Electronic supplementary information

Direct magnetic-field dependence of NMR chemical shift

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Experimental

The NMR sample consisted of saturated tris(acetylacetonate)cobalt(III) [Co(acac)₃] in CDCl₃ and natural xenon gas. The sample was placed in a 5-mm glass tube. Chemical shifts were measured relative to external xenon gas. Xenon gas (pressure 2 atm) was chosen as reference because its ¹²⁹Xe resonance signal is practically independent of environmental effects, such as temperature¹ and magnetic-field strength.²

⁵⁹Co and ¹²⁹Xe NMR experiments were carried out at four magnetic fields on Bruker Avance III spectrometers as listed in Table S1. Both nuclei are favourable from the NMR point of view, as comes out from Table S2: Their natural abundance is high as well as their receptivity. The large quadrupole moment of ⁵⁹Co ($Q = 420 \times 10^{-31}$ m², Ref. 3) leads, however, to enhanced T_2 relaxation and, consequently, to line broadening. Resonance peak positions were determined on the dmfit programme⁴ using Lorentzian line shape function for each case: ¹²⁹Xe gas, ¹²⁹Xe in solution and ⁵⁹Co in solution, with linewidths approximately 3...4, 6...7 and 70...100 Hz, respectively. Despite the wide resonance lines, their position could be obtained with better than a few hundreds of a hertz accuracy. All the spectra were recorded using the simple 'pulse - acquire' -sequence with a 90-degree

pulse. The number of scans recorded for ¹²⁹Xe (both the gas reference as well as the actual sample) and for ⁵⁹Co were 4 and 16, respectively, and the corresponding relaxation delays used were 120 and 1 seconds, in this order. Experiments for both nuclei were run at five different temperatures corresponding to spectrometer temperature settings of 300, 305, 310, 315 and 320 K and the sample temperature was allowed to stabilise for two hours before recording the spectra.

Table S1. NMR spectrometers, their magnetic flux densities and resonance frequencies for 59 Co and 129 Xe.^{*a*}

Spectrometer ^b	Magnetic flux density B_0 (T)	⁵⁹ Co frequency (MHz)	¹²⁹ Xe frequency (MHz)
Avance III-800	18.7914	188.926	221.3068
Avance III-600	14.0943	141.702	165.5891
Avance III-400	9.39725	94.478	110.6714
Avance III-300	7.05151	70.895	83.0456

^{*a*} Computed from the resonance frequency of ¹²⁹Xe gas using gyromagnetic ratios of 6.317×10⁻⁷ rad/Ts and -7.3997×10⁻⁷ rad/Ts for ⁵⁹Co and ¹²⁹Xe, respectively.

^{*b*} All spectrometers were delivered by Bruker.

Table S2. Properties of ⁵⁹Co and ¹²⁹Xe.

Nucleus	Spin	Natural abundance (%)	Receptivity relative to ¹³ C
⁵⁹ Co	7/2	100	1640
¹²⁹ Xe	1/2	26.4	33

To guarantee that experiments at different magnetic fields correspond to each other, ¹²⁹Xe chemical shift in the solution was used, instead of using sample temperature which is a less accurate parameter than the xenon shift. Temperatures can, however, be estimated from the ¹²⁹Xe chemical shifts in the solution as described below.

⁵⁹Co shift relates linearly to the ¹²⁹Xe chemical shift (both shifts are relative to the xenon gas):

$$\delta_{Co}^{exp} = \delta_{Co}(0) + a\delta_{Xe}^{exp},\tag{S1}$$

where $\delta_{C_0}(0)$ is the ⁵⁹Co chemical shift at $\delta_{X_e}^{exp} = 0$. We are, however, interested in the δ_{C_0} values in conditions where the ¹²⁹Xe chemical shifts in the solution correspond to approximate temperatures in the range 300...320 K. Then

$$\delta_{Co}^{exp} = \delta_{Co}^{s} \left(\delta_{Xe}^{fixed} \right) + a \left(\delta_{Xe}^{exp} - \delta_{Xe}^{fixed} \right).$$
(S2)

Least-squares fit of function (S2) to the experimentally obtained chemical shifts reveals the ⁵⁹Co chemical shift $\delta_{Co}^{s} \left(\delta_{Xe}^{fixed} \right)$ and slope *a* at the chosen, fixed ¹²⁹Xe chemical shift, in other words at fixed temperature, at each magnetic field. We have chosen $\delta_{Xe}^{fixed} = 200, 202, 205, 206$ and 208 ppm, but any other value within the range 200...208 ppm would be possible. The above-described procedure was repeated for each magnetic field strength. Consequently, there are five $\delta_{Co} \left(\delta_{Xe}^{fixed} \right)$ values at each of the four magnetic fields. Equation (7) in the main text was used in the determination of the parameter τ_{Co} corresponding to the chosen ¹²⁹Xe chemical shift values.

It turns out that τ_{Co} is dependent on the xenon-129 chemical shift and, consequently, on temperature. Using the results of Ref. 5, the sample temperature in the CDCl₃/Xe solution [*i.e.*, without Co(acac)₃] is obtained from

$$T = -2.5898 \frac{K}{ppm} \delta_{Xe} + 837.87 K,$$
(S3)

where $[\delta_{Xe}] = ppm$. Application of Eqn. (S3) to the present case results in the correspondence between the ¹²⁹Xe chemical shift and temperature shown in Table S3.

¹²⁹ Xe chemical shift (ppm)	Temperature (K)
200	319.9
202	314.7
205	307.0
206	304.4
208	299.2

Table S3. Approximate experimental temperatures corresponding to the fixed ¹²⁹Xe chemical shifts used.

Small contributions to the field-dependence coefficient

The response-theory formulae for the three smaller contributions to the field-dependence tensor τ are as follows 6

$$\tau_{K,\alpha\beta\gamma\delta}^{dia} = \frac{1}{3!\hbar\gamma_K} P_{\beta\gamma\delta} \left(\left\langle h_{KB_0,\alpha\beta}^{DS}; h_{B_0^2,\gamma\delta}^{SUSC} \right\rangle \right)_0$$
(S4)

$$\tau^{dia-para}_{K,\alpha\beta\gamma\delta} = \frac{1}{3!\hbar\gamma_{K}} \frac{1}{2!} \frac{P_{\beta\gamma\delta}}{\langle h_{KB_{0},\alpha\beta}; h_{B_{0},\gamma}^{OZ}, h_{B_{0},\delta}^{OZ} \rangle \rangle_{0,0}$$
(S5)

$$\tau^{para-dia}_{K,\alpha\beta\gamma\delta} = \frac{1}{3!\hbar\gamma_{K}} P_{\beta\gamma\delta} \left(\left(h^{PSO}_{K,\alpha}; h^{OZ}_{B_{0},\beta}, h^{SUSC}_{B_{0}^{2},\gamma\delta} \right) \right)_{0,0},$$
(S6)

where the notations $\langle\langle A;B \rangle\rangle_0$ and $\langle\langle A;B,C \rangle\rangle_{0,0}$ stand for linear and quadratic response functions⁷ involving as static (zero-frequency) perturbations the following magnetic operators:

$$H^{DS} = \sum_{\alpha\beta} h_{KB_{0},\alpha\beta}^{DS} B_{0,\alpha} I_{K,\beta} \quad ; \quad h_{KB_{0},\alpha\beta}^{DS} = \frac{e^{2} \hbar \mu_{0}}{2m_{e} 4\pi} \gamma_{K} \sum_{i} \frac{\delta_{\alpha\beta} (r_{i0} \cdot r_{iK}) - r_{iK,\alpha} r_{i0,\beta}}{r_{iK}^{3}}$$

$$H^{SUSC} = \sum_{\gamma\delta} h_{B_{0}^{2}\gamma\delta}^{SUSC} B_{0,\gamma} B_{0,\delta} \quad ; \quad h_{B_{0}^{2}\gamma\delta}^{SUSC} = \frac{e^{2}}{8m_{e}} \sum_{i} [\delta_{\gamma\delta} (r_{i0} \cdot r_{i0}) - r_{i0,\gamma} r_{i0,\delta}]$$
(S7)
$$(S7)$$

$$H^{OZ} = \sum_{\gamma} h_{B_0,\gamma}^{OZ} B_{0,\gamma} \quad ; \quad h_{B_0,\gamma}^{OZ} = \frac{e}{2m_e} \sum_{i} l_{iO,\gamma}$$
(S9)

$$H^{PSO} = \sum_{\alpha} h_{I_{K},\alpha}^{PSO} I_{K,\alpha} \quad ; \quad h_{K,\alpha}^{PSO} = \frac{e\hbar\,\mu_0}{m_e 4\pi} \gamma_K \sum_i \frac{l_{iK,\alpha}}{r_{iK}^3}, \tag{S10}$$

where γ_K is the gyromagnetic ratio of nucleus *K* and $\delta_{\alpha\beta}$ is the Kronecker delta for the Cartesian components α and β , the sums run over all electrons *i*, and the natural constants *e*, \hbar , m_e , and μ_0 have their usual meanings.

The DS operator is bilinear in the nuclear spin I_K and magnetic field B_0 and, *e.g.*, responsible for the diamagnetic part of conventional, field-independent nuclear shielding tensor.⁸ It involves the location vectors of the electrons $r_{i0} = r_i - 0$ and $r_{iK} = r_i - R_K$ measured from the common gauge origin O and nucleus K, respectively (these coincide in our present investigation of ⁵⁹Co shielding). r_{iK} is the length of the latter vector. The SUSC operator is quadratic in B_0 and gives the corresponding, diamagnetic contribution to the magnetizability tensor. The OZ and PSO operators involve the electronic angular momenta $l_{i0} = -i\hbar(r_i - 0) \times \nabla_i$ and $l_{iK} = -i\hbar(r_i - R_K) \times \nabla_i$ with respect to O and R_K , respectively, and constitute together the paramagnetic part of the field-independent shielding tensor.

Construction of the computational model

We first optimised the geometry of Co(acac)₃ and a truncated model thereof, on the Turbomole programme⁹ using DFT with the PBE0 exchange-correlation functional,¹⁰ the D3 dispersion correction,¹¹ and def2-QZVP basis set.¹² The D₃ point-group symmetry was enforced in the optimisation. The truncated model, in which the methyl groups of the acac groups were replaced by protons, was constructed to be able to run the costly electron-correlated calculations of the leading field-dependence term. Tables S4 and S5 list the optimised atomic coordinates of both models and Figure S1 illustrates them. Comparison of the full and truncated models at the Hartree-Fock level (Table S6) reveals that truncation increases the computed τ by 8%, which is acceptable taken the larger dependence of the results on the choice of the reference wave function (see the main text).

Table S4. Geometry of $Co(acac)_3$ as optimised at the PBE0-D3/def2-QZVP level of theory. Atomic coordinates in Å in the .xyz format.

43			
Со	0.000000	0.000000	0.000000
0	-1.255218	0.828104	-1.128097
0	-1.255218	-0.828104	1.128097
0	-0.089550	-1.501103	-1.128097
0	1.344768	-0.672999	1.128097
0	-0.089550	1.501103	1.128097
0	1.344768	0.672999	-1.128097
С	-2.504178	0.725953	-0.993195
С	-2.504178	-0.725953	0.993195
С	0.623395	-2.531658	-0.993195
С	1.880783	-1.805705	0.993195
С	0.623395	2.531658	0.993195
С	1.880783	1.805705	-0.993195
С	-3.161871	0.000000	0.000000
С	-3.306811	1.468588	-2.019461
С	-3.306811	-1.468588	2.019461
С	1.580936	-2.738261	0.000000
С	0.381571	-3.598076	-2.019461
С	2.925239	-2.129488	2.019461
С	1.580936	2.738261	0.000000
С	0.381571	3.598076	2.019461
С	2.925239	2.129488	-2.019461
Н	-4.240974	0.000000	0.000000
Н	-3.026186	2.522411	-1.999605
Н	-3.056410	1.086056	-3.009961
Н	-4.377323	1.373415	-1.854004
Н	-4.377323	-1.373415	1.854004
Н	-3.026186	-2.522411	1.999605
Н	-3.056410	-1.086056	3.009961
Н	2.120487	-3.672792	0.000000
Н	0.999249	-4.477580	-1.854004
Н	-0.671380	-3.881959	-1.999605
Н	0.587653	-3.189957	-3.009961
Н	2.468757	-2.103901	3.009961
Н	3.378074	-3.104165	1.854004
Н	3.697565	-1.359548	1.999605
Н	2.120487	3.672792	0.000000

Н	0.999249	4.477580	1.854004
Н	-0.671380	3.881959	1.999605
Н	0.587653	3.189957	3.009961
Н	2.468757	2.103901	-3.009961
Н	3.378074	3.104165	-1.854004
Н	3.697565	1.359548	-1.999605

Table S5. Geometry of a truncated model of $Co(acac)_3$ as optimised at the PBE0-D3/def2-QZVP level of theory. Atomic coordinates in Å in the .xyz format.

25			
Со	0.000000	0.000000	0.000000
0	-1.252406	0.835166	-1.135147
0	1.349478	0.667033	-1.135147
0	-1.252406	-0.835166	1.135147
0	-0.097072	-1.502198	-1.135147
0	1.349478	-0.667033	1.135147
0	-0.097072	1.502198	1.135147
С	-2.492490	0.720545	-0.980886
С	-3.162328	0.000000	0.000000
С	-2.492490	-0.720545	0.980886
С	1.870255	1.798288	-0.980886
С	0.622235	-2.518832	-0.980886
С	1.870255	-1.798288	0.980886
С	0.622235	2.518832	0.980886
С	1.581164	-2.738656	0.000000
С	1.581164	2.738656	0.000000
Н	-4.241779	0.000000	0.000000
Н	2.120889	-3.673488	0.000000
Н	2.120889	3.673488	0.000000
Н	-3.097959	1.260379	-1.716663
Н	-3.097959	-1.260379	1.716663
Н	2.640500	2.052721	-1.716663
Н	0.457459	-3.313101	-1.716663
Н	2.640500	-2.052721	1.716663
Н	0 457459	3.313101	1 716663



Figure S1. Co(acac)₃ and its truncated model. Yellow=cobalt, red=oxygen, brown=carbon, white=hydrogen.

Table S6. Comparison of the calculated field-dependence coefficient τ of ⁵⁹Co nuclear shielding constant using the full vs. the truncated computational model (Figure S1). All the contributions in equation (9) of the paper are included at the Hartree-Fock-level. Results at geometry optimised at the PBE0-D3-BJ/def2-QZVP level using the pcSseg-2/pcseg-2 basis set for Co/other atoms.

τ (10 ⁻³ ppm / T ²)			
Full model Truncated mode			
-1.324	-1.426		

Name	Correlated electrons	RAS1 ^b	RAS2 ^c	RAS3 ^d	Configurations
RASSCF (18 el.)	18	3, 3	3, 3	3, 3	207 776
RASSCF (32 el.)	32	7,6	3, 3	7, 7	4 476 090
RASSCF' (32 el.)	32	7,6	3, 3	9, 10	8 107 566
RASSCF (38 el.)	38	8, 8	3, 3	9, 10	12 127 578

Table S7. Specification of the restricted active-space multiconfigurational self-consistent field (RASSCF) wave functions used in the present work.^{*a*}

^{*a*} Calculations in the C₂ subgroup of the full D₃ molecular point group. In the RAS1—3 subspaces the number of orbitals in the A, B symmetry species are denoted. The orbital spaces were selected based on the natural occupation numbers obtained at the second-order Møller-Plesset many-body perturbation theory level.

^b Maximum of two holes were allowed in the RAS1 orbital subspace.

^c All symmetry-allowed orbital occupations were included in the RAS2 subspace.

^d Maximum of two electrons were allowed in the RAS3 orbital subspace.

Basis sets used in the calculations

The starting basis set in our calculations was the pcSseg-2 basis¹³ at the Co centre, for which τ was calculated, and the pcseg-2¹⁴ set for the other atoms. It was possible to use cubic response theory with large RASSCF wave functions (Table S7) to calculate the dominating τ^{para} term for the truncated molecular model, only by using a smaller, locally dense¹⁵ basis set consisting of the pcSseg-1 set¹³ for Co, pcseg-1¹⁴ for O, whereas STO-2G¹⁶ was used otherwise. The change of results associated with this simpler basis set is a few percent at the HF level (Table S8). In all the calculations of τ , a common gauge origin was used for the vector potential corresponding to the external magnetic field, placed at the Co centre.

In the calculations of the standard shielding and susceptibility anisotropies, the optimized, full molecular model and the pcSseg-2/pcseg-2 basis set were employed, using the gauge-including atomic orbital ansatz¹⁷ to remove the gauge-origin dependence of the results.

Table S8. Comparison of the calculated field-dependence coefficient τ of ⁵⁹Co nuclear shielding constant using a basis set of uniform quality vs. a smaller, locally dense basis set. All the contributions in equation (9) of the paper are included at the Hartree-Fock level. Results for the full molecular model with geometry optimised at the PBE0-D3-BJ/def2-QZVP level.

τ (10 ⁻³ ppm / T ²)			
Uniform basis ^{<i>a</i>} Locally dense basis ^{<i>b</i>}			
-1.324	-1.421		

^a Co: pcSseg-2 / COH: pcseg-2 basis sets.

^bCo: pcSseg-1 / O: pcseg-1 / C,H: STO-2G basis sets.

Table S9. Physical contributions [equation (9) in the paper] to the calculated field-dependence coefficient τ of ⁵⁹Co nuclear shielding constant at various computational levels. Results using the full molecular model unless otherwise noted.

	Term in τ [see equation (9)] (10 ⁻³ ppm/T ²)				
Computational method	dia	dia-para	para-dia	para	total
	8.342 × 10-	5.347×10^{-1}	4.318 × 10-		
HF ^a	7	5	3	-1.328	-1.324
	6.066 × 10-	4.772×10^{-1}	3.812×10^{-10}		
RASSCF $(32 \text{ el.})^b$	7	5	3	-0.843	-0.839
	9.389 × 10-	1.284×10^{-1}	1.614 × 10-		
DFT/BHandHLYP ^a	7	5	3	-0.090	-0.089
	9.956 × 10-	1.102×10^{-1}	1.082×10^{-1}		
DFT/B3LYP ^a	7	5	3	-0.026	-0.025
	1.011×10^{-1}	7.669×10^{-1}	7.951×10^{-1}		
DFT/BLYP ^a	6	6	4	-0.011	-0.010

^{*a*} Co: pcSseg-2 / COH: pcseg-2 basis sets.

^b Using the truncated model and Co: pcSseg-1 / O: pcseg-1 / C,H: STO-2G basis sets.

Table S10. Calculated dependence of the coefficient τ on the stretched Co-O bond length. Results at

the Hartree-Fock level of theory.^a

Geometry	<i>r</i> (Co-O) (Å)	$\tau (10^{-3} \text{ ppm/T}^2)$
$r_{\rm e} ({\rm small \ model})^b$	1.885	-1.379
$r_{\rm exp}$ (full model) ^c	1.8781.889	-1.401
$r_{\rm e}$ (full model) ^b	1.880	-1.328
$r_{\rm e}$ (full model) + Δr (Co-O) ^d	1.900	-2.068
	1.920	-3.190
	1.940	-5.034
	1.960	-8.169

^{*a*}Co: pcSseg-2 / COH: pcseg-2 basis sets.

^b Computationally optimised geometry of Tables S4 and S5.

^c Experimental x-ray geometry of Ref. 18. A range of Co-O bond lengths was given.

^{*d*} Equilibrium geometry of Table S4 with symmetrically stretched Co-O bond length and other degrees of freedom reoptimized.

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