

Electronic Supporting Information for

The Molecular-Level Effect of Alkoxide Additives in Iron-Catalyzed Kumada Cross-Coupling with Simple Ferric Salts and MeMgCl

Nikki J. Bakas,^{+a} Pablo Chourreu,^{+b,c} Eric Gayon,^c Guillaume Lefèvre,^{*b} and Michael L. Neidig^{*a,d}

^a Department of Chemistry, University of Rochester, Rochester, NY 14627 USA

^b CRNS, Institute of Chemistry for Life and Health sciences, CSB2D, Chimie ParisTech, PSL Research University, 75005 Paris, France

^c M2i Development, Bâtiment ChemStart'Up, Allée Le Corbusier, 64170 Lacq, France

^d Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3QR, United Kingdom

⁺ These authors contributed equally to this work

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1. Experimental Procedures

- 1.1. General Considerations.** All chemical reagents and solvents were purchased from commercial sources. All air and moisture sensitive manipulations were carried out in an MBraun inert-atmosphere (N₂) dry box equipped with a direct liquid nitrogen inlet line. All solvents used in air-sensitive manipulations were sparged using dry N₂ atmosphere before being utilized. All anhydrous solvents were further dried using activated alumina/4Å molecular sieves and stored under N₂-atmosphere over 4Å molecular sieves. Low-temperature reactions (-5 °C) were performed in the glovebox using a Huber ministat 230-cc-NR recirculating bath combined with a Syrris hot/cold plate fit with a PT100 thermocouple for direct measurement and control of the reaction temperature. Additional infrastructure for low-temperature reactions and manipulations (less than -25 °C) was provided by dry gloveboxes equipped with cold wells. Appropriate solvent-dry ice or -liquid N₂ formulations were utilized to achieve temperatures as low as -80 °C.
- 1.2. Preparation of Mössbauer samples.** Solution samples for ⁵⁷Fe Mössbauer spectroscopy were prepared from Fe-57 labeled salts such as ⁵⁷Fe(acac)₃. All samples were prepared in an inert atmosphere dry glovebox equipped with a liquid N₂ fill port to enable sample freezing to 77 K. Each sample was loaded into a Mössbauer sample cup manufactured from Delrin and stored, handled, and loaded under liquid N₂. Low-temperature ⁵⁷Fe Mössbauer measurements were performed using a See Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N₂ cryostat for measurements at 5 & 80 K. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo). Errors of the fit analyses were the following: $\delta \pm 0.02$ mm/s and $\Delta E_Q \pm 3\%$. For multicomponent fits, the quantitation errors of individual components were $\pm 3\%$.
- 1.3. Preparation of Electron Paramagnetic Resonance (EPR) samples.** All samples for EPR spectroscopy were prepared in an N₂ atmosphere glove box equipped with a liquid N₂ fill port to enable sample freezing to 77 K. EPR samples were prepared in 4 mM OD suprasil quartz EPR tubes from Wilmad Labglass. Samples for spin integration utilized high precision suprasil quartz tubes to allow for direct comparison of intensities between different samples. All samples for EPR spectroscopy were 3-5 mM iron. X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat. The instrumental parameters employed for all samples were as follows: 1 mW power; time constant 41 ms; modulation amplitude 8 G; 9.38 GHz; modulation frequency 100 kHz. Samples exhibiting S = 3/2 EPR spectra were spin integrated using a 3 mM CuSO₄ standard under non-saturating conditions. Identical instrumentation parameters were used for both the iron and standard samples.
- 1.4. Preparation of Nuclear Magnetic Resonance (NMR) samples.** All the samples were prepared at 25°C in a recirculating Jacomex Campus inert atmosphere (Ar) glovebox and vacuum Schlenk lines. Glassware was dried overnight at 120 °C before use. Deuterated solvents were thoroughly degassed and dried overnight on 4Å molecular sieves. All non-deuterated solvents were dried over a Na/benzophenone mixture, and distilled before used; NMR tubes equipped with a J. Young valve were used for all ¹H NMR experiments. All chemicals were used as purchased, unless specified otherwise.

2. Supplementary Data

2.1. ^{57}Fe Mössbauer spectra

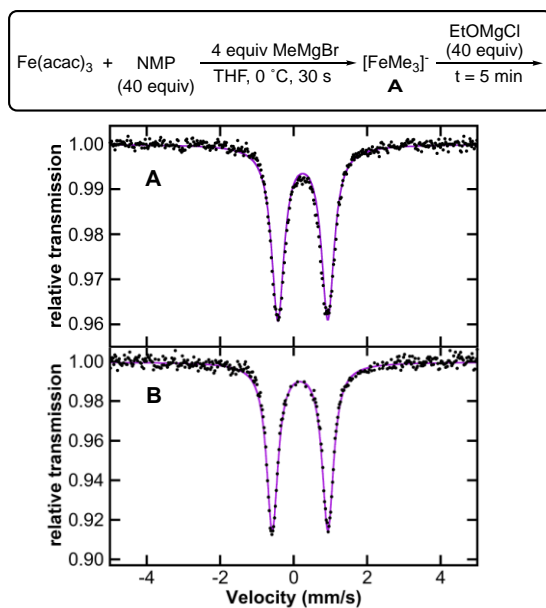


Figure S1. 80 K Mössbauer spectrum of a frozen solution of A) in situ generated $[\text{FeMe}_3]^-$ with 40 equiv NMP (with respect to Fe to match catalytic conditions) and B) plus 40 equiv of EtOMgCl after 5 min, (black dots), total fit (purple line). Note that the addition of 40 equiv EtOMgCl to a solution of $[\text{FeMe}_3]^-$ initially generated with 40 equiv NMP present led to no change in the observed iron speciation.

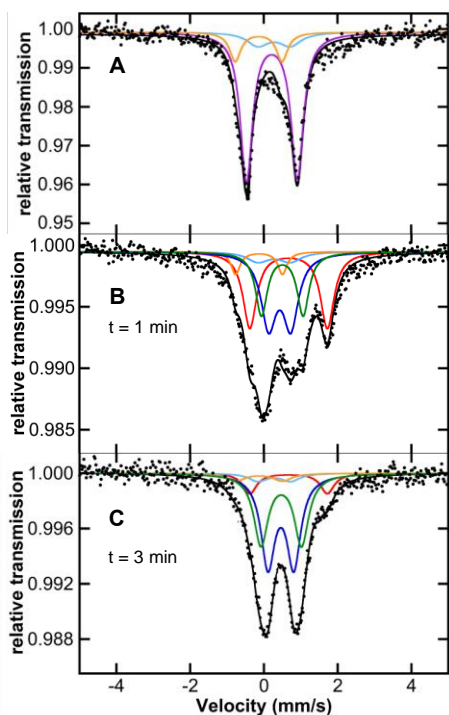
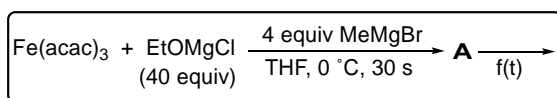


Figure S2. 80 K Mössbauer spectrum of a frozen solution of A) in situ generated $[\text{FeMe}_3]^-$ with alkoxide, B) $t = 1$ min, and C) $t = 3$ min after the formation of in situ generated $[\text{FeMe}_3]^-$, (black dots), total fit (black line), individual components shown.

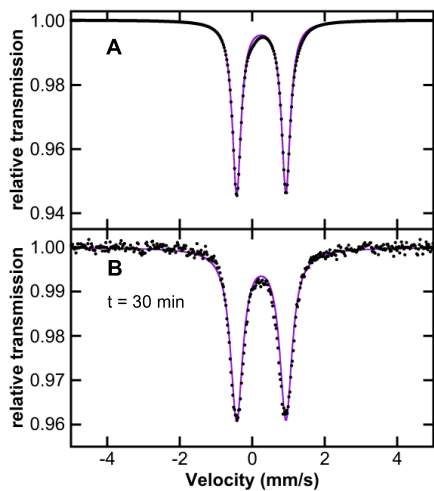
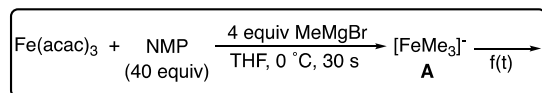


Figure S3. 80 K Mössbauer spectrum of a frozen solution of A) in situ generated $[\text{FeMe}_3]^-$ with NMP and B) $t = 30$ min, (black dots), total fit (black line), individual components shown.

2.2. Summary of ^{57}Fe Mössbauer parameters

Fig.	^{57}Fe Mössbauer Parameters ^a	Total %Fe
1A	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	80
	$\delta = 0.30$ mm/s and $\Delta E_Q = 0.85$ mm/s	12
	$\delta = -0.14$ mm/s and $\Delta E_Q = 1.19$ mm/s	8
1B	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	98
	$\delta = 0.64$ mm/s and $\Delta E_Q = 1.27$ mm/s	2
S1A	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	100
S1B	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	100
S2A	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	80
	$\delta = 0.30$ mm/s and $\Delta E_Q = 0.85$ mm/s	12
	$\delta = -0.14$ mm/s and $\Delta E_Q = 1.19$ mm/s	8
S2B	$\delta = 0.67$ mm/s and $\Delta E_Q = 2.10$ mm/s	30
	$\delta = 0.30$ mm/s and $\Delta E_Q = 0.85$ mm/s	8
	$\delta = -0.14$ mm/s and $\Delta E_Q = 1.19$ mm/s	8
	$\delta = 0.46$ mm/s and $\Delta E_Q = 0.60$ mm/s	32
	$\delta = 0.50$ mm/s and $\Delta E_Q = 1.13$ mm/s	22
S2C	$\delta = 0.67$ mm/s and $\Delta E_Q = 2.10$ mm/s	10
	$\delta = 0.30$ mm/s and $\Delta E_Q = 0.85$ mm/s	6
	$\delta = -0.14$ mm/s and $\Delta E_Q = 1.19$ mm/s	5
	$\delta = 0.46$ mm/s and $\Delta E_Q = 0.60$ mm/s	44
	$\delta = 0.50$ mm/s and $\Delta E_Q = 1.13$ mm/s	35
S3A	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	100
S3B	$\delta = 0.25$ mm/s and $\Delta E_Q = 1.36$ mm/s	100

[a] Isomer shifts were determined relative to $\alpha\text{-Fe}$ at 298 K.

2.3. NMR spectra

2.3.1. Variable-temperature ^1H NMR observation of $[\text{FePh}_3]^-$

In the absence of EtOMgBr

In a J. Young NMR tube, 5 mg $\text{Fe}(\text{acac})_3$ (14 μmol) dissolved in ca. 800 μL of d_8 -THF were added. The sealed tube was cooled down at $-50\text{ }^\circ\text{C}$ and further connected to a Schlenk line before addition of 4.5 equiv. PhMgBr (63 μmol = 63 μL from a commercial THF solution) under a flow of argon. VT ^1H NMR spectra were then recorded by 10-minute warming steps between $-50\text{ }^\circ\text{C}$ and $10\text{ }^\circ\text{C}$. $[\text{FePh}_3]^-$ was characterized by its *meta*-H downfielded and *para*-H highfielded signals (resp. 109 and -39 ppm at 273 K). All spectra were gathered on a Bruker 400 MHz spectrometer.

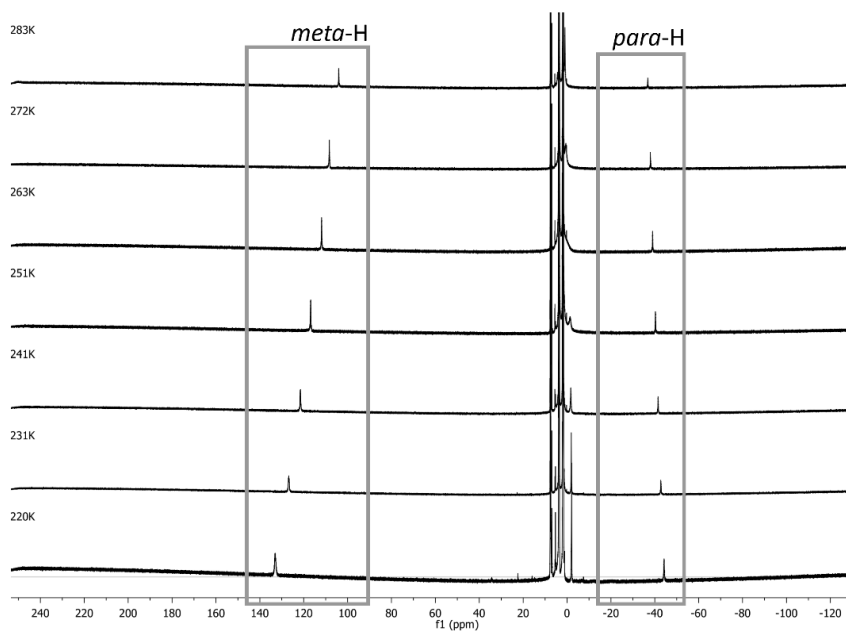


Figure S3. Variable-temperature ^1H -NMR of $[\text{FePh}_3]^-$ in the absence of EtOMgCl.

In the presence of EtOMgBr

In a J. Young NMR tube, 28 μmol EtOH (1.6 μL , 2 equiv. versus Fe, *vide infra*) were added in ca. 800 μL $\text{d}_8\text{-THF}$. PhMgBr (98 μmol , 7 equiv. versus Fe, 98 μL of a THF solution) were then added to generate 28 μmol EtOMgBr. The solution was stirred at room temperature during 5 minutes. The sealed tube was cooled down at -50°C and further connected to a Schlenk line before addition of $\text{Fe}(\text{acac})_3$ (5 mg dissolved in ca. 100 μL $\text{d}_8\text{-THF}$, 14 μmol) under a flow of argon. VT ^1H NMR spectra were then recorded by 10-minute warming steps between -50°C and 10°C . All spectra were gathered on a Bruker 400 MHz spectrometer.

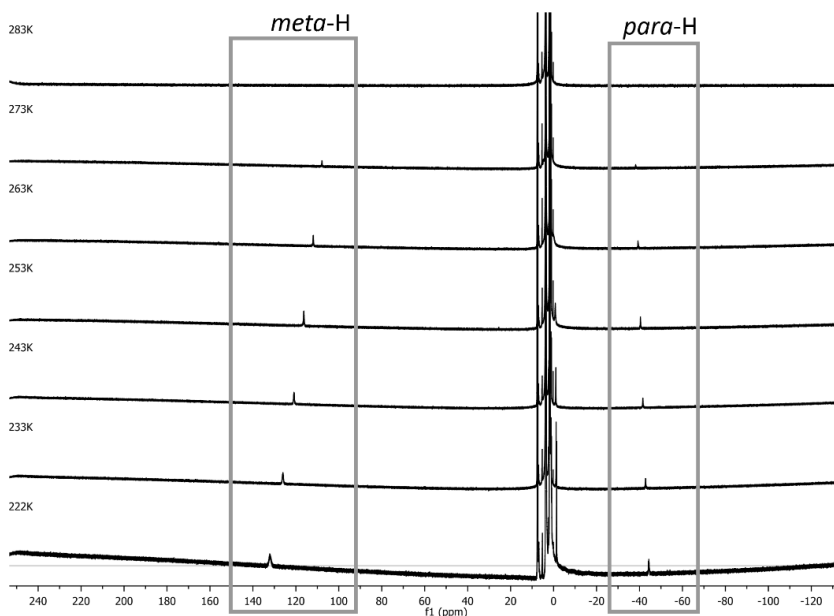


Figure S3. Variable-temperature ^1H -NMR of $[\text{FePh}_3]^-$ in the presence of EtOMgCl.

2.3.2. Reaction of Fe_2Mes_4 with EtOMgBr

Dinuclear complex Fe_2Mes_4 was synthesized according to the procedure reported by Floriani (A.Klose et al *J. Am. Chem. Soc.*, **1994**, 116, 9123-9135). To a $\text{d}_8\text{-THF}$ solution of Fe_2Mes_4 (17 μmol ; 10 mg in ca. 2 mL), two equivalents of EtOMgBr formed in situ by deprotonation of EtOH (34 μmol ; 2 μL) with MesMgBr (34 μmol = 2 equiv. from a commercial THF solution) were added. ^1H NMR spectrum was then recorded after 10 minutes at room temperature; the starred peaks on the NMR spectrum belong to $[\text{FeMes}_3]^-$.

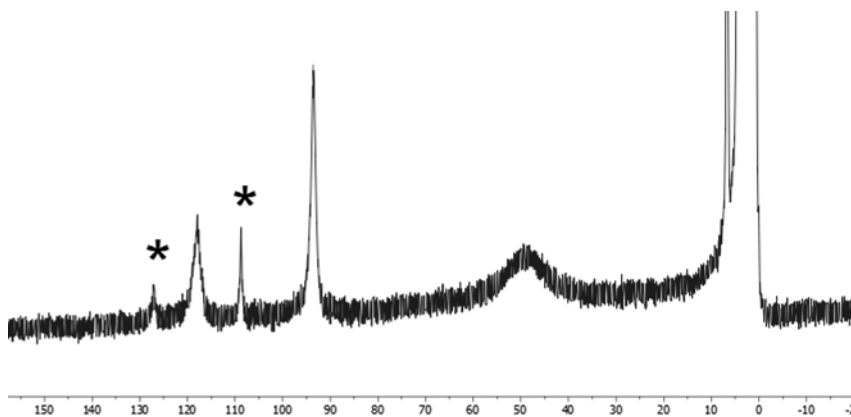


Figure S5. ^1H -NMR of the reaction of Fe_2Mes_4 with 2 equiv EtOMgCl after 10 min at RT.