The Addition of Grignard Reagents to Carbodiimides. The Synthesis, Structure and Potential Utilization of Magnesium Amidinates

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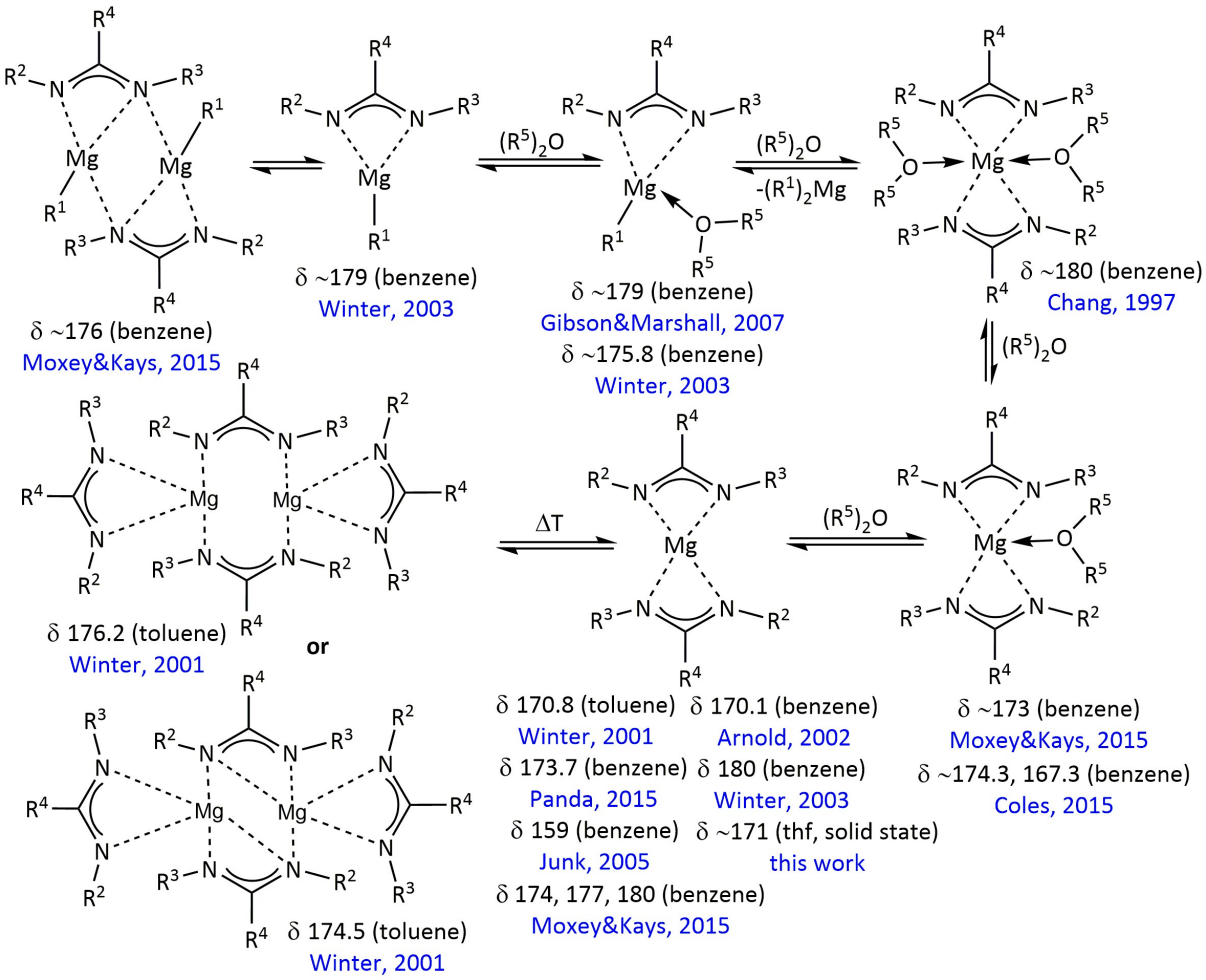

Scheme S1: Possible structural motifs and ^{13}C NMR shifts of the central carbon atom of the amidinato ligand of known organomagnesium amidinates and bisamidinates – references are given in the article.

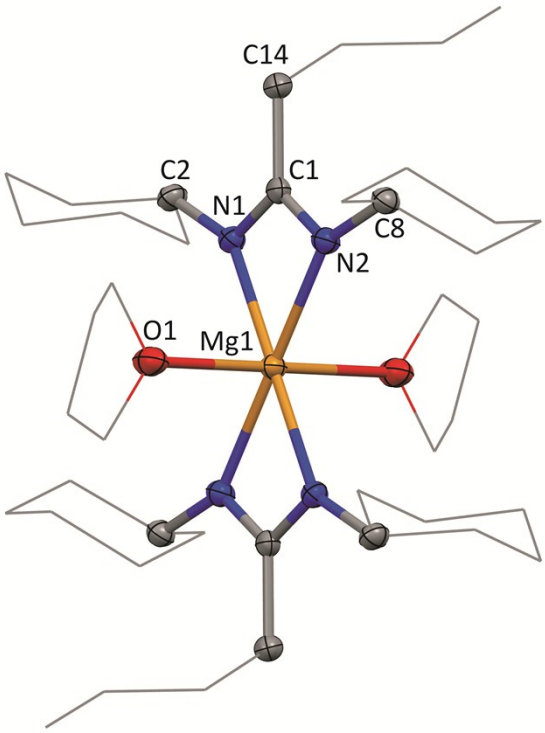

Fig. S1 The molecular structure of **8** (ORTEP view, 50% probability level). Hydrogen atoms and the second independent molecule are omitted for clarity. Symmetry operation: -x, -y, ½-z. Selected interatomic distances [Å] and angles [°], values of the second independent molecule are given in italics: N1-C1 1.327(3) *1.330(3)*; N2-C1 1.332(3) *1.328(4)*; N1-Mg1 2.152(2) *2.177(2)*; N2-Mg1 2.174(2) *2.163(2)*; N1-C1-N2 113.7(2) *113.9(2)*.

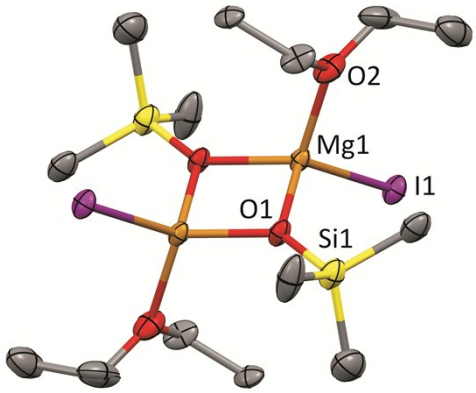

Fig. S2 The molecular structure of **[MgI(Et$_2$O)-μ-OSiMe$_3$]$_2$** (ORTEP view, 40% probability level). Hydrogen atoms are omitted for clarity. Symmetry operation: -x, -y, ½-z. Selected interatomic distances [Å] and angles [°]: O1-Mg1 1.936(6); O1-Mg1a 1.956(6); I1-Mg1 2.663(2); Si1-O1a 1.616(6); Mg1-O1-Mg1a 92.9(3); O1a-Mg1-O1 87.1(3); I1-Mg1-O1a 118.4(2).

Comparison of the PBE0/6-31G(d) and B3LYP/6-31G(d) results:

	1	THF	-$^{n}Bu_2Mg$	-----> **8**	
PBE0	-1132.11610	-232.04617	-514.96569	-2213.38868	ΔH = -18.7 kcal/mol
B3LYP	-1133.3688	-232.31858	-515.49769	-2215.89394	ΔH = -10.6 kcal/mol

	MeMgI	$(MeMgI)_2$	
PBE0	-7158.946551	-14317.93893	ΔH =-28.8 kcal/mol
B3LYP	-7159.55394	-14319.1442	ΔH =-22.8 kcal/mol

	$(MeMgI)_2$	Et_2O	*p*TolNCN*p*Tol	-----> **9**	
PBE0	-14317.93893	-233.22967	-688.427965	-15472.99242	ΔH = -104.3 kcal/mol
B3LYP	-14319.14420	-233.51412	-689.241599	-15475.55908	ΔH = - 91.0 kcal/mol

Table S1: Polymerization of TMC catalyzed by magnesium complexes

Run	Cat.	Conversion %	M_n[1] [kg.mol^{-1}]	Đ[1]
23	**1**	78	11.4	1.50
24	**9**	81	9.5	1.39

90 min, 80°C, n(cat)=18 μmol, [TMC]=6.8 mol.l^{-1}, TMC/**1** or **9**=450

[1] Number average molar mass and dispersity (M_w/M_n) determined by SEC-MALLS

Table S2: Polymerization of LLA catalyzed by magnesium complexes

Run	Cat.	[LLA]	*n* (BnOH)	Conversion %	M_n[1] [kg.mol^{-1}]	Đ[1]
25[2]	**1**	1.1	-	36	15.0	2.26
26	**1**	1.7	18	55	11.1	1.85
27[3]	**1**	1.7	19	75	10.6	2.07
28[3]	**1**	0.9	19	77	11.6	2.27
29[3,4]	**1**	0.9	19	75	11.6	2.33
30	**9**	1.7	16	-	-	-

100°C, 90 min, n(cat)=20 μmol; LLA/cat=160-200; [1] Number average molar mass and dispersity (M_w/M_n) determined by SEC against polystyrene calibration; [2] RT for 140 min. [3] LLA recrystalized from ethylacetate; [4] 45 min of polymerization

Table S3: Esterification of LLA catalyzed by magnesium complexes

Molar ratio (LLA : MeOH : catalyst)	Catalyst	Reaction time	% LLA	% MeLacH	% $Me(Lac)_2H$	% $Me(Lac)_3H$
100:400:1	**4**	1 min.	74.43	0	22.46	3.1
		30 min.	3.8	0.32	78.6	17.24
		2 hrs.	8.97	0.82	74.31	15.9
		24 hrs.	9.62	0	47.23	43.14
50:200:1	**4**	1 min.	0.51	93.46	6.03	0
		30 min.	0.48	89.94	23.1	8.86
		2 hrs.	0.54	93.95	5.51	0
		24 hrs.	0.44	90.88	8.68	0
100:400:1	MeMgI	1 min.	0	19.02	57.34	23.64
		30 min.	0	3.42	89.33	7.24
		2 hrs.	0	0.14	94.95	4.91
		24 hrs.	0	0	93.4	6.6
50:200:1	MeMgI	1 min.	0	58.83	27.47	13.7
		30 min.	0	0	91.04	8.96
		2 hrs.	0	0	95.03	4.97
		24 hrs.	0	0	93.21	6.79

Table S4: Esterification of LLA catalyzed by magnesium complexes - continued

Ratio (LLA : MeOH : catalyst)	Catalyst	Reaction time	% LLA	% MeLacH	% $Me(Lac)_2H$
100:400:1	**1**	1 min.	0	93.23	6.77
		30 min.	0	94.03	5.97
		2 hrs.	0	97.63	2.37
		24 hrs.	0	55.91	44.09
50:200:1	**1**	1 min.	0	67.23	32.77
		30 min.	0	96.53	3.47
		2 hrs.	0	97.54	2.46
		24 hrs.	0	97.47	2.53
100:400:1	**9**	1 min.	0	64.73	35.27
		30 min.	0	76.42	23.58
		2 hrs.	0	76.69	23.31
		24 hrs.	0	95.84	4.16
50:200:1	**9**	1 min.	0	82.09	17.91
		30 min.	0	76.97	23.03
		2 hrs.	0	81.66	18.34
		24 hrs.	0	95.17	4.83

General methods

All syntheses were performed using standard Schlenk techniques under an inert argon atmosphere. All solvents and reagents were purchased from commercial sources. Solvents were dried using the solvent purification system PureSolv MD 7 supplied by Innovative Technology, Inc., degassed and then stored under an argon atmosphere over a potassium mirror. The melting points were measured in inert perfluoroalkylether oil and are uncorrected. The elemental analyses (C, H and N) of new compounds were performed under an inert argon atmosphere on an automatic analyzer EA 1108 by FISONS Instruments. Deuterated solvents for NMR samples preparation were distilled, degassed and stored over a potassium mirror under an argon atmosphere.

TMC was kindly supplied by Labso Chimie Fine (France) and used as received (water content 200 ppm), Cyclohexene oxide (CHO, Aldrich 98%), propylene oxide (Aldrich, 99%), CL (Aldrich, 97%) were dried over CaH_2 and vacuum distilled prior to use (water content: CHO 8 ppm, PPO 10 ppm, CL 74 ppm), LLA (Aldrich) was used as received. Toluene was refluxed on sodium and distilled prior to use (4 ppm water content). Karl-Fischer titration was used to determine the water content in monomers and solvent.

NMR spectra of appropriate compounds in C_6D_6, THF-d_8, Tol-d_8 or $CDCl_3$ solutions were recorded on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5mm probe) with a resonance frequency of 500.13 MHz for ^{1}H and 125.76 MHz for $^{13}C\{^1H\}$ at 295 K. Values of ^{1}H and ^{13}C chemical shifts were calibrated to residual signals of benzene ($\delta(^1H)$ = 7.16 / $\delta(^{13}C)$ = 128.4), THF ($\delta(^1H)$ = 3.58 / $\delta(^{13}C)$ = 67.57), chloroform ($\delta(^1H)$ = 7.27 / $\delta(^{13}C)$ = 77.23) and toluene ($\delta(^1H)$ = 7.00 / $\delta(^{13}C)$ = 137.9). All ^{13}C NMR spectra were recorded under standard gated proton-decoupling; CH and CH_3 vs. C and CH_2 moieties were differentiated using the APT method[1].

The solid state NMR spectra were measured on a Bruker Avance III HD 500 WB/US spectrometer at 11.7 T in a double-resonance 4-mm probe head at 300 K. Standard cross-polarization experiments were used to record ^{13}C CP/MAS NMR spectra at MAS frequency of 10 kHz (the intensities of excitation and spin-locking fields $B_1(^{13}C)$ expressed in frequency units $\omega_1/2\pi = \gamma B_1$ were 62.5 kHz and the duration of cross-polarization contact time pulse was 1.7 ms, recycle delay of 5 - 10 s). The ^{13}C NMR scale was calibrated with glycine as an external standard (176.03 ppm - low-field carbonyl signal).

The ^{13}C NMR spectra of methylmagnesium chloride and methylmagnesium iodide, respectively, in the solid state as well as in solutions were recorded for the study of the reactivity towards starting *N*,*N*-disubstituted carbodiimides. **CH_3MgCl**: ^{1}H NMR (THF/THF-d_8 [9/1], 500 MHz, 295 K) δ: -1.79 (s, 3H, CH_3). ^{13}C NMR (THF/THF-d_8 [9/1], 125 MHz, 295 K) δ: -17.0 (*C*H_3). ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: -12.6 (*C*H_3); -13.6 (*C*H_3); -15.7 (*C*H_3). **CH_3MgI**: ^{1}H NMR (Et_2O/internal capillary with THF-d_8, 500 MHz, 295 K) δ: -1.82 (s, 3H, CH_3). ^{13}C NMR (Et_2O/ internal capillary with THF-d_8, 125 MHz, 295 K) δ: -12.4 (*C*H_3). ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: -9.4 (*C*H_3).

General procedure of attempt for preparation of [RNC(Me)NR]MgX (2 - 7)

One equivalent of commercial 3M methylmagnesium iodide solution in Et_2O or 3M methylmagnesium chloride solution in THF was added using a Hamilton syringe to a colourless solution of the appropriate starting *N*,*N*'-disubstitued carbodiimide in hexane cooled approximately to 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. All solvents were evaporated under vacuo.

Preparation of 1

1M di-*n*-butylmagnesium solution in heptane (4.67 ml, 4.64 mmol) was added using a Hamilton syringe to a solution of *N,N'*-dicyclohexylcarbodiimide (0.958 g, 4.64 mmol) in hexane (30 ml) cooled approximately to 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting white precipitate of **1** was obtained. All solvents were evaporated under vacuo and the crude product of **1** was extracted with hexane (15 ml). All volatiles were evaporated under vacuo to give 0.983 g (60 %) of pure white powder of **1**. Single crystals suitable for XRD analyses were obtained from a saturated solution of **1** in hexane at -30 °C. mp 240 - 241 °C. ^{1}H NMR (C_6D_6, 500.13 MHz, 295 K) δ: 3.17 (m, 2H, Cy*H*); 2.29 (t, ^{3}J = 8.1 Hz, 2H, $^{\alpha}CH_2$); 2.11 - 1.49 (br m, 14H; $^{\beta}CH_2$ + Cy*H*); 1.43 - 1.06 (br m, 10H, $^{\gamma}CH_2$ + Cy*H*); 0.89 (t, ^{3}J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6, 125.76 MHz, 295 K) δ: 181.7 (N*C*N); 56.8 (Cy); 36.9 (Cy); 31.0 ($^{\alpha}CH_2$); 28.0 ($^{\beta}CH_2$); 26.6 (Cy); 26.3 (Cy); 23.9 ($^{\gamma}CH_2$); 14.2 (*C*H_3). Anal. Calcd for $C_{42}H_{80}Mg_2N_4$ of single crystals: C 73.14; H 11.69; N 8.12. Found: C 73.23; H 11.76; N 7.81.

Attempt for preparation of [^{i}PrNC(Me)N^{i}Pr]MgI (2) leading to the mixture of [^{i}PrNC(Me)N^{i}Pr]$_2$Mg(Et$_2$O)$_n$ and MgI$_2$(Et$_2$O)$_3$

N,*N*′-diisopropylcarbodiimide (0.505 g, 0.62 ml, 4.00 mmol); 3M methylmagnesium iodide solution (1.33 ml, 4.00 mmol); hexane (30 ml). 1.157 g (99 %) of **2**. mp > 250 °C. ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: 180.0 (N*C*N); 179.1 (N*C*N); 47.7 (br s, *C*H); 26.6 (*C*H$_3$); 26.1 (*C*H$_3$); 25.4 (*C*H$_3$); 25.2 (*C*H$_3$); 24.1 (*C*H$_3$); 18.0 (NC(*C*H$_3$)N). Preparation of the sample for solution NMR measurement in the donor solvent THFd$_8$ led to the formation of [^{i}PrNC(Me)N^{i}Pr]$_2$Mg(Et$_2$O)$_n$ and MgI$_2$(Et$_2$O)$_3$ - ^{1}H NMR (THF-d$_8$, 500.13 MHz, 295 K) δ: 3.47 (m, 2H, C*H*); 1.81 (s, 3H, NC(C*H*$_3$)N); 1.02 (d, ^{3}J = 6.4 Hz, 12H, C*H*$_3$). ^{13}C NMR (THF-d$_8$, 125.76 MHz, 295 K) δ: 171.0 (N*C*N); 47.1 (*C*H); 26.9 (*C*H$_3$); 10.9 (NC(*C*H$_3$)N).

Attempt for preparation of [^{i}PrNC(Me)N^{i}Pr]MgCl (3) leading to the mixture of [^{i}PrNC(Me)N^{i}Pr]$_2$Mg(THF)$_n$ and MgCl$_2$(THF)$_4$

N,*N*′-diisopropylcarbodiimide (1.002 g, 1.23 ml, 7.94 mmol); 3M methylmagnesium chloride solution (2.65 ml, 7.94 mmol); hexane (30 ml). 1.578 g (99 %) of **3**. mp > 250 °C. ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: 170.4 (N*C*N); 45.9 (*C*H); 45.7 (*C*H); 26.5 (*C*H$_3$); 26.0 (*C*H$_3$); 25.8 (*C*H$_3$); 25.5 (*C*H$_3$); 24.9 (*C*H$_3$); 9.8 (NC(*C*H$_3$)N). Preparation of the sample for solution NMR measurement in the donor solvent THFd$_8$ led to the formation of [^{i}PrNC(Me)N^{i}Pr]$_2$Mg(THF)$_n$ and MgCl$_2$(THF)$_4$ - ^{1}H NMR (THF-d$_8$, 500.13 MHz, 295 K) δ: 3.46 (m, 2H, C*H*); 1.80 (s, 3H, NC(C*H*$_3$)N); 1.01 (d, ^{3}J = 5.9 Hz, 12H, C*H*$_3$). ^{13}C NMR (THF-d$_8$, 125.76 MHz, 295 K) δ: 170.7 (N*C*N); 47.1 (*C*H); 26.9 (*C*H$_3$); 26.6 (*C*H$_3$); 10.6 (NC(*C*H$_3$)N).

Attempt for preparation of [CyNC(Me)NCy]MgI (4) leading to the mixture of [CyNC(Me)NCy]$_2$Mg(Et$_2$O)$_n$ and MgI$_2$(Et$_2$O)$_3$

N,N′-dicyclohexylcarbodiimide (1.464 g, 7.10 mmol); 3M methylmagnesium iodide solution (2.36 ml, 7.10 mmol); hexane (30 ml). 2.619 g (99 %) of **4**. mp 119 - 120 °C. Preparation of the sample for solution NMR measurement in the donor solvent THFd$_8$ led to the formation of [CyNC(Me)NCy]$_2$Mg(Et$_2$O)$_n$ and MgI$_2$(Et$_2$O)$_3$ - ^{1}H NMR (THF-d$_8$, 500.13 MHz, 295 K) δ: 3.00 (m, 2H, Cy*H*); 1.80 (s, 3H, NC(C*H*$_3$)N); 1.75 - 1.16 (br m, 20H, Cy*H*). ^{13}C NMR (THF-d$_8$, 125.76 MHz, 295 K) δ: 170.7 (N*C*(CH$_3$)N); 56.2 (Cy); 37.9 (Cy); 27.3 (Cy); 27.2 (Cy); 11.0 (NC(*C*H$_3$)N).

Attempt for preparation of [CyNC(Me)NCy]MgCl (5) leading to the mixture of $[CyNC(Me)NCy]_2Mg(THF)_n$ and $MgCl_2(THF)_4$

N,N'-dicyclohexylcarbodiimide (1.496 g, 7.25 mmol); 3M methylmagnesium chloride solution (2.42 ml, 7.25 mmol); hexane (30 ml). 2.018 g (99 %) of **5**. mp > 250 °C. Preparation of the sample for solution NMR measurement in the donor solvent $THFd_8$ led to the formation of $[CyNC(Me)NCy]_2Mg(THF)_n$ and $MgCl_2(THF)_4$ - ^{1}H NMR (THF-d_8, 500.13 MHz, 295 K) δ: 2.98 (br s, 2H, Cy*H*); 1.66 - 1.51 (br m, 11H, NC(CH_3)N + Cy*H*); 1.26 (br s, 10H, Cy*H*); 1.10 (br s, 2H, Cy*H*). ^{13}C NMR (THF-d_8, 125.76 MHz, 295 K) δ: 170.7 (N*C*N); 56.2 (br s, Cy); 37.8 (br s, Cy); 27.2 (br s, Cy); 27.1 (br s, Cy); 10.9 (br s, NC(*C*H_3)N).

Attempt for preparation of [*p*TolNC(Me)N*p*Tol]MgI (6) leading to the mixture of $[pTolNC(Me)NpTol]_2Mg(Et_2O)_n$ and $MgI_2(Et_2O)_3$

N,N'-bis(4-methylphenyl)carbodiimide (0.843 g, 3.79 mmol); 3M methylmagnesium iodide solution (1.26 ml, 3.79 mmol); hexane (30 ml). 1.458 g (99 %) of **6**. mp > 250 °C. ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: 170.6 (N*C*N); 147.0 (Ar); 132.0 (Ar); 131.7 (Ar); 129.2 (Ar); 125.2 (Ar); 123.9 (Ar); 123.2 (Ar); 22.9 (*C*H_3); 19.2 (NC(*C*H_3)N). Preparation of the sample for solution NMR measurement in the donor solvent $THFd_8$ led to the formation of $[pTolNC(Me)NpTol]_2Mg(Et_2O)_n$ and $MgI_2(Et_2O)_3$ - ^{1}H NMR (THF-d_8, 500.13 MHz, 295 K) δ: 6.88 (d, ^3J = 5.4 Hz, 4H, Ar*H*); 6.68 (d, ^3J = 5.7 Hz, 4H, Ar*H*); 2.21 (s, 6H, CH_3); 1.88 (s, 3H, NC(CH_3)N). ^{13}C NMR (THF-d_8, 125.76 MHz, 295 K) δ: 170.6 (N*C*N); 147.0 (Ar); 132.0 (Ar); 131.7 (Ar); 129.2 (Ar); 125.2 (Ar); 123.9 (Ar); 123.2 (Ar); 22.9 (*C*H_3); 19.2 (NC(*C*H_3)N).

Preparation of 7

N,N'-bis(4-methylphenyl)carbodiimide (1.597 g, 7.18 mmol); 3M methylmagnesium chloride solution (2.39 ml, 7.18 mmol); hexane (30 ml). 2.112 g (99 %) of **7**. Single crystals suitable for XRD analyses were obtained from saturated solution of **7** in hexane at -30 °C. mp 235 - 236 °C. ^{1}H NMR (THF-d_8, 500.13 MHz, 295 K) δ: 6.93 (br s, 4H, Ar); 6.74 (br s, 4H, Ar); 2.21 (s, 6H, CH_3); 1.88 (s, 3H, NC(CH_3)N). ^{13}C NMR (THF-d_8, 125.76 MHz, 295 K) δ: 168.5 (br s, N*C*N); 149.9 (br s, Ar); 129.6 (s, Ar); 125.2 (br s, Ar); 21.0 (*C*H_3); 16.2 (NC(*C*H_3)N). ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: 169.2 (N*C*N); 167.3 (N*C*N); 146.2 (Ar); 144.9 (Ar); 129.5 (Ar); 128.3 (Ar);

127.3 (Ar); 122.6 (Ar); 122.0 (Ar); 22.9 (*C*H_3); 19.5 (NC(*C*H_3)N). Anal. Calcd for $C_{44}H_{58}Cl_2N_2Mg_2N_4O_3$ of single crystals: C 65.21; H 7.21; N 6.91. Found: C 65.30; H 7.25; N 6.79.

Preparation of 8

A THF (1 ml) was added using a Hamilton syringe to a colourless solution of **1** (0.415 g, 1.20 mmol) in hexane (15 ml). The reaction mixture was filtrated and concentrated under vacuo to the saturated solution (ca 10 ml) and then left in the freezer at – 30°C for couple of days. 0.193 g (23 %) of colourless single crystals of **8** suitable for XRD analyses were obtained. mp < 25 °C. Anal. Calcd for $C_{42}H_{78}N_4MgO_2$ of single crystals: C 72.54; H 11.31; N 8.06. Found: C 72.66; H 11.36; N 7.94.

Preparation of 9

3M methylmagnesium iodide solution in Et_2O (1.49 ml, 4.46 mmol) was added using a Hamilton syringe to a colourless solution of *N,N'*-bis(4-methylphenyl)carbodiimide (0.496 g, 2.23 mmol) in hexane (30 ml) cooled approximately to 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting pale yellow precipitate of **9** was filtrated and washed with hexane (15 ml). All volatiles were evaporated under vacuo to give 1.335 g (85 %) of pure yellow powder of **9**. Single crystals suitable for XRD analyses were obtained from saturated solution of **9** in hexane at -30 °C. mp 145 - 146.5 °C. ^{1}H NMR (Tol-d_8, 500.13 MHz, 295 K) δ: 7.28 (d, ^3J = 7.9 Hz, 4H, Ar); 6.89 (d, ^3J = 7.9 Hz, 4H, Ar); 3.37 (br s, 8H, Et_2O); 2.12 (s, 6H, C*H*$_3$); 1.55 (s, 3H, NC(C*H*$_3$)N); 0.73 (br s, 12H, Et_2O); -0.32 (s, 3H, MgC*H*$_3$Mg). ^{13}C NMR (Tol-d_8, 125.76 MHz, 295 K) δ: 177.1 (N*C*N); 146.6 (Ar); 137.4 (br s, Ar); 133.8 (Ar); 129.9 (br s, Ar); 127.4 (Ar); 127.0 (br s, Ar); 66.6 (br s, Et_2O); 20.8 (*C*H_3); 18.0 (NC(*C*H_3)N); 14.1 (br s, Et_2O); -6.7 (br s, Mg*C*H_3Mg). ^{13}C CP/MAS NMR (10 kHz, 300 K) δ: 175.6 (N*C*N); 145.9 (Ar); 145.2 (Ar); 134.2 (Ar); 131.1 (Ar); 125.4 (Ar); 67.1 (Et_2O); 21.3 (*C*H_3); 20.6 (*C*H_3); 18.8 (NC(*C*H_3)N); 15.2 (Et_2O); -7.5 (Mg*C*H_3Mg). Anal. Calcd for $C_{25}H_{40}I_2Mg_2N_2O_2$ of single crystals: C 42.71; H 5.74; N 3.98. Found: C 42.77; H 5.82; N 3.90.

Preparation of 10

An off-white powder of **4** (0.627 g, 1.68 mmol - prepared by the procedure above) was dissolved in THF (15 ml) and the reaction was stirred overnight with subsequent filtration. All solvents were evaporated under vacuo to give 0.416 g (91 %) of pale yellow crystalline material of **10**. Single crystals suitable for XRD analyses were obtained from saturated solution of **10** in THF at -30 °C. mp 195 - 196 °C. ^{1}H NMR (THF-d_8, 500.13 MHz, 295 K) δ: 2.95 (m, 4H, Cy*H*); 1.68 (s, 6H, CH_3); 1.66 - 1.52 (br m, 20H, Cy*H*); 1.34 - 1.14 (br m, 16H, Cy*H*); 1.07 (m, 4H, Cy*H*). ^{13}C NMR (THF-d_8, 125.76 MHz, 295 K) δ: 170.7 (N*C*N); 56.2 (Cy); 37.9 (Cy); 27.3 (Cy); 27.2 (Cy); 11.0 (NC(*C*H_3)N). Anal. Calcd for $C_{36}H_{66}MgN_4O_2$ of single-crystals: C 70.74; H 10.88; N 9.17. Found: C 70.91; H 11.02; N 8.98.

Typical polymerization procedure for CL

To a flame dried Schlenk tube catalyst solution in toluene (10-90 μmol), toluene and benzyl alcohol solution in toluene (15-20 μmol) were added. Polymerization was initiated by fast injection of ε-caprolactone (1-2.5 g) under stirring. The ampoule was then placed into the oil bath at 100°C or kept at room temperature. After the desired polymerization time the ampoule was cooled by cold water, the product was dissolved in $CHCl_3$ (10-20 ml) and the polymer was precipitated in 300 ml of methanol. The polymer was filtered, washed with methanol and dried in a vacuum oven (100 Pa) at 50°C for 24h.

Typical polymerization procedure for TMC and LLA

Trimethylenecarbonate (~0.9 g) or L-lactide (~0.5 g) were placed into a Schlenk ampoule followed by addition of toluene and benzyl alcohol solution. Polymerization was started by the injection of a catalyst solution in toluene (~20 μmol in 0.4 ml) at room temperature under stirring and heating to the desired temperature in an oil bath (80°C for TMC, RT or 100°C for LLA). Polymer workup was the same as in the case of the CLO polymerization.

Copolymerization of epoxides with CO_2

A purified Fischer-Porter bottle was loaded with the catalyst solution which was evaporated to dryness. The nitrogen atmosphere was replaced by CO_2, epoxide (1.5-2 mL) was added, then the bottle was pressurized to 1 MPa CO_2 and heated to 75°C for 16h. Polymerization

was stopped by cooling to room temperature and releasing CO_2 pressure. A small aliquot of the reaction mixture was taken for ^{1}H NMR analysis. Polymer work-up was the same as in the case of CLO polymerization.

Esterification of LLA

The LLA esterification attempts were performed as follows: one molar equivalent of appropriate catalyst in dichlormethane (10 mL), LLA (50 mol. eq., 1,02 g, 7.06 mmol) and MeOH (50 or 200 mol. eq., 0.285 or 1.14 mL, 7 or 28 mmol) were mixed together and 1mL aliquots were taken after 1, 30 min., 2 and 24 h, the reaction was quenched with addition of one drop of glacial acetic acid.

Polymer characterization

Polymers molar mass and dispersity values of PCLO, PTMC and PLLA were determined by SEC (Waters 1515 pump, Waters 2410 refractive index detector working at 880 nm, Waters 717plus Autosampler, column heater) equipped with three-angle LS detector (Wyatt, miniDawn TREOS at 658 nm) using THF for sample solutions (3 mg/ml) as well as a mobile phase (1 ml/min). Separation was performed on two PSS Lux linear columns (LIN M, 5 mm, 7.8 mmx300 mm). dn/dc=0.079 ml/g for poly(ε-caprolactone) and dn/dc=0.056 ml/g for poly(L-lactide) were used.[2,3] dn/dc=0.051 ml/g for poly(trimethylenecarbonate) was obtained as an average value from measurements of a series of samples (molar mass 20-100 kg/mol) by on-line method.[3,4] LS data were evaluated using the Astra 5.3.4.14 software. The apparent molar mass of poly(cyclohexene oxide) and poly(L-lactide) was evaluated from a PS calibration on the same instrument. The molar mass of polyamide 6 extracted 3 times in methanol was determined by viscometry of tricresol solutions (2 mg/ml) using relationships published in ref. [5,6]

X-ray structure determination

Compounds **1**, **7**, **8** (Fig. S1), **9**, **10** and **[MgI(Et$_2$O)-μ-OSiMe$_3$]$_2$** (Fig. S2) have been characterized by single crystal X-ray crystallography techniques. The crystallographic details are summarized in Table S5. All diffraction experiments were performed under an inert oil using the Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer

with a Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode at 150K. Data reductions were done with DENZO-SMN[7]. The absorption was corrected by integration methods[8]. Structures were solved by direct methods (Sir92) [9] and refined by a full matrix least-square based on F^2 (SHELXL97) [10]. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure uniformity of the crystal treatment, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = 1.2 U_{eq} (pivot atom) or of 1.5U_{eq} (methyl). The H atoms in methyl, methylene, methine and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98 and 0.93 Å. The peripheral alkyl ether groups in **[MgI(Et_2O)-μ-$OSiMe_3$]$_2$** were disordered. Treatment of this disorder by standard methods has been employed – splitting ethyl groups to two positions with nearly equal occupancy.

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 1898542-1898547 for **1**, **7** - **10** and **[MgI(Et_2O)-μ-$OSiMe_3$]$_2$**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table S5: Crystallographic data for **1**, **7** - **10** and **[MgI(Et$_2$O)-μ-OSiMe$_3$]$_2$**.

Compound reference	**1**	**7**	**8**	**9**	**10**	**[MgI(Et$_2$O)-μ-OSiMe$_3$]$_2$**
Formula	$C_{42}H_{80}Mg_2N_4$	$C_{41}H_{51}Cl_2Mg_2N_4O_3,C_6H_{12}$	$C_{42}H_{78}MgN_4O_2$	$C_{25}H_{40}I_2Mg_2N_2O_2$	$C_{36}H_{66}MgN_4O_2$	$C_{14}H_{38}I_2Mg_2O_4Si_2$
M_r [g.mol^{-1}]	689.72	853.55	695.39	703.01	611.24	629.04
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
a [Å]	15.2640(11)	15.2300(14)	10.5000(6)	28.361(2)	12.2379(10)	13.9819(9)
b [Å]	16.4970(15)	16.8731(8)	12.2960(10)	8.5970(9)	15.8571(13)	13.6630(7)
c [Å]	16.9821(19)	22.9250(14)	16.7670(9)	26.456(3)	16.2460(6)	14.2620(9)
α [°]	90	90	84.125(6)	90	99.671(7)	90
β [°]	90	129.661(7)	80.152(4)	99.168(7)	111.819(8)	90
γ [°]	90	90	75.609(6)	90	104.575(6)	90
V [Å^3]	4276.3(7)	4535.2(6)	2061.9(2)	6368.1(11)	2710.0(4)	2724.6(3)
Space group	*Pca*2$_1$	*P*2$_1$/*c*	*P*-1	*P*2$_1$/*c*	*P*-1	*Pbca*
Crystal colour	colourless	colourless	colourless	colourless	colourless	colourless
T_{min}/T_{max}	0.972/0.982	0.940/0.970	0.981/0.991	0.600/0.609[d]	0.980/0.991	0.577/ 0.666
Z	4	4	2	8	3	4
μ/mm^{-1}	0.088	0.215	0.081	2.036	0.085	2.455
reflns measured	22670	36542	39582	32656	48185	12331
independent reflns	8033	10249	9110	11280	12222	2935
R_{int}[a]	0.063	0.068	0.056	0.074	0.051	0.073
GOF on F^2 (S)[b]	1.162	1.132	1.092	1.141	1.126	1.128
Final R_1 ($I > 2\sigma(I)$)[c]	0.067	0.063	0.074	0.060	0.060	0.059
Final $wR(F^2)$ ($I > 2\sigma(I)$)[c]	0.153	0.119	0.158	0.134	0.114	0.141

[a] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$. [b] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{½}$. [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{½}$;[d] absorption corrections performed by SADABS[11]

DFT Calculations

The Gaussian16 package (Rev. A.03)[12] was used to perform all quantum chemical calculations employing the hybrid functionals PBE0[13] and B3LYP[14] together with a 6-31G(d)[15] basis set. Iodine was described using a 6-311 G triple zeta basis set[16]. No symmetry or internal coordinate constraints were applied during optimizations. All reported structures were verified as true minima by the absence of imaginary eigenvalues in the vibrational frequency analysis. Approximate free energies were obtained through thermochemical analysis, using the thermal correction to Gibbs free energy as reported by Gaussian16. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. For visualization GaussView[17] and CYLview[18] were used.

Optimized structures for DFT calculations

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8	0.000000	1.248878	0.000000
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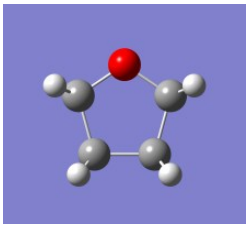

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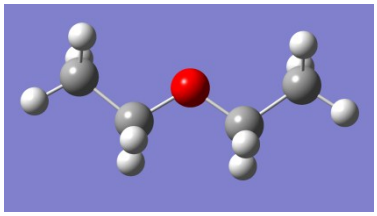
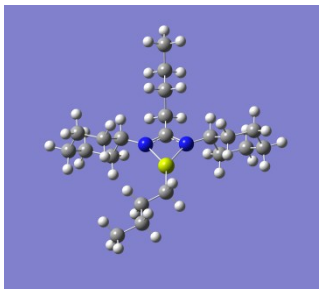


Complex 1



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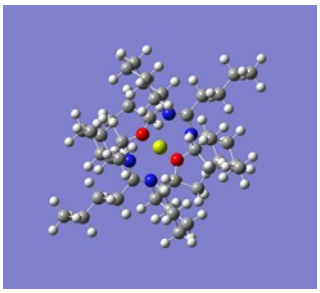
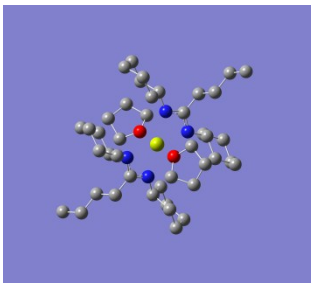
Complex 8





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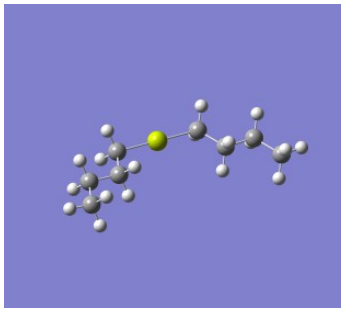
1	1.921652	1.133773	3.020189
1	0.284713	-2.349219	3.646854
1	-0.166142	-1.492745	5.135920
1	2.453259	-1.477797	4.199738
1	1.767747	-0.069464	5.013861
1	1.483620	0.275116	-2.886107
1	0.599289	-1.108487	-3.571901
1	-2.059249	-0.739517	-3.188784
1	-2.369734	0.592489	-2.033777
1	-0.059535	0.245301	-5.356253
1	0.596504	1.695986	-4.594134
1	-2.191218	1.143440	-4.737314
1	-1.440303	2.230342	-3.555835

$^{n}Bu_2Mg$



6	-2.794090	-0.205298	0.000303
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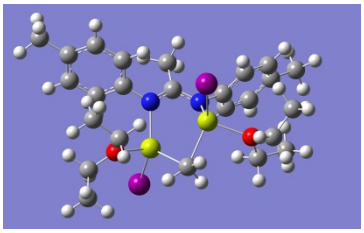
1	-2.475051	-0.790856	0.877129
6	-2.113000	1.169480	-0.001295
1	-2.465806	1.744188	0.870864
1	-2.464899	1.741718	-0.875441
6	2.113001	1.169481	0.000917
1	2.464902	1.741981	0.874892
1	2.465805	1.743927	-0.871415
6	2.794090	-0.205298	-0.000251
1	2.475064	-0.791128	-0.876900
1	2.474152	-0.793056	0.874774
6	4.322788	-0.142002	0.000616
1	4.652849	0.430647	0.879078
1	4.653765	0.432560	-0.876252
6	-4.322788	-0.142002	-0.000558
1	-4.652864	0.430371	-0.879195
1	-4.653750	0.432835	0.876135
6	-4.987574	-1.513868	0.001033
1	-4.696886	-2.093254	0.886139
1	-6.080692	-1.435274	0.000373
1	-4.695997	-2.095735	-0.882151
6	4.987573	-1.513868	-0.000533
1	4.696902	-2.093532	-0.885463
1	4.695979	-2.095459	0.882828
1	6.080692	-1.435275	0.000124
12	0.000000	1.168244	-0.000198

Complex 9



53	1.480540	-3.632156	-0.740866
53	-0.820148	3.387096	-0.874130
12	1.264465	-0.962264	-0.818752
12	-1.137927	0.715040	-0.951814
8	3.095967	-0.166656	-1.385473
8	-2.996131	0.326667	-1.805413
7	0.958551	0.013581	0.999451
7	-1.297726	-0.264708	0.867114
6	-0.211519	-0.121715	1.624472
6	2.087111	0.486005	1.712959
6	-3.495367	0.342057	1.758049
1	-3.264651	1.389739	1.577473
6	-5.045481	-1.367423	2.527934
6	-2.533940	-0.626973	1.455616
6	-2.846364	-1.972754	1.682741
1	-2.109344	-2.732573	1.432125
6	-6.366266	-1.760523	3.130391
1	-6.724295	-2.713729	2.726908
1	-7.134431	-1.003579	2.942033
1	-6.285767	-1.879727	4.218641
6	4.393653	1.455517	3.033613
6	-0.317363	-0.108013	3.126414
1	-0.787164	0.823963	3.460570
1	0.661174	-0.197180	3.598994
1	-0.960265	-0.927263	3.459232
6	-4.680338	2.099382	-1.857136
1	-5.451169	1.472187	-1.400515
1	-5.166265	2.819651	-2.524989
1	-4.168978	2.661958	-1.070347
6	3.173016	-0.358474	1.967400
1	3.115056	-1.402773	1.665744
6	-4.081422	-2.330982	2.213045
1	-4.302312	-3.382967	2.382539
6	-4.730120	-0.027682	2.284874
1	-5.462255	0.743624	2.515503
6	2.170426	1.823657	2.116686
1	1.345640	2.494883	1.889199
6	0.032400	-0.292734	-2.562867
6	4.306343	0.124468	2.615093
1	5.136902	-0.551782	2.807606
6	3.140037	1.231767	-1.728375
1	2.171386	1.628422	-1.408112
1	3.191142	1.324514	-2.820059
6	4.287803	-0.931359	-1.622868
1	4.057423	-1.923888	-1.227001
1	5.099774	-0.504855	-1.024080
6	-4.802783	-1.332062	-1.524006
1	-4.942234	-1.048626	-0.476835
1	-4.994126	-2.406627	-1.617620
1	-5.542534	-0.809657	-2.139674
6	-3.386447	-1.046564	-1.973209
1	-2.675916	-1.619965	-1.370855
1	-3.234727	-1.319350	-3.026290
6	4.654831	-1.019906	-3.089227
1	3.827111	-1.438416	-3.671176

1	5.517219	-1.685302	-3.202970
1	4.928567	-0.048271	-3.513820
6	3.305203	2.293410	2.769818
1	3.349103	3.337706	3.072640
6	-3.681288	1.279025	-2.642297
1	-4.154791	0.728847	-3.463970
1	-2.909952	1.929076	-3.067761
6	5.604661	1.963619	3.766526
1	5.470039	1.890952	4.853630
1	5.802031	3.015651	3.534873
1	6.499808	1.387168	3.511148
6	4.262545	1.991242	-1.054535
1	4.246032	1.836366	0.028389
1	4.120827	3.059854	-1.247714
1	5.248870	1.714812	-1.441809
1	-0.600473	-1.122790	-2.905325
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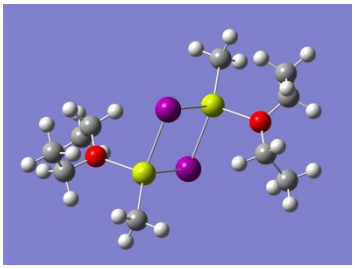
1	-0.307663	0.607367	-3.103968

MeMgI-Dimer with Et_2O



12	1.563685	0.084060	1.115244
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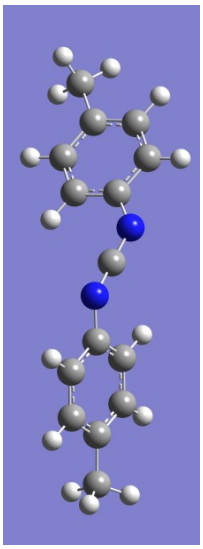
12	-1.553162	0.079351	-1.112872
8	-3.193456	0.037311	0.173559
6	-4.466131	-0.334747	-0.382507
6	-3.143408	0.093669	1.608458
1	-4.474431	0.086758	-1.390954
6	-3.647001	1.418944	2.138072
1	-3.711397	-0.752622	2.012150
1	-2.093520	-0.060740	1.872155
1	-3.573309	1.428381	3.231014
1	-3.042503	2.241875	1.745436
8	3.189505	0.038327	-0.190072
6	4.469236	-0.327475	0.353854
6	3.124146	0.088358	-1.624571
6	4.656864	-1.829397	0.400991
1	5.249805	0.163221	-0.238798
1	4.487179	0.098461	1.360302
1	2.072119	-0.070962	-1.876633
1	3.890615	-2.293384	1.030149
1	5.638278	-2.064805	0.827103
6	2.241028	0.068802	3.101652
1	2.826424	-0.830490	3.344467
1	2.875375	0.936231	3.337207
1	1.410202	0.094902	3.820429
6	-2.206460	0.057105	-3.107344
1	-2.787021	-0.844074	-3.354721
1	-2.839850	0.922548	-3.352606
1	-1.367381	0.083191	-3.816488
1	4.605650	-2.281706	-0.594750
1	-4.694794	1.595585	1.872629
1	-5.254494	0.156216	0.199506
6	-4.648838	-1.837425	-0.425032
1	-3.874627	-2.301979	-1.043960
1	-4.606869	-2.285201	0.573186
1	-5.624994	-2.077601	-0.860462
6	3.617528	1.413019	-2.165246
1	3.014481	2.235641	-1.769738
1	4.667486	1.594267	-1.911732
1	3.532180	1.417447	-3.257373
1	3.690793	-0.757711	-2.030616

*p*TolNCN*p*Tol



6	-0.000307	-1.178027	-0.004892
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7	-1.097663	-1.277627	0.523785
6	-2.306129	-0.620431	0.271050
6	-3.384950	-0.885170	1.115746
6	-2.472997	0.280159	-0.787364
6	-4.606935	-0.257711	0.904710
1	-3.247871	-1.583250	1.935877
6	-3.699550	0.898269	-0.986147
1	-1.636686	0.491600	-1.449284
6	-4.790626	0.641642	-0.148420
1	-5.436756	-0.472248	1.574449
1	-3.812893	1.598067	-1.811505
6	2.306197	-0.620878	-0.275432
6	2.474471	0.268345	0.792372
6	3.387086	-0.885246	-1.117548
6	3.703555	0.878056	1.000983
1	1.639627	0.471021	1.458874
6	4.611689	-0.266296	-0.896559
1	3.251909	-1.582573	-1.938632
6	4.794628	0.627554	0.161328
1	3.819853	1.563780	1.837666
1	5.444992	-0.485539	-1.560416
6	-6.122677	1.294352	-0.392565
1	-6.702448	0.744252	-1.145227
1	-6.724691	1.329415	0.521032
1	-6.005993	2.319546	-0.759963
6	6.112268	1.317469	0.380045
1	6.116876	2.317935	-0.071984
1	6.327059	1.443528	1.446638
1	6.937893	0.754119	-0.066315

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