Supporting Information

Mössbauer and mass spectrometry support for iron(II) catalysts in enantioselective C–H activation

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General Remarks

In all cases, standard Schlenk techniques were applied. THF was obtained from a MBRAUN MB SPS-800 solvent purification system, or dried over sodium/benzophenone and freshly distilled before use. TMEDA was dried first over calcium hydride, then over sodium, and finally distilled. **L** and **1a** were synthesized as previously reported.[1] Grignard reagents were used as purchased: CyMgCl (1.0 M in THF) and PhMgCl (1.9 M in THF). $^{57}FeCl_2$ was synthesized from ^{57}Fe-enriched metal powder (95%, Isoflex) according to the literature.[2] Sample solutions were injected into the ESI source of an HCT quadrupole-ion trap mass spectrometer (Bruker Daltonics) at a flow-rate of 8.0 µL min^{-1} and transferred into the helium-filled ion trap under mild conditions.[3] Mass spectra were recorded over an *m/z* range of 50−1200. Mössbauer spectra were recorded with a ^{57}Co source in a Rh matrix using an alternating constant acceleration *Wissel* Mössbauer spectrometer operated in the transmission mode and equipped with a *Janis* closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature. Simulation of the experimental data was performed with the *Mfit* program using *Lorentzian* line doublets.[4]

Sample Preparation

ESI-MS

Standard sample solutions were prepared by the addition of the Grignard reagent (8.0 equiv) to a solution of $Fe(acac)_3$ (1.0 equiv), TMEDA (4.0 equiv) in THF at –78 °C, and dilution to 10 mM. **L** and **1a** were added before the Grignard reagent.

Mössbauer Spectroscopy

Mössbauer sample solutions were prepared by the addition of the Grignard reagent (8.0 equiv) to solutions of $^{57}FeCl_2$ (5.0 mM, 1.0 equiv) and TMEDA (4.0 equiv) in THF in a N_2-filled glovebox (unless specified otherwise: at –20 °C for CyMgCl, and at 23 °C for PhMgCl) and directly transferred into the Mössbauer sample cell before *immediately* freezing in liquid nitrogen (outside of the glovebox). **L** and **1a** were added before the Grignard reagent.

Mössbauer Parameters

Table S1. Reactions with CyMgCl

Reaction	Figure	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	Rel. int. [%]	Color	Assignment
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + CyMgCl (8.0 equiv)	Fig. 1b	0.48	0.89	84	blue	$Cy_4Fe(III)^-$
		0.21	1.56	16	red	$Cy_3Fe(II)^-$
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + CyMgCl (8.0 equiv)[a]	Fig. S2	0.48	0.88	85	blue	$Cy_4Fe(III)^-$
		0.24	1.59	15	red	$Cy_3Fe(II)^-$
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + CyMgCl (8.0 equiv)[b]	Fig. S3	0.19	0.86	68	gray	---
		0.48	0.91	28	blue	$Cy_4Fe(III)^-$
		−0.10	1.10	3	yellow	---
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + **L** (1.0 equiv) + CyMgCl (8.0 equiv)	Fig. 2b	0.18	1.59	36	red	$Cy_3Fe(II)^-$
		0.39	3.19	27	green	$Cy_2Fe(II)(NHC)$
		0.46	0.98	19	blue	$Cy_4Fe(III)^-$
		0.54	2.04	11	magenta	$Cy_3Fe(II)(NHC)^-$
		0.24	0.40	7	cyan	---
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + **L** (1.0 equiv) + CyMgCl (8.0 equiv)[b]	Fig. S10	0.22	1.57	47	red	$Cy_3Fe(II)^-$
		0.22	0.57	34	cyan	---
		0.75	1.57	10	purple	---
		0.37	3.20	9	green	$Cy_2Fe(II)(NHC)$
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + **L** (1.0 equiv) + **1a** (1.0 equiv) + CyMgCl (8.0 equiv)	Fig. S13	0.20	1.71	53	red	$Cy_3Fe(II)^-$
		0.43	3.13	21	green	$Cy_2Fe(II)(NHC)$
		0.58	2.04	18	magenta	$Cy_3Fe(II)(NHC)^-$
		0.47	0.84	8	blue	$Cy_4Fe(III)^-$

[a] Recorded at 7 K. [b] Prepared at 23 °C. NHC = $C_{49}H_{54}N_2$.

Table S2. Reactions with PhMgCl

Reaction	Figure	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	Rel. int. [%]	Color	Assignment
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + PhMgCl (8.0 equiv)	Fig. S4	0.54	1.12	78	blue	$Ph_4Fe(III)^-$
		0.20	1.44	13	red	$Ph_3Fe(II)^-$
		0.46	2.61	9	dark yellow	---
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + **L** (1.0 equiv) + PhMgCl (8.0 equiv)	Fig. S9	0.51	1.09	40	blue	$Ph_4Fe(III)^-$
		0.22	4.25	39	green	$Ph_2Fe(II)(NHC)$
		0.56	2.62	14	light green	---
		0.32	1.70	4	orange	---
		1.10	4.30	3	wine	---
$^{57}FeCl_2$ (5.0 mM) + TMEDA (4.0 equiv) + **L** (1.0 equiv) + **1a** (1.0 equiv) + PhMgCl (8.0 equiv)	Fig. S14	0.51	1.09	52	blue	$Ph_4Fe(III)^-$
		0.22	4.21	36	green	$Ph_2Fe(II)(NHC)$
		0.57	2.64	7	light green	---
		0.32	1.70	4	orange	---
		1.10	4.30	2	wine	---

Additional Spectra

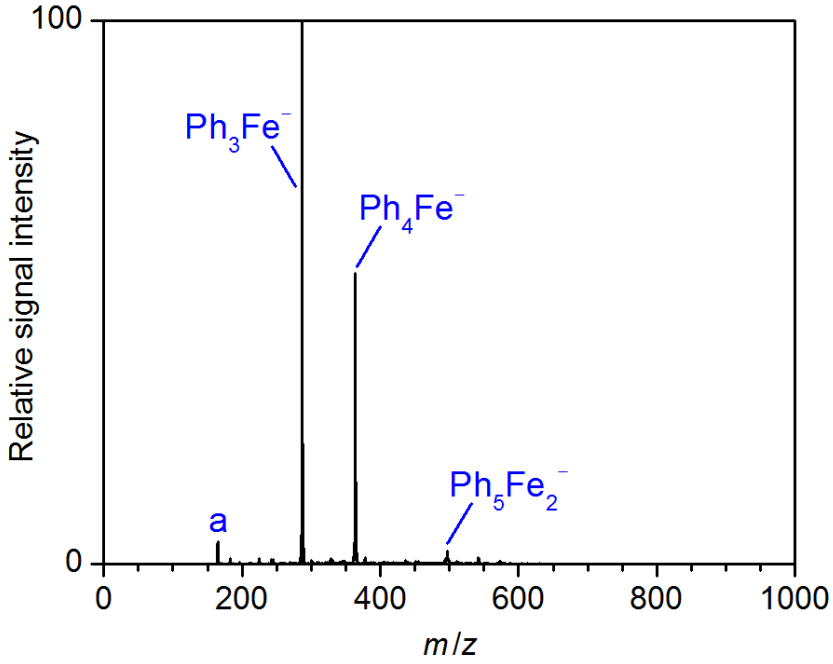

Fig. S1. Negative-ion mode ESI spectrum of a solution of the products formed in the reaction of $Fe(acac)_3$ (10 mM) with TMEDA (4.0 equiv) and PhMgCl (8.0 equiv) in THF; *a* = $[Ph,Fe,O_2]^-$.

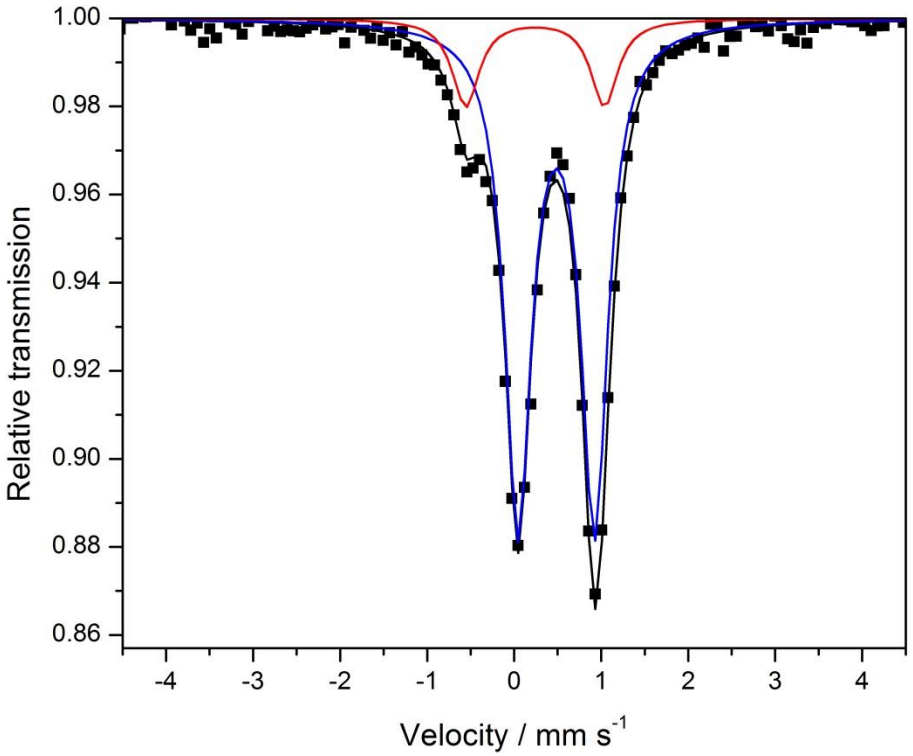

Fig. S2. Mössbauer spectrum and components of the fit of a frozen solution (*T* = 7 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv) and CyMgCl (8.0 equiv) in THF; components of the fit: δ(blue) = 0.48 mm s^{-1}, ΔE_Q(blue) = 0.88 mm s^{-1}, rel. int. = 85%; δ(red) = 0.24 mm s^{-1}, ΔE_Q(red) = 1.59 mm s^{-1}, rel. int. = 15%.

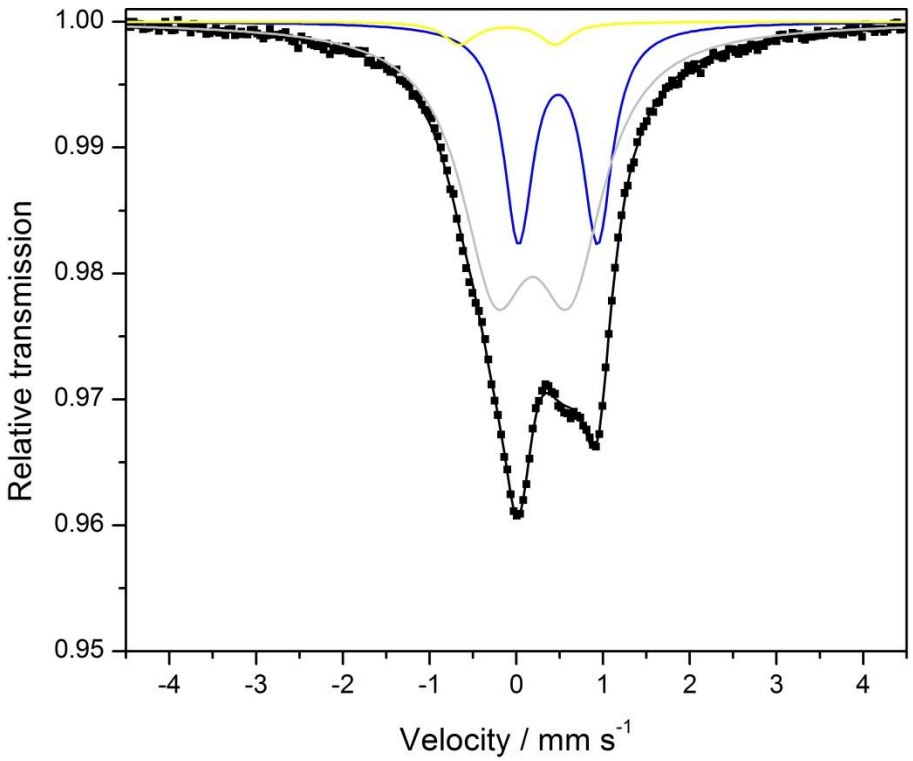

Fig. S3. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv) and CyMgCl (8.0 equiv) in THF at 23 °C; components of the fit: δ(gray) = 0.19 mm s^{-1}, ΔE_Q(gray) = 0.86 mm s^{-1}, rel. int. = 68%; δ(blue) = 0.48 mm s^{-1}, ΔE_Q(blue) = 0.91 mm s^{-1}, rel. int. = 28%; δ(yellow) = −0.10 mm s^{-1}, ΔE_Q(yellow) = 1.10 mm s^{-1}, rel. int. = 3%.

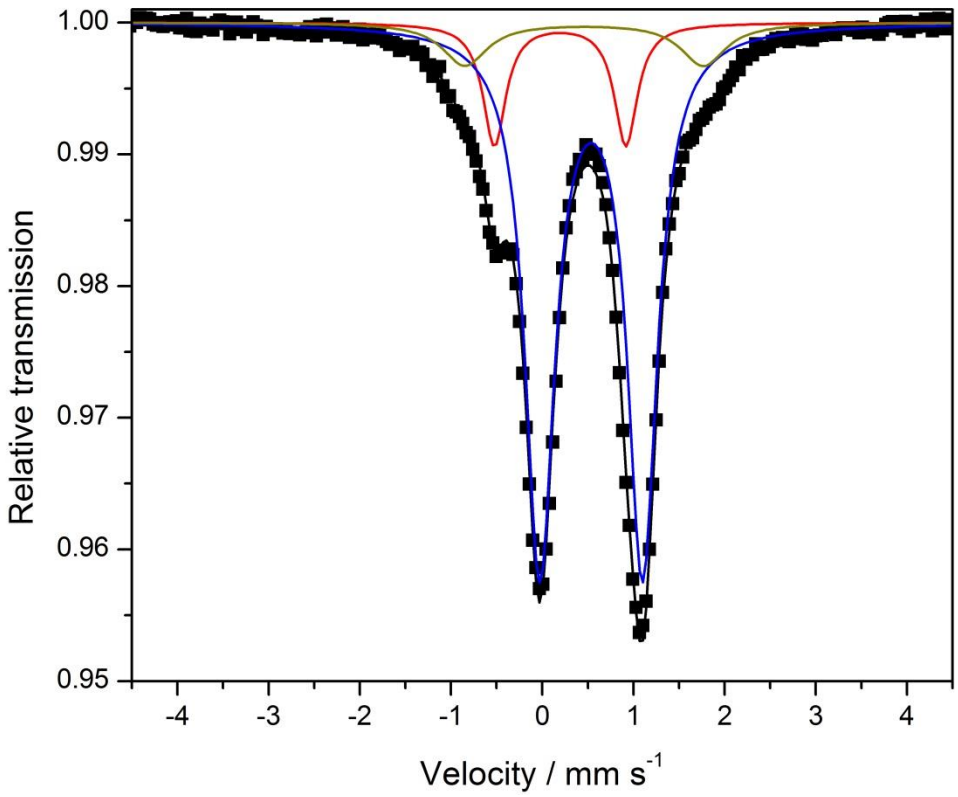

Fig. S4. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv) and PhMgCl (8.0 equiv) in THF; components of the fit: δ(blue) = 0.54 mm s^{-1}, ΔE_Q(blue) = 1.12 mm s^{-1}, rel. int. = 78%; δ(red) = 0.20 mm s^{-1}, ΔE_Q(red) = 1.44 mm s^{-1}, rel. int. = 13%; δ(dark yellow) = 0.46 mm s^{-1}, ΔE_Q(dark yellow) = 2.61 mm s^{-1}, rel. int. = 9%.

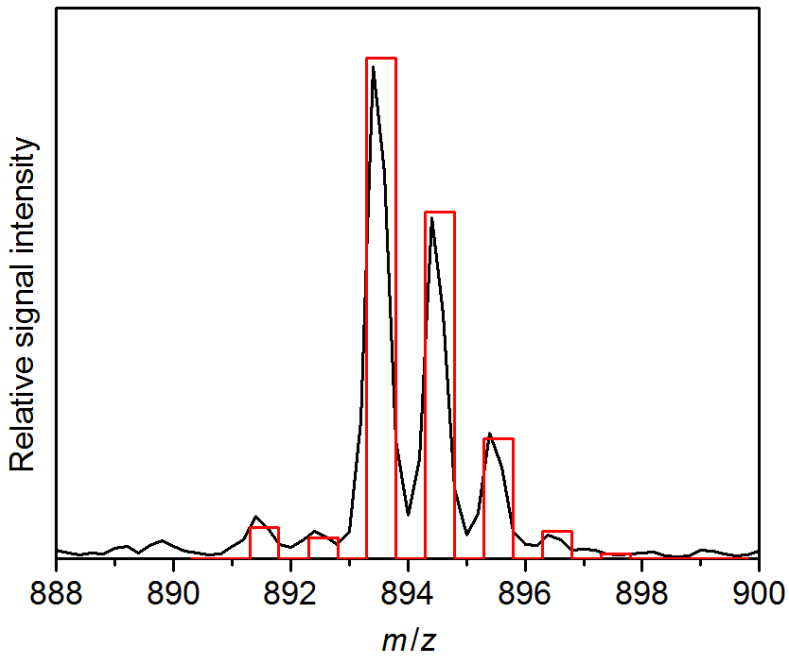

Fig. S5. Comparison of the observed (black) and simulated (red) isotope pattern of $Cy_2FeH(NHC)^-$; NHC = $C_{49}H_{54}N_2$.

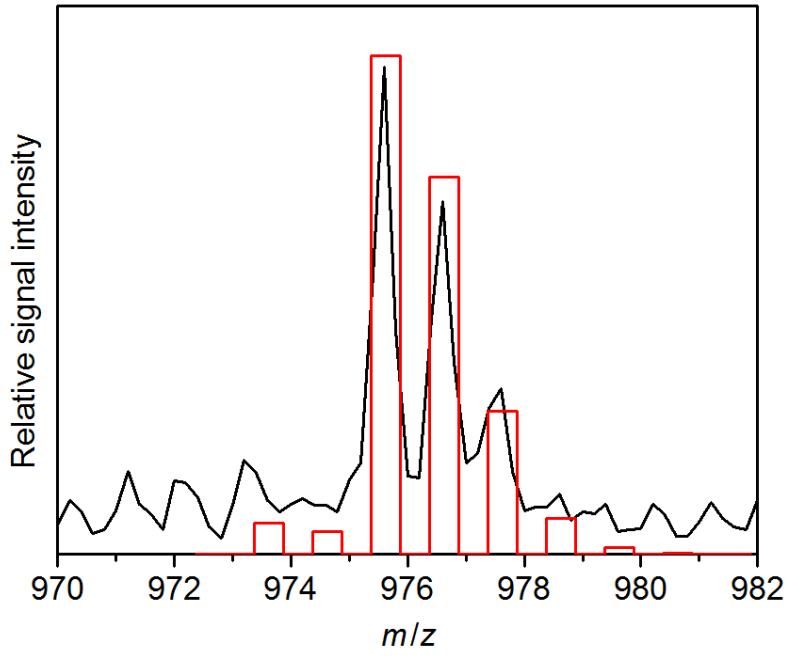

Fig. S6. Comparison of the observed (black) and simulated (red) isotope pattern of $Cy_3Fe(NHC)^-$; NHC = $C_{49}H_{54}N_2$.

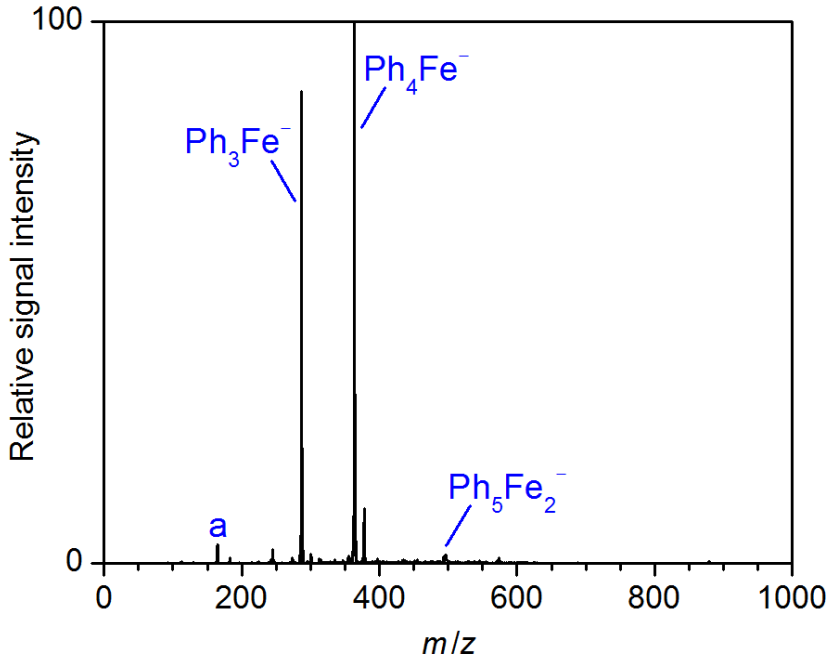

Fig. S7. Negative-ion mode ESI spectrum of a solution of the products formed in the reaction of $Fe(acac)_3$ (10 mM) with TMEDA (4.0 equiv), PhMgCl (8.0 equiv) and **L** (1.0 equiv) in THF; *a* = $[Ph,Fe,O_2]^-$.

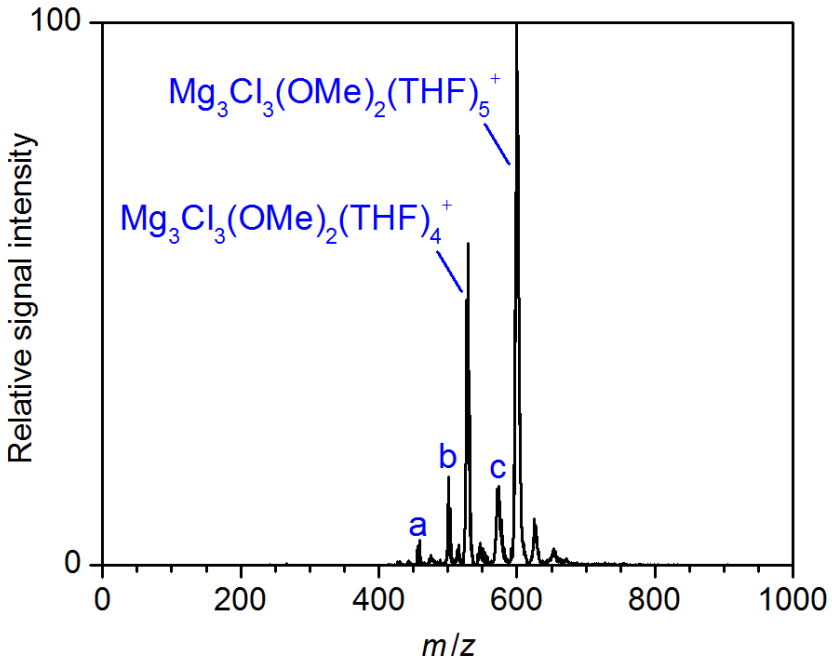

Fig. S8. Positive-ion mode ESI spectrum representative of all experiments; *a* = $Mg_3Cl_3(OMe)(OH)(TMEDA)^{2+}$, *b* = $Mg_3Cl_3(OMe)_2(THF)_2(TMEDA)^+$, *c* = $Mg_3Cl_3(OMe)_2(THF)_3(TMEDA)^+$. The incorporated methoxide originates from traces of methanol as reported previously.[5]

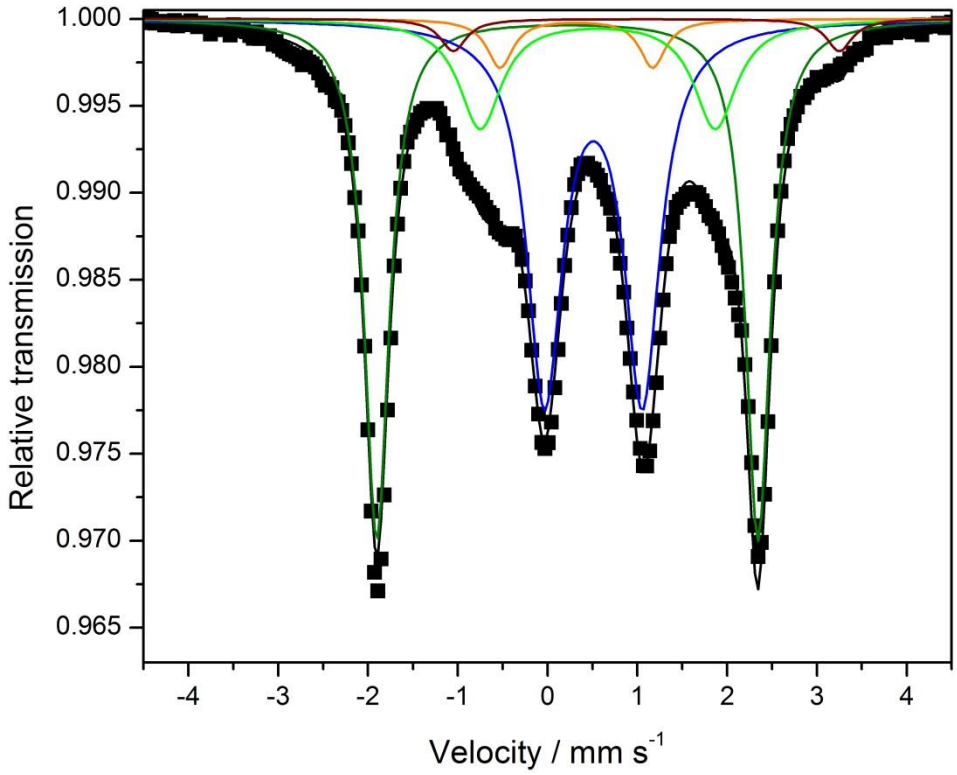

Fig. S9. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv), PhMgCl (8.0 equiv) and **L** (1.0 equiv) in THF; components of the fit: δ(blue) = 0.51 mm s^{-1}, ΔE_Q(blue) = 1.09 mm s^{-1}, rel. int. = 40%; δ(green) = 0.22 mm s^{-1}, ΔE_Q(green) = 4.25 mm s^{-1}, rel. int. = 39%; δ(light green) = 0.56 mm s^{-1}, ΔE_Q(light green) = 2.62 mm s^{-1}, rel. int. = 14%; δ(orange) = 0.32 mm s^{-1}, ΔE_Q(orange) = 1.70 mm s^{-1}, rel. int. = 4%; δ(wine) = 1.10 mm s^{-1}, ΔE_Q(wine) = 4.30 mm s^{-1}, rel. int. = 3%.

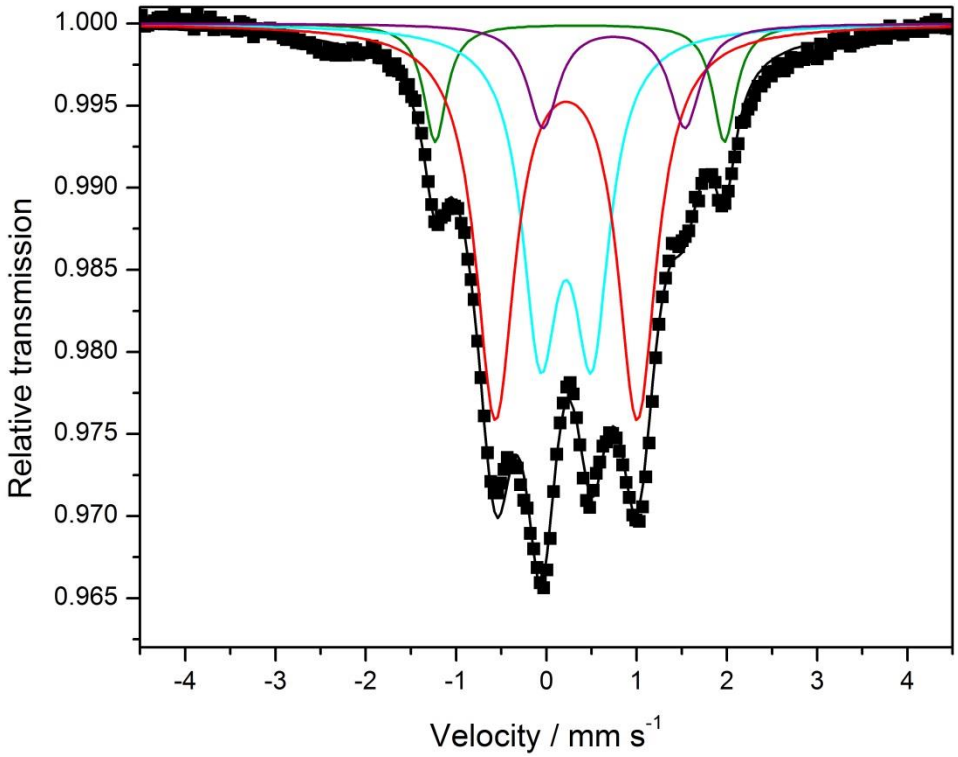

Fig. S10. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv), CyMgCl (8.0 equiv) and **L** (1.0 equiv) in THF at 23 °C; components of the fit: δ(red) = 0.22 mm s^{-1}, ΔE_Q(red) = 1.57 mm s^{-1}, rel. int. = 47%; δ(cyan) = 0.22 mm s^{-1}, ΔE_Q(cyan) = 0.57 mm s^{-1}, rel. int. = 34%; δ(purple) = 0.75 mm s^{-1}, ΔE_Q(purple) = 1.57 mm s^{-1}, rel. int. = 10%; δ(green) = 0.37 mm s^{-1}, ΔE_Q(green) = 3.20 mm s^{-1}, rel. int. = 9%.

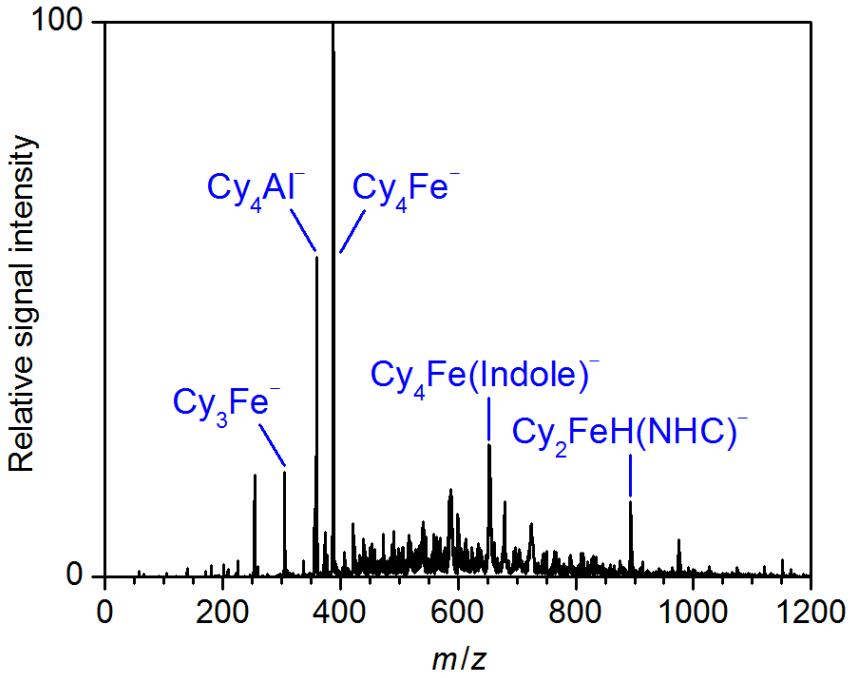

Fig. S11. Negative-ion mode ESI spectrum of a solution of the products formed in the reaction of $Fe(acac)_3$ (10 mM) with TMEDA (4.0 equiv), CyMgCl (8.0 equiv), **L** (1.0 equiv) and **1a** (1.0 equiv) in THF.

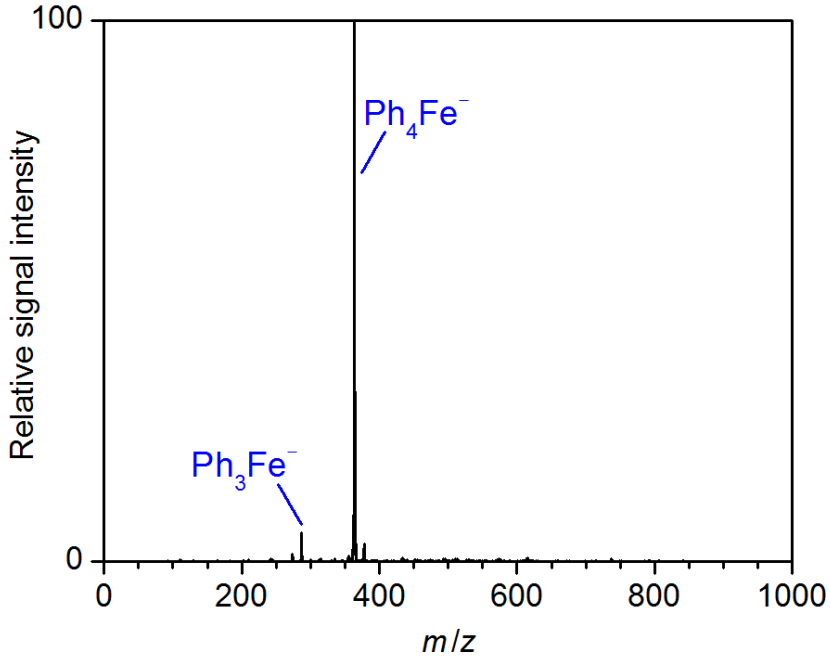

Fig. S12. Negative-ion mode ESI spectrum of a solution of the products formed in the reaction of $Fe(acac)_3$ (10 mM) with TMEDA (4.0 equiv), PhMgCl (8.0 equiv), **L** (1.0 equiv) and **1a** (1.0 equiv) in THF.

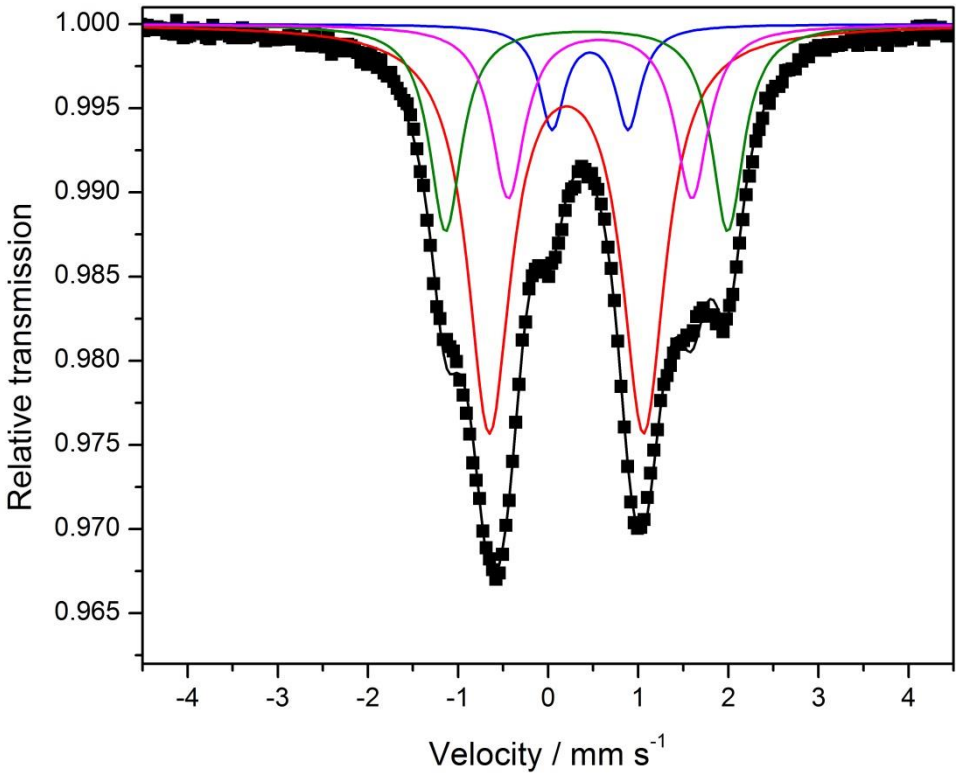

Fig. S13. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv), CyMgCl (8.0 equiv), **L** (1.0 equiv) and **1a** (1.0 equiv) in THF; components of the fit: δ(red) = 0.20 mm s^{-1}, ΔE_Q(red) = 1.71 mm s^{-1}, rel. int. = 53%; δ(green) = 0.43 mm s^{-1}, ΔE_Q(green) = 3.13 mm s^{-1}, rel. int. = 21%; δ(magenta) = 0.58 mm s^{-1}, ΔE_Q(magenta) = 2.04 mm s^{-1}, rel. int. = 18%; δ(blue) = 0.47 mm s^{-1}, ΔE_Q(blue) = 0.84 mm s^{-1}, rel. int. = 8%.

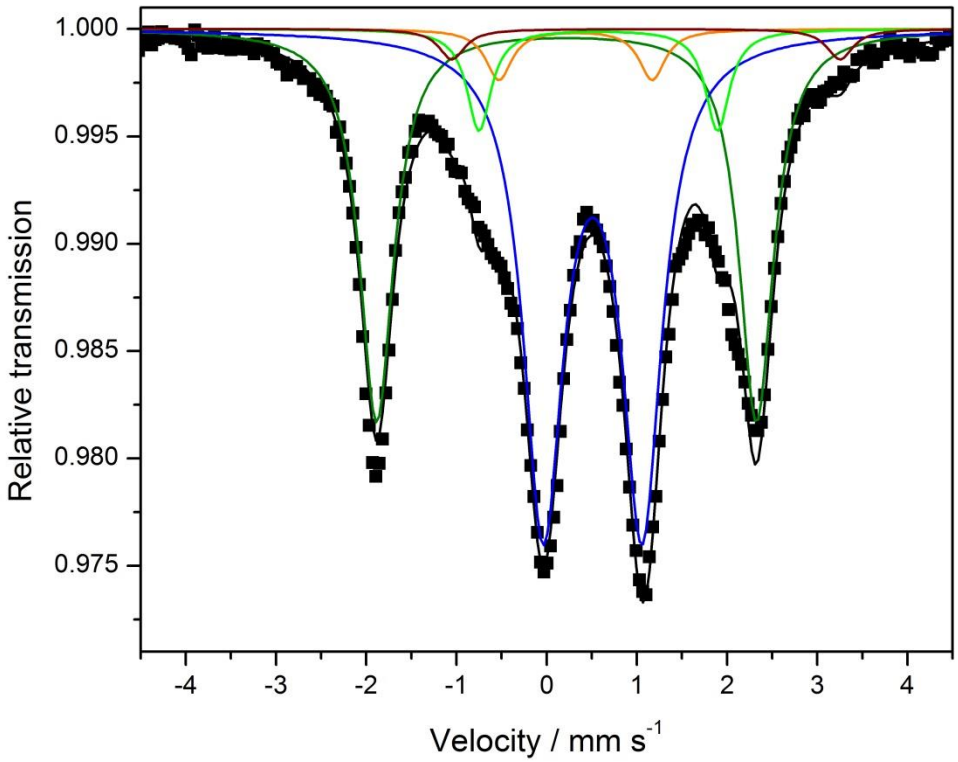

Fig. S14. Mössbauer spectrum and components of the fit of a frozen solution (T = 80 K) of the products formed in the reaction of $^{57}FeCl_2$ (5.0 mM), TMEDA (4.0 equiv), PhMgCl (8.0 equiv), **L** (1.0 equiv) and **1a** (1.0 equiv) in THF; components of the fit: δ(blue) = 0.51 mm s^{-1}, ΔE_Q(blue) = 1.09 mm s^{-1}, rel. int. = 52%; δ(green) = 0.22 mm s^{-1}, ΔE_Q(green) = 4.21 mm s^{-1}, rel. int. = 36%; δ(light green) = 0.57 mm s^{-1}, ΔE_Q(light green) = 2.64 mm s^{-1}, rel. int. = 7%; δ(orange) = 0.32 mm s^{-1}, ΔE_Q(orange) = 1.70 mm s^{-1}, rel. int. = 4%; δ(wine) = 1.10 mm s^{-1}, ΔE_Q(wine) = 4.30 mm s^{-1}, rel. int. = 2%.

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