The Schlenk equilibrium and the composition of Grignard Reagents in ethereal solutions

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SUPPORT INFORMATION

S1. Optimized bond distance (Å) for Grignard reagents RMgX, as monomeric species, at different levels of calculation. All calculations performed with the aug-cc-pVTZ basis set (*a*), excepting at MP2 level that was also performed with the cc-pVTZ basis set (*b*).

	C- Mg [a]	Mg-X [a]		
		F	Cl	Br
HF	2.09	1.74	2.20	2.35
GVB-PP	2.12	1.76	2.21	2.37
GVB-RCI	2.12	1.77	2.22	2.37
MP2	2.09 (2.09) [b]	1.78 (1.77) [b]	2.20 (2.20) [b]	2.36 (2.36) [b]

S2. Optimized bond distance (Å) for MgX_2 and MgR_2 species, at different levels of calculation. All calculations performed with the aug-cc-pVTZ basis set.

	C- Mg	Mg-X		
		F	Cl	Br
GVB-PP	2.13	1.75	2.18	2.34
GVB-RCI	2.13	1.76	2.18	2.34
MP2	2.10	1.77	2.19	2.34

S3. Optimized bond distance (Å) for Grignard reagents as monomeric (M) and dimeric species (D), at different basis sets, aug-cc-pVTZ basis set, cc-pVTZ basis set and 6-311G* basis set. All calculations performed at MP2 level.

C-Mg							Mg-X					
	F(M)	F(D)	Cl(M)	Cl(D)	Br(M)	Br(D)	F(M)	F(D)	Cl(M)	Cl(D)	Br(M)	Br(D)
ACCT	2.09	2.09	2.08	2.09	2.08	2.09	1.78	1.93	2.21	2.39	2.36	2.55
CCT	2.09	2.09	2.08	2.08	2.08	2.08	1.77	1.92	2.20	2.39	2.36	2.55
6-311G*	2.09	2.09	2.09	2.09	2.09	2.09	1.80	1.94	2.20	2.38	2.36	2.55

S4. Optimized bond distance (Å) for Grignard reagents, at aug-cc-pVTZ basis set. All calculations performed at DFT (M-06) level.

L	Unsolvated		Et_2O		THF	
	C-Mg	Mg-X	C-Mg	Mg-X	C-Mg	Mg-X
CH_3MgF	2.06	1.76	2.07	1.79	2.07	1.80
MgF_2	-	1.75	-	1.78	-	1.79
$Mg(CH_3)_2$	2.08	-	2.09	-	2.09	-
CH_3MgCl	2.06	2.20	2.07	2.23	2.07	2.25
$MgCl_2$	-	2.17	-	2.21	-	2.21
CH_3MgBr	2.06	2.34	2.07	2.38	2.07	2.39
$MgBr_2$	-	2.32	-	2.35	-	2.36
$(CH_3MgF)_D$	2.07	1.92	2.08	1.93	2.11	1.93
$(CH_3MgCl)_D$	2.06	2.39	2.07	2.40	2.07	2.40
$(CH_3MgBr)_D$	2.06	2.54	2.07	2.55	2.07	2.55

(*D*): Dimeric species.

S5. Optimized bond distance (Å) for Grignard reagents, at 6-311G* basis set. All calculations performed at DFT (M-06) level.

	S. *n* Et2O					
	(Mg-O)		(Mg-X)		(C-Mg)	
	n=1	n=2	n=1	n=2	n=1	n=2
CH_3MgF	2.06	2.13; 2.09	1.82	1.84	2.09	2.12
MgF_2	-	2.06; 2.08	-	1.83	-	-
$Mg(CH_3)_2$	-	2.15	-	-	-	2.14
CH_3MgCl	2.07	2.13; 2.11	2.25	2.29	2.09	2.11
$MgCl_2$	-	2.07	-	2.27	-	-
CH_3MgBr	2.07	2.11; 2.13	2.40	2.45	2.09	2.11
$MgBr_2$	-	2.06; 2.09	-	2.42	-	-
$(CH_3MgF)_D$	-	2.12; 2.14	-	1.96	-	2.09
$(CH_3MgCl)_D$	-	2.08	-	2.43; 2.45	-	2.09
$(CH_3MgBr)_D$	-	2.07; 2.08	-	2.58; 2.61	-	2.09

(*D*): Dimeric species, (*S*): Organomagnesium compound.

S6. Optimized bond distance (Å) for Grignard reagents, at 6-311G* basis set. All calculations performed at DFT (M-06) level.

	S. *n* THF					
	(Mg-O)		(Mg-X)		(C-Mg)	
	n=1	n=2	n=1	n=2	n=1	n=2
CH_3MgF	2.06	2.10; 2.11	1.81	1.85	2.09	2.12
MgF_2	-	2.06	-	1.83	-	-
$Mg(CH_3)_2$	-	2.13	-	-	-	2.13
CH_3MgCl	2.06	2.09; 2.11	2.25	2.30	2.09	2.11
$MgCl_2$	-	2.05; 2.07	-	2.26; 2.27	-	-
CH_3MgBr	2.06	2.09; 2.12	2.39	2.45	2.09	2.10
$MgBr_2$	-	2.06	-	2.41	-	-
$(CH_3MgF)_D$	-	2.09; 2.10	-	1.95; 1.96	-	2.10
$(CH_3MgCl)_D$	-	2.07	-	2.44	-	2.09
$(CH_3MgBr)_D$	-	2.07	-	2.59	-	2.09

(*D*): Dimeric species, (*S*): Organomagnesium compound.

S7. Spin density values of possible radical species in Grignard reagent. All calculations performed at DFT (M-06) and CASSCF levels.

radical	σ_{CASSCF}			σ_{DFT}		
	C	Mg	X	C	Mg	X
CH_3	2×10^{-6}	-	-	0.0520	-	-
MgF	-	0.9012	0.0419	-	1.1111	0.0577
MgCl	-	0.8793	0.0570	-	1.1275	0.0982
MgBr	-	0.9410	0.0950	-	1.1424	0.1586

S8. Autocatalytic process Gibbs energies (ΔG^0_{13}) for tert-butyl radical and carbanionic species in ethereal solvents performed at DFT (M-06) level with the 6-311G** basis set. [a] The subscript on the ΔG^0 refers to the reaction depicted in Scheme 1.

X	THF	Et_2O
F	+4.55	+7.36
Cl	-21.18	-13.06
Br	-13.25	-13.27

(a) All values are in kcal/mol.