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Supporting information for article:

Insight into the local environment of magnesium and calcium in low-coordination number organo-complexes using ^{25}Mg and ^{43}Ca solid-state NMR: a DFT study

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Supporting information

S1. Additional DFT calculations on organocalcium and organomagnesium complexes

Table S1 DFT calculations on magnesium complex CCDC 198354: influence of the k-point mesh, the energy cut-off, and the optimization of unit cell parameters.

Optimization	H atoms		H atoms		H atoms		All atoms		All atoms + cell parameters	
k-point grid	(1x1x1)		(1x1x1)		(2x2x2)		(1x1x1)		(1x1x1)	
Energy cut-off (Ry)	60		80		60		80		80	
Site	Mg(1)	Mg(2)	Mg(1)	Mg(2)	Mg(1)	Mg(2)	Mg(1)	Mg(2)	Mg(1)	Mg(2)
δ_{iso} (ppm)	46.3	49.0	46.3	49.0	50.0	50.7	43.3	45.5	43.7	45.0
C_Q (MHz)	-44.80	-45.69	-44.79	-45.68	-44.70	-45.71	-43.36	-44.15	-43.59	-44.39
η_Q	0.23	0.23	0.23	0.23	0.24	0.22	0.24	0.23	0.24	0.23

Table S2 DFT calculations on Mg and Ca complexes 198354, 266468, 745088 and 255195: influence of the dispersion correction.

CCDC	198354		266468		745088		255195			
Optimization	All atoms		All atoms		All atoms		All atoms			
k-point grid	(1x1x1)		(1x1x1)		(1x1x1)		(1x2x1)			
Energy cut-off (Ry)	80		60		60		80			
Dispersion	-	yes	-	yes	-	yes	-	yes		
Site	Mg(1)	Mg(2)	Mg(1)	Mg(2)	Mg(1)	Mg(1)	Mg(1)	Ca(1)	Ca(1)	
δ_{iso} (ppm)	43.3	45.5	43.0	44.6	52.7	55.1	84.1	84.2	103.3	110.5
C_Q (MHz)	-43.36	-44.15	-43.13	-43.58	26.12	27.07	23.13	23.12	-6.11	-6.17
η_Q	0.24	0.23	0.24	0.23	0.85	0.84	0.90	0.88	0.85	0.86

Table S3 DFT calculations on calcium complex CCDC 247152: influence of the k-point mesh.

k-point grid	(1x1x1)	(2x2x2)
δ_{iso} (ppm)	102.1	102.1
C_Q (MHz)	7.22	7.22
η_Q	0.15	0.15

GIPAW calculations reported here were performed using an energy cut-off of 80 Ry and correspond to H-atom optimization only.

S2. Calibration of ^{43}Ca and ^{25}Mg NMR parameter calculations

Table S4 DFT-calculated ^{43}Ca NMR shieldings of a selection of crystalline phases, used for the calibration of ^{43}Ca NMR calculations, together with the previously reported experimental ^{43}Ca isotropic chemical shifts.

Structure	$\sigma_{\text{iso}}(\text{calc}) / \text{ppm}$	$\delta_{\text{iso}}(\text{exp}) / \text{ppm}$
CaO	951.8	136 (1)
$\text{Ca}(\text{OH})_2$	1027.2	71 (3)
CaCO_3 (calcite)	1100.0	22 (2)
CaCO_3 (aragonite)	1137.8	-26 (1)
Hydroxyapatite	1115.4	4.5 (1)
	1095.4	17.5 (1)
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	1136.5	-15 (5)
CaB_2O_4	1109.4	6 (5)
CaAl_4O_7	1055.6	54 (5)
$\alpha\text{-Ca}_2\text{P}_2\text{O}_7$	1145.7	-18 (5)
	1111.1	12 (5)

Experimental values taken from Laurencin, D. et al (2013) *Prog. Nucl. Magn. Reson. Spectrosc.* **68**, 1–40.

Figure S1 Plots of $\sigma_{\text{iso}}(\text{calc})$ as a function of $\delta_{\text{iso}}(\text{exp})$ (left), and $P_Q(\text{calc})$ as a function of $P_Q(\text{exp})$ (right), for the calcium compounds shown in Table S4 ($P_Q = C_Q(1 + \eta_Q^2/3)^{0.5}$)).

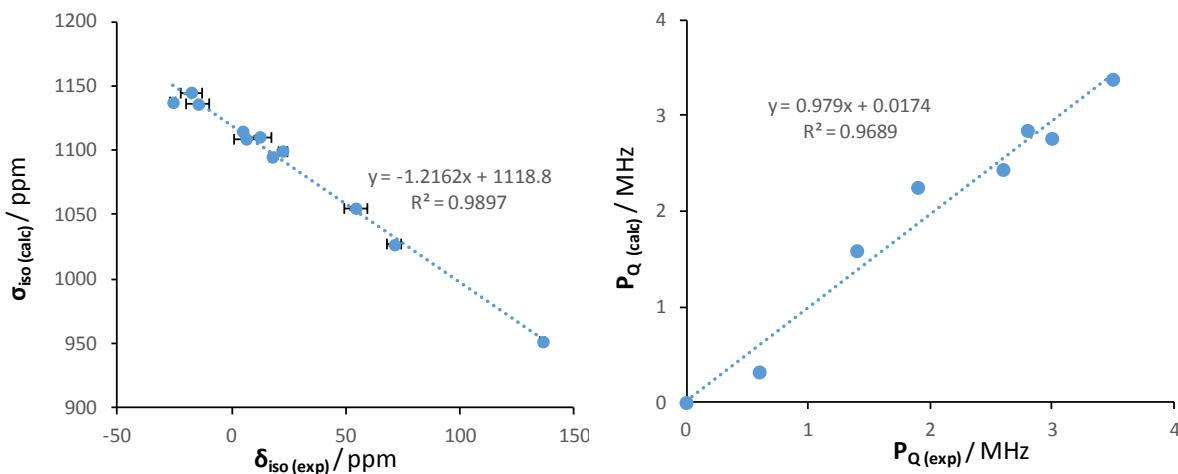
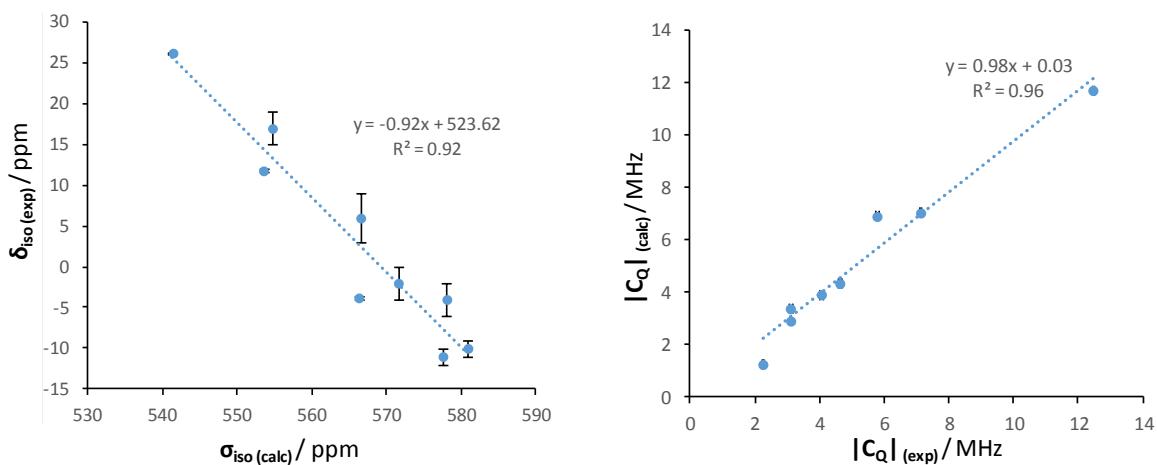


Table S5 DFT-calculated ^{25}Mg NMR shieldings and $|\mathbf{C}_Q|$ values of a selection of crystalline phases, used for the calibration of ^{25}Mg NMR calculations, together with the previously reported experimental ^{25}Mg isotropic chemical shifts and $|\mathbf{C}_Q|$ values (experimental errors are given in parenthesis).

Structure	ICSD	$\sigma_{\text{iso}}(\text{calc}) / \text{ppm}$	$\delta_{\text{iso}}(\text{exp}) / \text{ppm}$	$ \mathbf{C}_Q (\text{calc}) / \text{MHz}$	$ \mathbf{C}_Q (\text{exp}) / \text{MHz}$
MgO	52026	541.3	26.26 (5) ^a		
Mg(OH) ₂	203212	553.4	11.8 (2) ^a	2.95	3.09(1)
MgCO ₃	73731	566.2	-3.8 (2) ^a	1.29	2.24(2)
$\alpha\text{-Mg}_2\text{P}_2\text{O}_7$	15326	577.5	-11 (1) ^b	3.96	4.05 (4)
		566.5	-6 (3) ^b	11.76	12.45 (4)
Mg(PO ₃) ₂	4280	580.9	-10 (1) ^b	3.42	3.09 (4)
		571.5	-2 (2) ^b	4.38	4.62 (6)
Mg ₃ (PO ₄) ₂	31005	554.7	17 (2) ^b	7.08	7.12 (2)
		578.0	-4 (2) ^b	6.95	5.77 (6)

Experimental values taken from [a] Pallister, P. J. *et al* (2009), *Phys. Chem. Chem. Phys.* **11**, 11487–11500, and [b] Laurencin, D. *et al* (2012) *J. Phys. Chem. C*, **116**, 19984–19995.

Figure S2 Plots of $\delta_{\text{iso}}(\text{exp})$ as a function of $\sigma_{\text{iso}}(\text{calc})$ (left), and $|\mathbf{C}_Q(\text{calc})|$ as a function of $|\mathbf{C}_Q(\text{exp})|$ (right), for the magnesium compounds shown in Table S5.



S3. Local environments of calcium in the organocomplexes studied by DFT

Table S6 Closest neighbors around the 2 calcium sites (within a 3.0 Å radius) in the organocalcium structure CCDC 255198.

	H-optimization	Full -optimization
Ca Neighbor	Distance (Å)	Distance (Å)
N	2.32	2.34
N	2.33	2.34
O	2.38	2.43
H	2.67	2.68
C	2.86	2.86
H	2.86	2.90

Table S7 Closest neighbors around the 2 calcium sites (within a 3.0 Å radius) in the organocalcium structure CCDC 704097.

	H-optimization	Full -optimization
Ca Neighbor	Distance (Å)	Distance (Å)
N	2.29	2.29
N	2.29	2.29
C	2.60	2.61
H	2.76	2.78
H	2.76	2.78

Table S8 Closest neighbors around the calcium (within a 3.0 Å radius) in the organocalcium structure CCDC 255195.

	H-optimization	Full optimization
Ca Neighbor	Distance (Å)	Distance (Å)
N	2.35	2.33
N	2.36	2.37
N	2.52	2.53
N	2.55	2.57
H	2.73	2.74
H	2.76	2.77
H	2.83	2.84
C	2.94	2.95

Table S9 Closest neighbors around the calcium (within a 3.0 Å radius) in the organocalcium structure CCDC 255196.

	H-optimization	Full optimization
Ca Neighbor	Distance (Å)	Distance (Å)
N	2.36	2.37
N	2.37	2.39
N	2.47	2.50
N	2.52	2.57
H	2.66	2.67
H	2.87	2.90
H	2.89	2.97
C	2.98	2.99

Table S10 Closest neighbors around the 2 calcium sites (within a 3.0 Å radius) in the organocalcium structure CCDC 198356.

	H-optimization	Full optimization
Ca(1) Neighbor	Distance (Å)	Distance (Å)
N	2.33	2.35
N	2.33	2.35
O	2.35	2.39
O	2.37	2.44
C	2.95	2.98
C	2.98	2.99
Ca(2) Neighbor	Distance (Å)	Distance (Å)
N	2.32	2.34
N	2.33	2.36
O	2.35	2.40
O	2.36	2.41
C	2.84	2.87

Table S11 Closest neighbors around the calcium (within a 3.0 Å radius) in the organocalcium structure CCDC 247152.

	H-optimization	Full optimization
Ca Neighbor	Distance (Å)	Distance (Å)
N	2.30	2.31
N	2.31	2.32
O	2.34	2.39
O	2.35	2.41
H	2.97	2.87

S4. Simulation of ^{43}Ca NMR spectra based on the GIPAW calculated NMR parameters

Figure S3 Simulation of the ^{43}Ca MAS NMR spectra at 20 T, for structures CCDC 198356 (Ca (1) site) and 704097, based on the values calculated in Tables 1 and 2 for the H-relaxed structures. Simulations were performed assuming an “infinite” spinning speed; only central transitions are represented here.

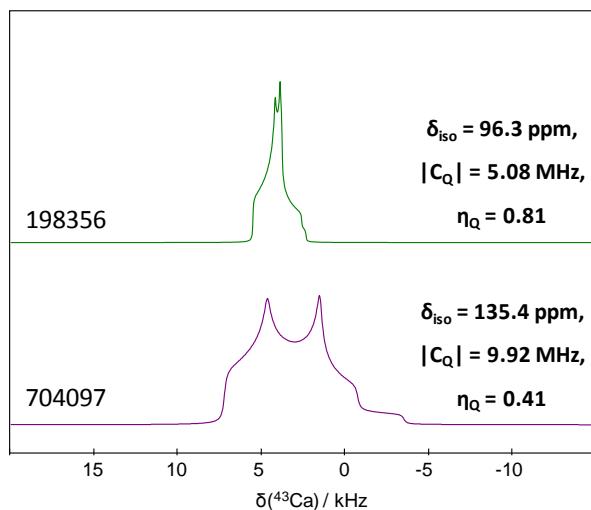
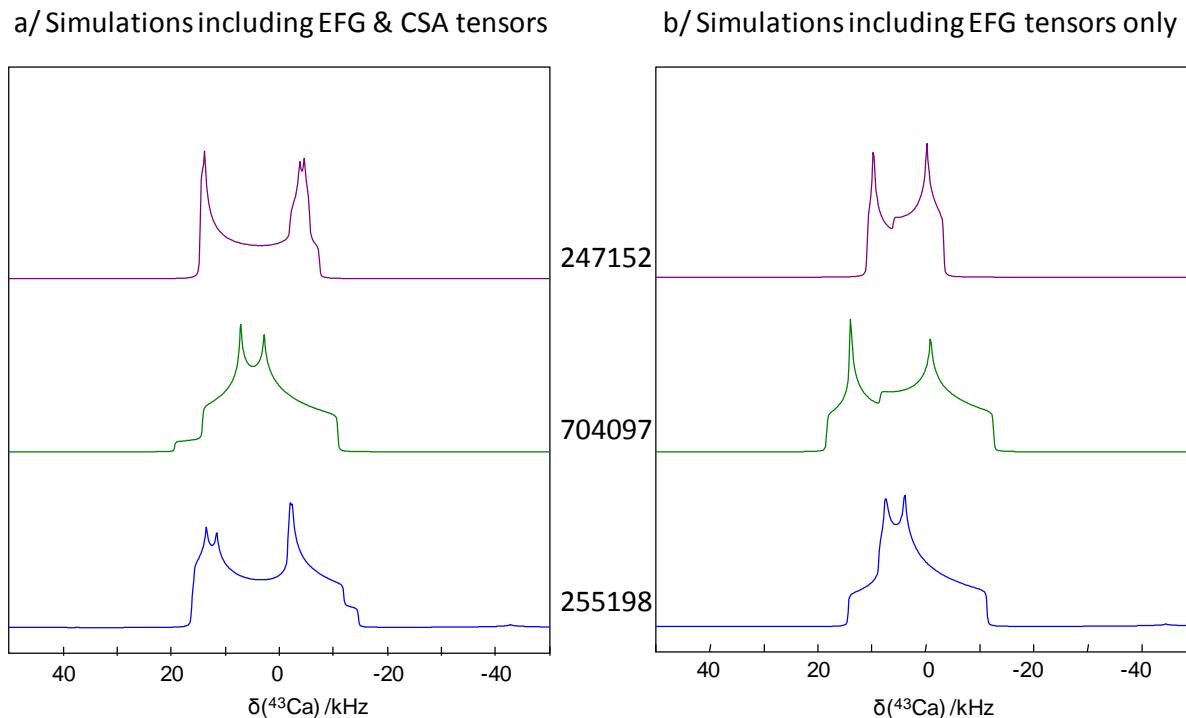


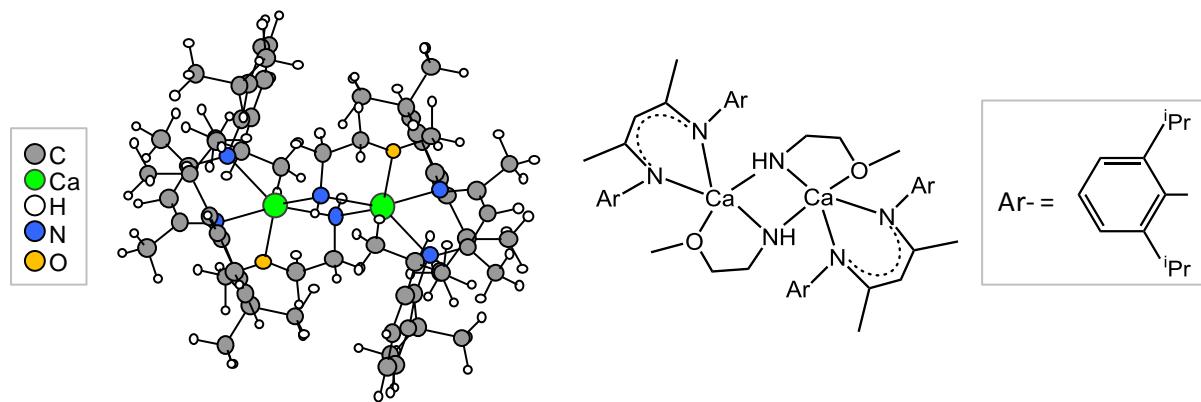
Table S12 Calculated ^{43}Ca NMR parameters after H-optimization of structures CCDC 255198, 704097 and 247152.

	255198	704097	247152
δ_{iso} (ppm)	99.5	135.4	102.1
$ C_Q $ (MHz)	8.0	9.9	7.2
η_Q	0.8	0.4	0.2
Ω (ppm)	286.5	310.2	224.6
κ	0.3	-0.7	0.8
α	-100	90	115
β	175	-90	175
γ	0	0	5

The relative orientation between the two tensors using three Euler angles (α, β, γ) was extracted from the first-principles calculations, which allows the simulation of the static spectra taking all these parameters into account. The QUEST software was used to simulate these spectra (Figure S4). The Euler angles reported therefore describe the relative orientation of the EFG tensor with respect to the shielding tensor along the following conventions : $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ and $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. Span $\Omega = \delta_{11} - \delta_{33}$ and skew $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.

Figure S4 Simulation of the static ^{43}Ca NMR spectra at 20 T, for structures CCDC 255198, 704097 and 247152, using the QUEST program. The NMR parameters calculated in Tables 1 and 2 for the H-relaxed structures were used. Only central transitions are represented here. Euler angles are given in Table S12 (above). The relative orientation of shielding and EFG tensors is shown in Figure 2. The simulations were performed with (a) and without (b) the shielding tensor, showing that for ^{43}Ca , it is necessary to take shielding tensors into account to properly interpret the static lineshape at high field.



S5. Local environments of calcium in a penta-coordinated diketiminato complex
Figure S5 Representation of the Ca local environment in the crystal structure CCDC 244505.

Table S13 Calculated ^{43}Ca NMR parameters after H-optimization or full optimization of structure CCDC 244505.

	H-optimization	Full optimization
δ_{iso} (ppm)	117.0	101.9
C_Q (MHz)	-7.13	-6.68
η_Q	0.62	0.66
Δ_{CSA} (ppm)	62.9	64.3
η_{CSA}	0.78	0.68
$d(\text{Ca...X})$ (Å)	2.41	2.45

$d(\text{Ca...X})$ corresponds to the average Ca...X distance ($X = \text{N}, \text{O}$). The equation used to derive calculated shifts from calculated shieldings can be found in supporting information (Figure S1).

Table S14 Closest neighbors around the calcium (within a 3.0 Å radius) in the organocalcium structure CCDC 244505.

H-optimization		Full optimization	
Ca Neighbor	Distance (Å)	Ca Neighbor	Distance (Å)
N	2.37	N	2.40
N	2.40	N	2.44
N	2.41	N	2.45
O	2.43	N	2.46
N	2.43	O	2.49
H	2.91	H	2.94
H	2.93	H	2.99

S6. Local environments of magnesium in the organocomplexes studied by DFT.**Table S15** Closest neighbors around the 2 Mg sites (within a 3.0 Å radius) in the organomagnesium structure CCDC 198354 (H-optimized structure).

Rel H		Rel tot		Rel H		Rel tot	
Mg(1) site				Mg(2) site			
Neighbor	Dist. (Å)	Neighbor	Dist. (Å)	Neighbor	Dist. (Å)	Neighbor	Dist. (Å)
N	1.92	N	1.94	N	1.91	N	1.93
N	1.92	N	1.94	N	1.91	N	1.93
H	2.82	H	2.84	H	2.65	H	2.67
H	2.82	H	2.84	H	2.65	H	2.67
H	2.85	H	2.85	H	2.69	H	2.69
H	2.85	H	2.85	H	2.69	H	2.69
H	2.88	H	2.90	C	2.86	C	2.86
H	2.88	H	2.90	C	2.86	C	2.86
C	2.94	C	2.94	C	2.97	C	2.98
C	2.94	C	2.94	C	2.97	C	2.98
H	2.97	H	2.98				
H	2.97	H	2.98				
C	2.98	C	2.99				
C	2.98	C	2.99				

Table S16 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 1207191.

		H-optimization	Full optimization
Mg	Neighbor	Distance (Å)	Distance (Å)
N		1.96	1.97
N		1.97	1.98
C		2.65	2.66
H		2.69	2.75
C		2.82	2.83
C		2.92	2.91
Si		2.93	2.93
C		2.96	2.96

Table S17 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266469.

H-optimization		Full optimization			
Mg	Neighbor	Distance (Å)	Mg	Neighbor	Distance (Å)
N		1.98	N		1.99
N		1.99	N		2.00
H		2.53	H		2.48
C		2.56	C		2.58
C		2.65	C		2.65
C		2.79	C		2.86
Si		2.89	Si		2.91
C		2.94	C		2.93
H		2.95			
Si		2.98			

Table S18 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266469.

H-optimization		Full optimization	
Mg(1) site			
Mg(1) Neighbor	Distance (Å)	Mg (1) Neighbor	Distance (Å)
N	1.99	N	2.00
H	2.74	C	2.73
C	2.77	H	2.75
Mg	2.85	Mg	2.86
H	2.92	H	2.89
C	2.93	C	2.93
C	2.96	H	2.99
Mg(2) site			
Mg (2) Neighbor	Distance (Å)	Mg (2) Neighbor	Distance (Å)
N	1.98	N	2.00
H	2.75	H	2.69
Mg	2.85	Mg	2.86
C	2.97	H	2.98
		C	2.99

Table S19 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 175074.

H-optimization		Full optimization	
Mg Neighbor	Distance (Å)	Mg Neighbor	Distance (Å)
N	1.98	N	2.00
N	1.99	N	2.00
O	2.53	O	2.07
H	2.56	C	2.81
C	2.65	H	2.84
H	2.79	H	2.87
H	2.89	C	2.91
H	2.94	H	2.91
C	2.95	H	2.98
H	2.98		

Table S20 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266470.

H-optimization		Full optimization	
Mg Neighbor	Distance (Å)	Mg Neighbor	Distance (Å)
N	1.99	N	2.00
N	1.99	N	2.00
N	2.13	N	2.15
H	2.73	H	2.75
H	2.73	H	2.75
H	2.93	H	2.99
H	2.93	H	2.99
C	2.97		
C	2.97		

Table S21 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266468.

H optimization		Full optimization	
Neighbor	Dist. (Å)	Neighbor	Dist. (Å)
N	1.97	N	1.99
N	2.10	N	2.11
N	2.13	N	2.15
H	2.41	H	2.43
H	2.46	H	2.46
H	2.56	H	2.57
H	2.73	H	2.75
H	2.78	C	2.82
C	2.80	H	2.82
C	2.85	C	2.88
C	2.86	C	2.88
Mg	2.94	Mg	2.96
C	2.96	C	2.98
C	2.99		

Table S22 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 745088.

H optimization		Full optimization	
Neighbor	Dist. (Å)	Neighbor	Dist. (Å)
N	2.04	N	2.05
N	2.04	N	2.06
Mg	2.81	Mg	2.80
C	2.96	C	2.95
C	2.96	C	2.96

Table S23 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 661565.

		H optimization	Full optimization
Mg	Neighbor	Distance (Å)	Distance (Å)
	N	2.07	2.09
	N	2.07	2.09
	C	2.49	2.50
	H	2.73	2.75
	H	2.73	2.75
	Mg	2.85	2.85

Table S24 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structures CCDC 247151 and 266465.

	CCDC 247151		CCDC 266465			
		H optimization		H optimization	Full optimization	
Mg	Neighbor	Distance (Å)	Distance (Å)	Distance (Å)	Distance (Å)	
	N	2.02	2.04	2.02	2.04	
	N	2.03	2.05	2.03	2.05	
	O	2.05	2.09	2.05	2.09	
	O	2.06	2.10	2.06	2.10	
	C	2.90	2.92	2.90	2.92	
	C	2.91	2.93	2.91	2.94	

Table S25 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266466.

H-optimization		Full optimization	
Mg(1) site			
Mg(1) Neighbor	Distance (Å)	Mg (1) Neighbor	Distance (Å)
N	2.03	N	2.05
N	2.03	N	2.05
N	2.17	N	2.18
N	2.19	N	2.22
H	2.83	H	2.83
C	2.91	C	2.93
C	2.93	C	2.95
H	2.94	H	2.98
Mg(1') site			
Mg (1') Neighbor	Distance (Å)	Mg (1') Neighbor	Distance (Å)
N	2.03	N	2.05
N	2.03	N	2.05
N	2.16	N	2.18
N	2.18	N	2.20
H	2.94	C	2.95
C	2.96	C	2.98
C	2.97	H	2.99

Table S26 Closest neighbors around the magnesium (within a 3.0 Å radius) in the organomagnesium structure CCDC 266464.

Mg	Neighbor	H optimization	Full optimization
		Distance (Å)	Distance (Å)
	N	2.01	2.03
	N	2.01	2.03
	N	2.14	2.17
	N	2.14	2.17
	H	2.97	
	H	2.97	

S7. Simulation of ^{25}Mg NMR spectra based on the GIPAW calculated NMR parameters
Table S27 Calculated ^{25}Mg NMR parameters after H-optimization of structures CCDC 198354, 1477718, 266470, 266465 and 266464.

	198354		1477718		266470	266465	266464
	Mg(1)	Mg(2)	Mg(1)	Mg(2)	Mg	Mg	Mg
δ_{iso} (ppm)	46.3	49.0	53.5	62.1	54.7	34.8	54.1
$ C_Q $ (MHz)	44.8	45.7	31.0	32.0	27.3	16.8	13.9
η_Q	0.2	0.2	0.2	0.1	1.0	0.3	0.5
Ω (ppm)	234.8	241.7	233.5	241.9	153.3	86.1	82.9
κ	0.7	0.6	0.8	0.9	0.6	0.8	0.4
α	80	70	125	80	-90	80	90
β	0	0	5	5	90	180	0
γ	-175	-155	10	140	180	-20	0

The relative orientation between the two tensors using three Euler angles (α, β, γ) was extracted from the first-principles calculations which allows the calculation of the static spectra taking all these parameters into account. The QUEST software was used to simulate spectra (Figure S6). The Euler angles reported therefore describe the relative orientation of the EFG tensor with respect to the shielding tensor along the following conventions: $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ and $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. Span $\Omega = \delta_{11} - \delta_{33}$ and skew $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.

Figure S6 Simulation of the static ^{25}Mg NMR spectra at 20 T, for structures CCDC 198354, 1477718, 266470, 266465, 266464, using the QUEST program. Simulations are performed considering a) both the EFG and shielding tensors, or b) only the EFG tensor, showing that for these compounds, the lineshape is dominated by quadrupolar effects. The values calculated in Tables 3-5 for the H-relaxed structures were used in both cases. Euler angles are given in Table S27 (above), while the relative orientation of the shielding and quadrupolar tensors is shown in Figure 4.

