

Supplementary Materials

Paramagnetic Solid-State NMR Study of Solid Solutions of Cobaltocene with Ferrocene and Nickelocene

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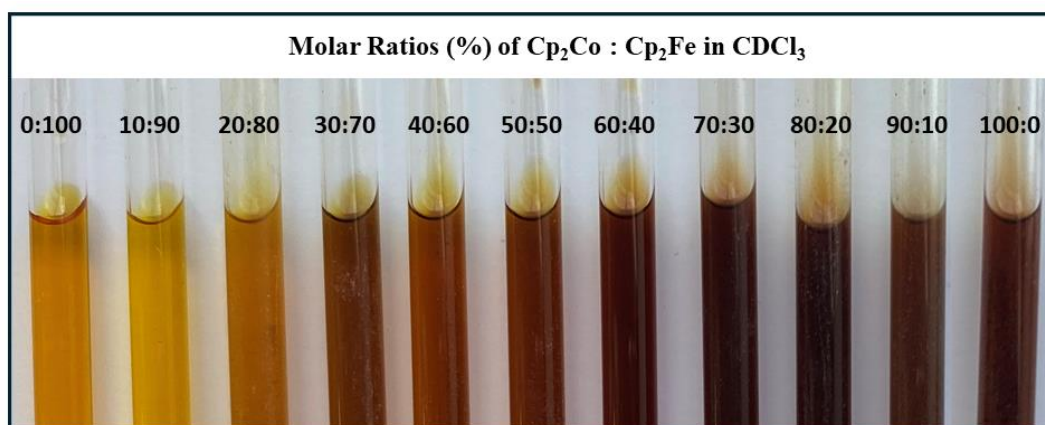


Figure S1. Mixtures with the indicated ratios of Cp_2Fe (1) and Cp_2Co (3) in CDCl_3 .

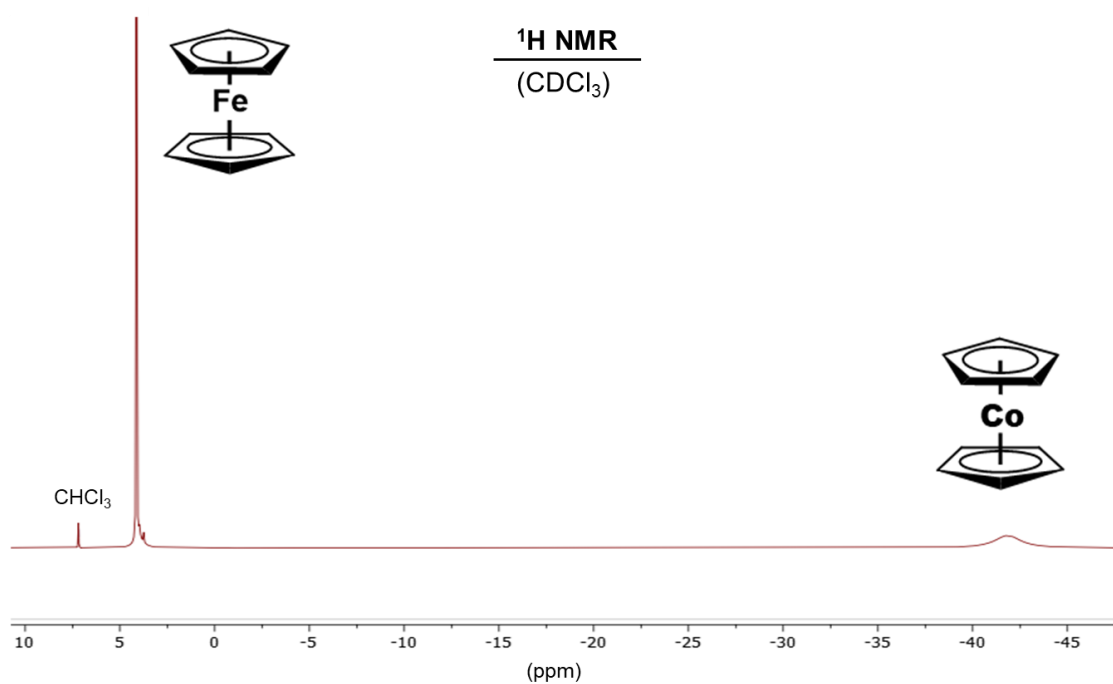


Figure S2. Solution ¹H NMR spectrum (295 K, CDCl₃) of a mixture of 60% Cp₂Fe (1) with 40% Cp₂Co (3).

Table S1. Chemical shifts of Cp₂Fe (1) and Cp₂Co (3) dissolved in CDCl₃ at 295 K with the indicated ratios.

Molar Ratio Cp ₂ Fe/Cp ₂ Co (%/%)	δ(¹ H) (ppm)	
	Cp ₂ Fe	Cp ₂ Co
100 / 0	4.16	–
90 / 10	4.15	–42.40
80 / 20	4.15	–41.60
70 / 30	4.13	–41.89
60 / 40	4.10	–41.76
50 / 50	4.07	–41.05
40 / 60	4.08	–41.79
30 / 70	4.06	–41.68
20 / 80	4.07	–41.70
10 / 90	4.01	–41.52
0 / 100	–	–42.14

Table S2. Halfwidths of Cp₂Fe (**1**) and Cp₂Co (**3**) dissolved in CDCl₃ with the indicated ratios.

Molar Ratio Cp ₂ Fe/Cp ₂ Co (%/%)	$\Delta\nu_{1/2}$ (Hz)	
	Cp ₂ Fe	Cp ₂ Co
100 / 0	2.0	–
90 / 10	2.2	307
80 / 20	2.3	311
70 / 30	2.8	317
60 / 40	3.4	303
50 / 50	4.2	304
40 / 60	5.1	302
30 / 70	4.8	306
20 / 80	5.5	312
10 / 90	5.5	309
0 / 100	–	300

Table S3. Relaxation times of Cp₂Fe (**1**) and Cp₂Co (**3**) dissolved in CDCl₃ with the indicated molar ratios.

Molar Ratio Cp ₂ Fe/Cp ₂ Co (%/%)	T ₁ (s)	T ₁ (ms)
	Cp ₂ Fe	Cp ₂ Co
100 / 0	4.9	–
90 / 10	2.54	9.57
80 / 20	1.52	9.56
70 / 30	1.25	9.58
60 / 40	1.23	9.63
50 / 50	1.05	9.57
40 / 60	0.80	9.41
30 / 70	0.33	9.66
20 / 80	0.27	9.44
10 / 90	0.21	9.78
0 / 100	–	9.58

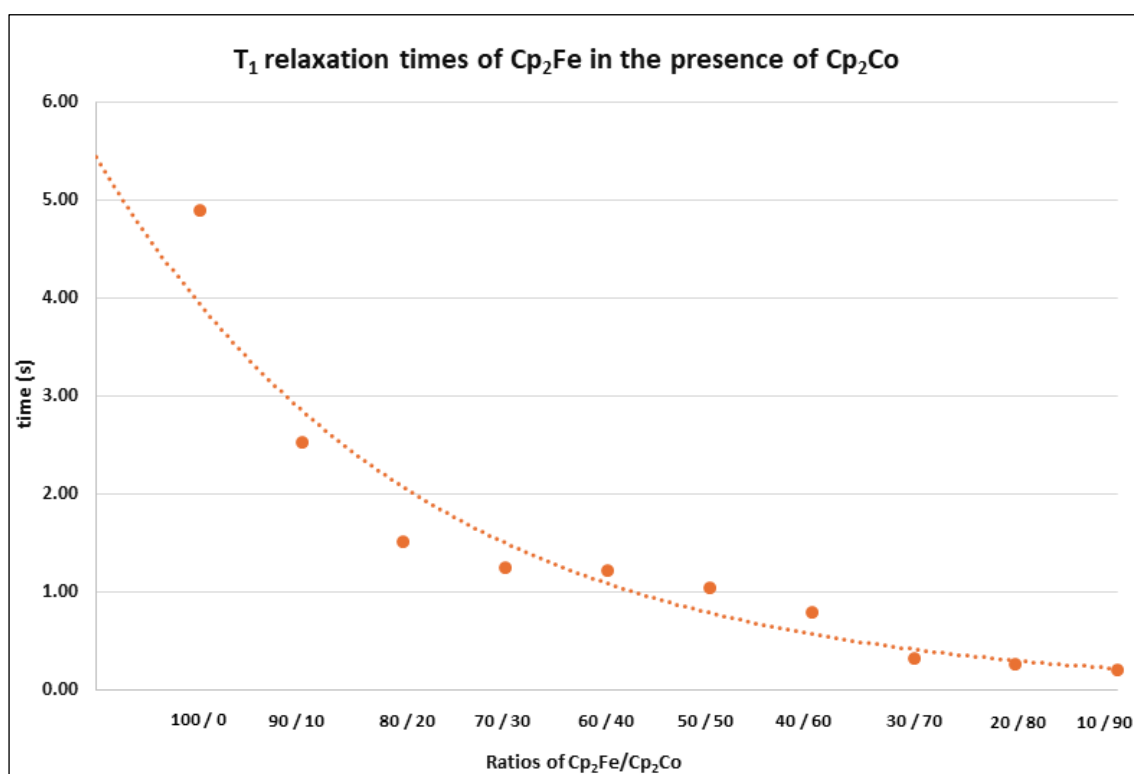


Figure S3. T_1 relaxation times of Cp_2Fe (1) dissolved in CDCl_3 together with Cp_2Co (3) with the indicated ratios.

Table S4. Melting points of mixed polycrystalline Cp_2Fe and Cp_2Co at the indicated molar ratios. The measurements were performed three times for each sample and the average value is reported. All melting point determinations were carried out using melting point capillaries closed in an inert gas atmosphere.

Molar Ratio $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Co}$ (%/%)	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
mp (°C)	174.0	174.4	174.9	174.9	175.3	175.3	176.0	177.8	177.3	178.0	180.1

Table S5. Intensities of the first and second-order rotational sidebands of the ^1H MAS NMR signal of Cp_2Fe (1) in the solid solution with Cp_2Co (3) with the indicated ratios. The intensities were measured with respect to the isotropic line set to intensity 1.00. The spectra were recorded at a rotational frequency of 6 kHz. The downfield sidebands of the first and second order are labeled I_1 and I_2 , and the sidebands on the upfield side are I_{-1} and I_{-2} . The intensities have been determined after background subtraction. For a graphical display of data see Figure 4.

Molar Ratio $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Co}$ (%/%)	Rotational sideband intensities of the Cp_2Fe signal			
	I_2	I_1	I_{-1}	I_{-2}
100 / 0	0.01	0.09	0.07	0.02
90 / 10	0.09	0.26	0.28	0.08
80 / 20	0.07	0.25	0.28	0.07
70 / 30	0.13	0.34	0.33	0.1
60 / 40	0.15	0.40	0.37	0.13
50 / 50	0.17	0.50	0.45	0.19
40 / 60	0.31	0.57	0.52	0.33
30 / 70	0.18	0.51	0.48	0.15
20 / 80	0.21	0.55	0.46	0.15
10 / 90	0.38	0.51	0.48	0.29
0 / 100	–	–	–	–

Table S6. Intensities of the first and second-order rotational sidebands of the ^1H MAS NMR signal of Cp_2Co (3) in the solid solutions with Cp_2Fe (1) at the indicated ratios. The intensities were measured with respect to the isotropic line set to intensity 1.00. The spectra were recorded at a 6 kHz rotational frequency in order to remove any overlap of sidebands. The downfield sidebands of the first and second order are labeled I_1 and I_2 , and the sidebands on the upfield side are I_{-1} and I_{-2} . The intensities have been determined after background subtraction. For a graphical display of the data see Figure S4.

Molar Ratio $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Co}$ (%/%)	Rotational sideband intensities of the Cp_2Co signal			
	I_2	I_1	I_{-1}	I_{-2}
100 / 0	–	–	–	–
90 / 10	0.14	0.36	0.34	0.18
80 / 20	0.14	0.27	0.28	0.11
70 / 30	0.11	0.31	0.40	0.11
60 / 40	0.18	0.41	0.40	0.13
50 / 50	0.24	0.53	0.56	0.13
40 / 60	0.27	0.56	0.51	0.26
30 / 70	0.16	0.51	0.52	0.18
20 / 80	0.20	0.55	0.53	0.24
10 / 90	0.27	0.66	0.57	0.25
0 / 100	0.19	0.53	0.46	0.16

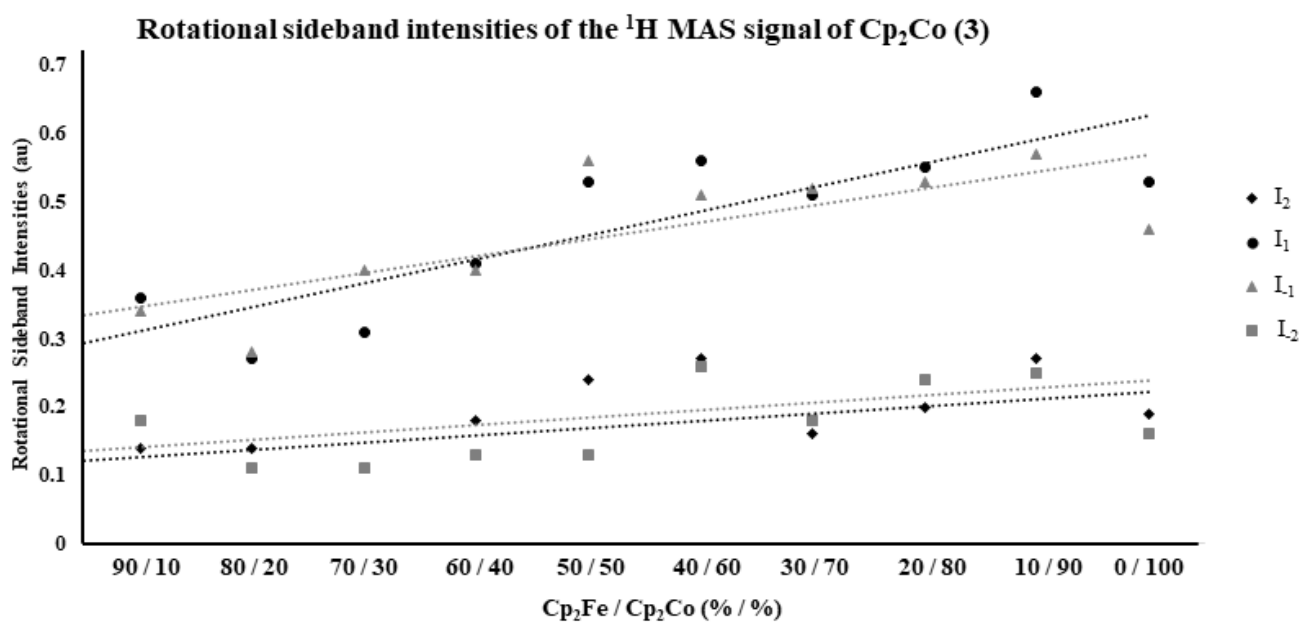


Figure S4. Graphical display of the rotational sideband intensities for the ^1H MAS signal of Cp_2Co (3), mixed with Cp_2Fe at the indicated molar ratios (Table S6).

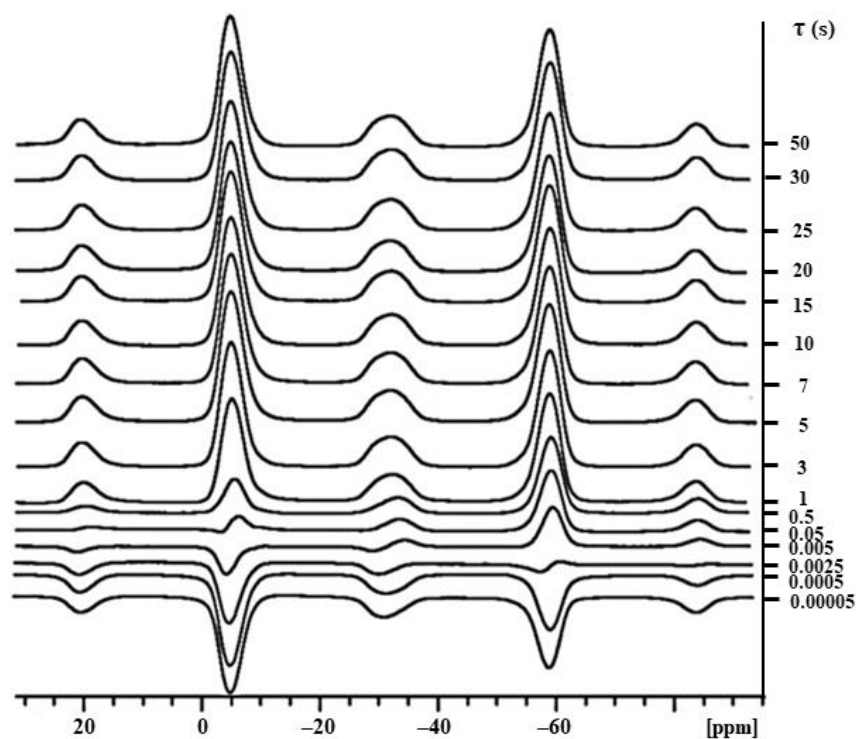


Figure S5. Inversion-recovery ^1H MAS NMR spectra recorded at a spinning rate of 10 kHz for a 50%/50% solid solution of Cp_2Fe and Cp_2Co . The solid solution was obtained by co-crystallization of the components from a CDCl_3 solution. The τ delay times were varied between 50 and 0.00005 s.

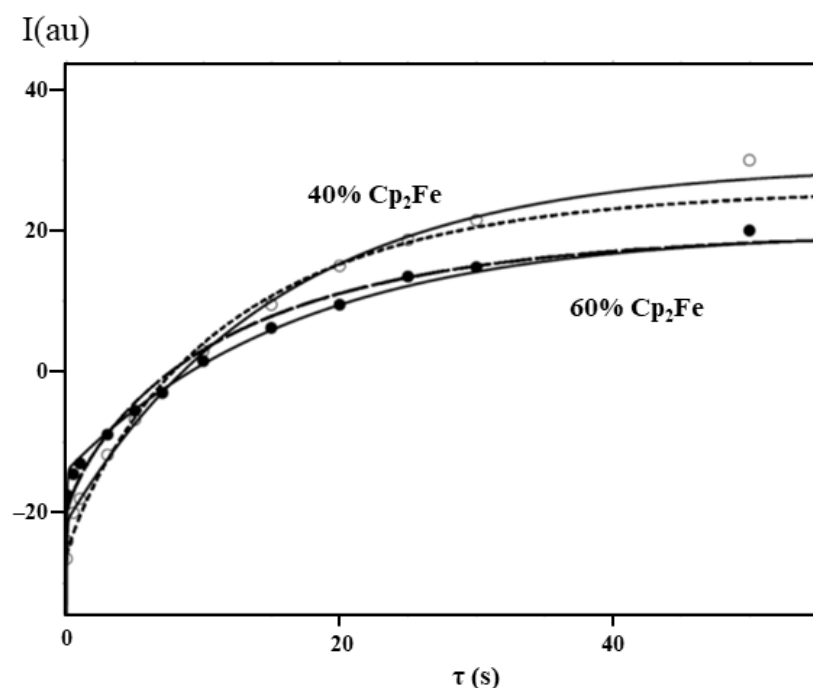


Figure S6. Experimental inversion-recovery curves obtained for the 40%/60% (top) and 60%/40% (bottom) $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Co}$ solid solutions after fittings to exponential (dotted lines) and stretched exponential functions with β parameters of 0.46 and 0.62, respectively (solid lines).

Table S7. Intensities of the first and second-order rotational sidebands of the ^1H MAS NMR signal of Cp_2Ni (**2**) in the solid solutions with Cp_2Co (**3**) at the indicated ratios. The intensities were measured with respect to the isotropic line set to intensity 1.00. The downfield sidebands of the first and second order are labeled I_1 and I_2 , and the sidebands on the upfield side are I_{-1} and I_{-2} . The intensities have been determined after background subtraction. For a graphical display of the data see Figure S7.

Molar Ratio $\text{Cp}_2\text{Ni}/\text{Cp}_2\text{Co}$ (%/%)	Rotational sideband intensities of the Cp_2Ni signal			
	I_2	I_1	I_{-1}	I_{-2}
100 / 0	0.39	0.73	0.66	0.36
90 / 10	0.55	0.91	0.62	0.31
80 / 20	0.51	0.90	0.63	0.34
70 / 30	0.42	0.84	0.62	0.33
60 / 40	0.34	0.71	0.60	0.31
50 / 50	0.35	0.72	0.61	0.34
40 / 60	0.50	0.76	0.64	0.47
30 / 70	0.39	0.77	0.61	0.33
20 / 80	0.52	0.74	0.58	0.47
10 / 90	0.49	0.87	0.65	0.39
0 / 100	–	–	–	–

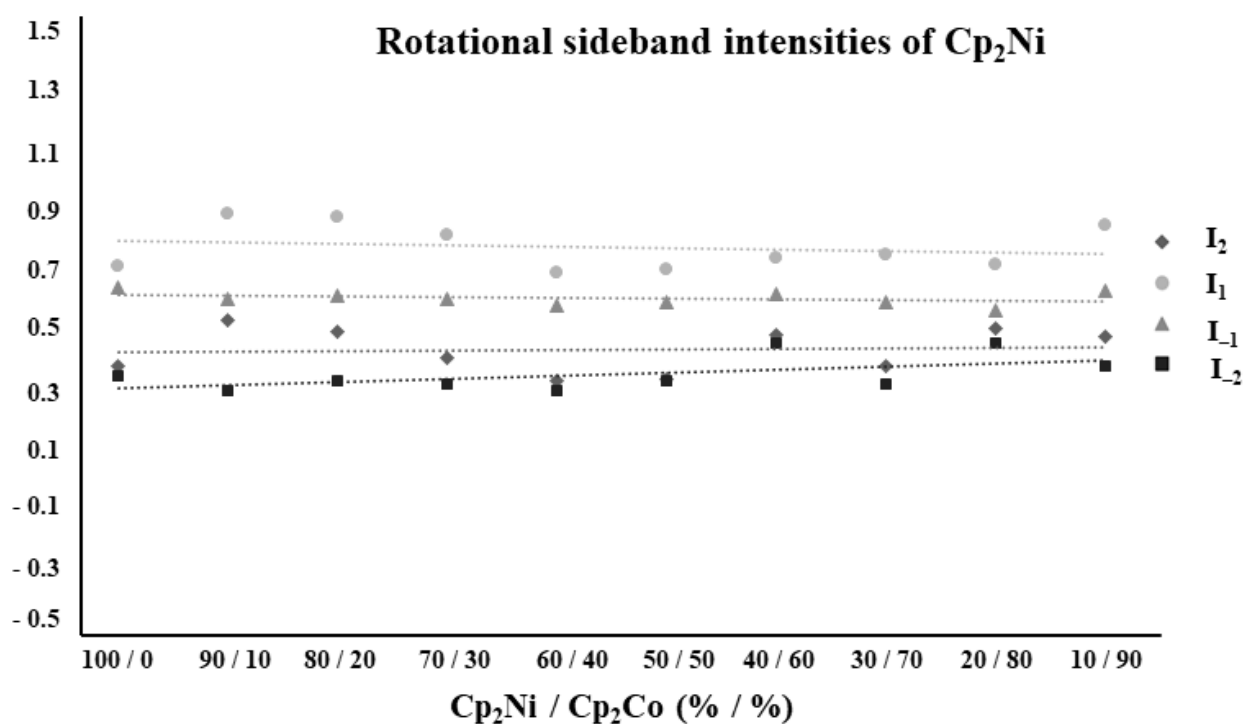


Figure S7. Graphical display of the rotational sideband intensities for the ^1H MAS signal of Cp_2Ni (2), mixed with Cp_2Co (3), at the indicated molar ratios (Table S7).

Table S8. ^1H T_1 relaxation times of the Cp resonances of solid solutions of Cp_2Ni (2) and Cp_2Co (3), prepared by grinding, with the indicated molar ratios. The T_1 times were obtained by fittings with a stretched exponential $f(t) = \exp(-t/T_1)^\beta$ for the Cp signals.

Molar Ratio $\text{Cp}_2\text{Co}/\text{Cp}_2\text{Ni}$ (% / %)	^1H T_1 (β) (ms)	
	Cp_2Co	Cp_2Ni
100 / 0	1.3 (0.35)	–
90 / 10	2.0 (0.65)	0.35 (0.65)
80 / 20	1.7 (0.60)	0.27 (0.45)
70 / 30	2.3 (0.74)	0.38 (0.65)
60 / 40	2.8 (0.69)	0.47 (0.77)
50 / 50	2.2 (0.52)	0.38 (0.62)
40 / 60	2.8 (0.64)	0.45 (0.60)
30 / 70	2.4 (0.55)	0.38 (0.52)
20 / 80	2.8 (0.62)	0.46 (0.59)
10 / 90	–	0.27 (0.70)

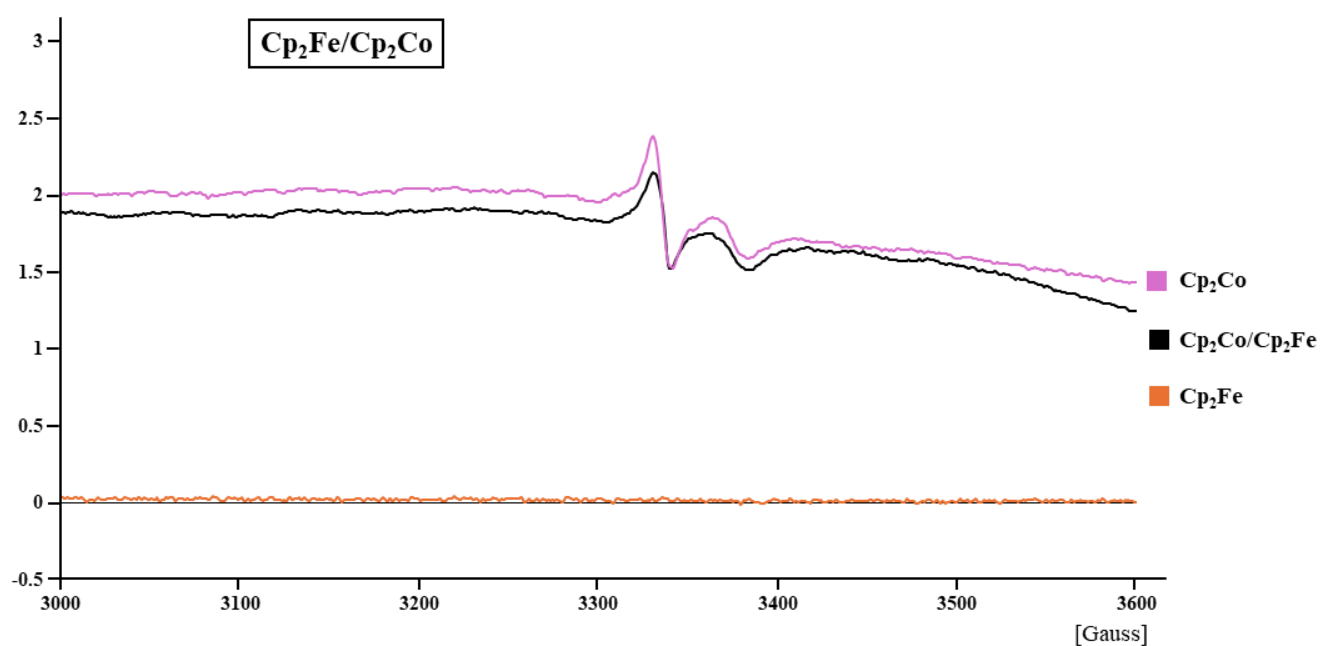


Figure S8. EPR spectra of Cp_2Fe (bottom), Cp_2Co (top), and a 50%/50% solid solution of both metallocenes (middle), obtained by crystallization from a CDCl_3 solution.

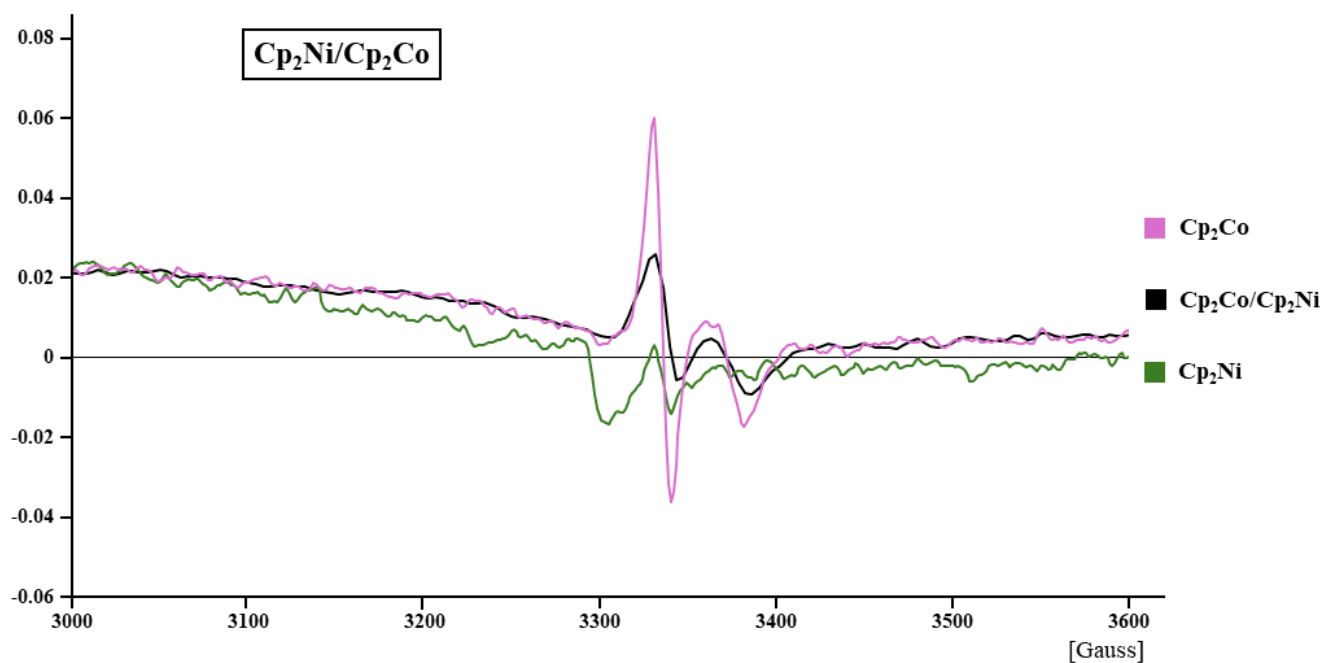


Figure S9. EPR spectra of Cp_2Co , Cp_2Ni , and a 50%/50% solid solution of both metallocenes, obtained by crystallization from CDCl_3 solution.