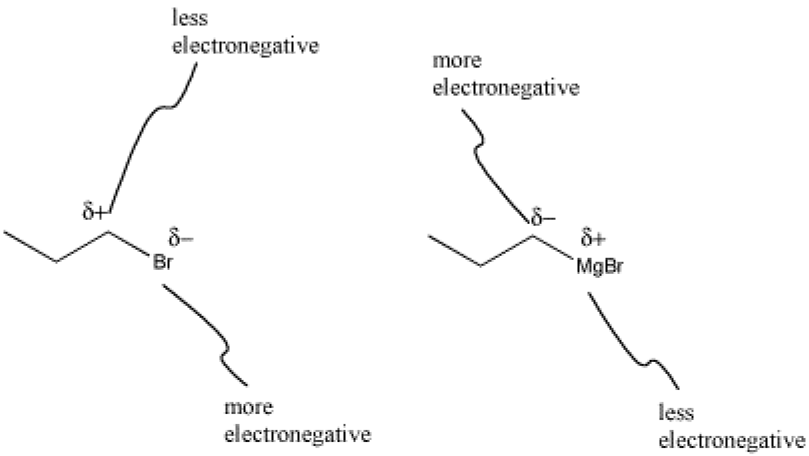


1 **H** 1.00797																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.0001	7 **N** 14.0067	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.453	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.64	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.79
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.27	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.5	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)	112 **Cn** (277)						
		⇧															
			58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0	
			90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)	

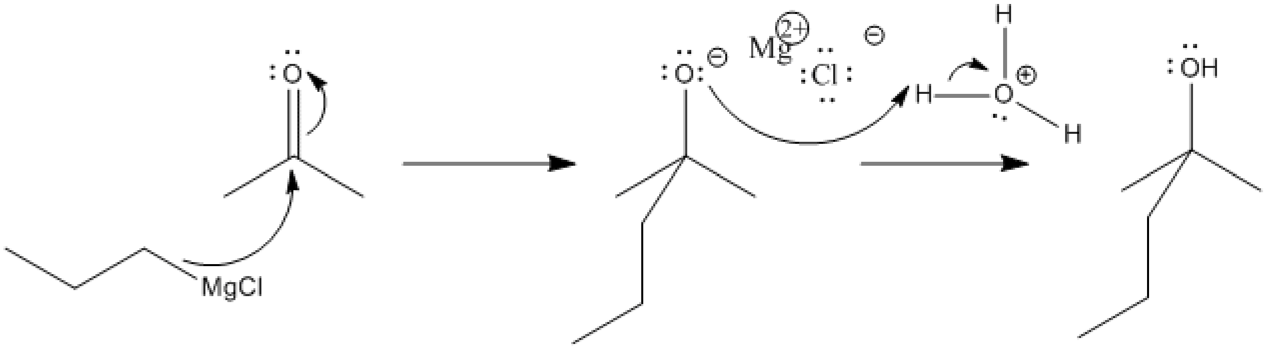
One of the most common classes of this type of compounds is the family of organomagnesium halides or Grignard reagents (Green-yard reagents). Victor Grignard was awarded the Nobel Prize in Chemistry for his development of these reagents. These compounds are made by reacting an alkyl halide (such as $CH_3CH_2CH_2Cl$) with magnesium metal. The metal undergoes an insertion into the C-Cl bond, forming $CH_3CH_2CH_2MgCl$. (You don't need to worry about how this happens.) Because magnesium is less electronegative than carbon, the C-Mg bond acts as though it were a lone pair on the carbon and the magnesium acts as though it were a cation.



What's striking about Grignard formation is that polarity is reversed in this reaction. In the alkyl halide, the carbon attached to the halogen has a partially positive charge, because carbon is further to the left than halogens in the periodic table. After magnesium insertion, this same carbon has a partial negative charge, because carbon is farther to the right in the periodic table than magnesium. This sort of reversal in reactivity is sometimes called "umpolung chemistry".



Propylmagnesium chloride and other Grignard reagents can deliver alkyl nucleophiles to carbonyls. Just like with simple anionic nucleophiles, an alkoxide ion results. Subsequent treatment of the alkoxide with acid provides a proton, resulting in an alcohol.



Remember, the order of these two steps is very important. Adding the acid before the Grignard reagent would not work, because the Grignard reagent would become protonated at the carbon. Although the Mg-C bond is covalent, it is still polar enough so that the carbon can act as a nucleophile or as a base. Once propylmagnesium has become protonated, it forms propane, which isn't likely to act as a nucleophile.

Source : http://employees.csbsju.edu/cschaller/Reactivity/carbonyl/COsemianion.htm