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Catalytic Silylation of Dinitrogen by a Family of Triiron Complexes

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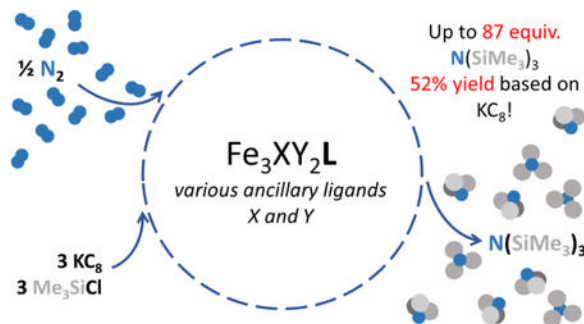
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Abstract

A series of triiron complexes supported by a tris(β -diketiminate)cyclophane (L^{3-}) catalyze the reduction of dinitrogen to tris(trimethylsilyl)amine using KC_8 and Me_3SiCl . Employing Fe_3Br_3L affords 83 ± 7 equiv. NH_4^+ /complex after protonolysis, which is a 50% yield based on reducing equivalents. The series of triiron compounds tested evidences the subtle effects of ancillary donors, including halides, hydrides, sulfides, and carbonyl ligands, and metal oxidation state on $N(SiMe_3)_3$ yield, and highlight $Fe_3(\mu_3-N)L$ as a common species in product mixtures. These results suggest that ancillary ligands can be abstracted with Lewis acids under reducing conditions.

Graphical Abstract



Keywords

N_2 reduction; N_2 silylation; iron clusters; trinuclear clusters; multinucleating ligand

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information. Experimental details. Characterization of new compounds. Additional results for the catalytic silylation of dinitrogen, 1H -NMR spectra of reaction mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Industrialization of ammonia production was realized from Haber's and Bosch's discoveries over 100 years ago, and the eponymous process is hitherto largely un-changed.¹⁻⁴ Despite the high efficiency and yields afforded by the Haber-Bosch process, several environmental and economic problems remain unresolved (e.g., carbon foot-print and transportation and distribution costs). Developing new approaches for N₂ fixation that address these problems are, therefore, of great interest. Many current strategies are inspired by the proposed mechanism of N₂ fixation by the FeMo co-factor of nitrogenase.^{5,6} There are several reports of molecular complexes that yield ammonia from electron and proton sources; however, these catalysts usually require cryogenic temperatures and proton reduction can be competitive with N₂ reduction.⁷⁻¹² To circumvent H₂ production, trimethylsilyl chloride (Me₃SiCl) has been employed as a proton surrogate in these reactions to afford tris(trimethylsilyl)amine instead of ammonia; N(SiMe₃)₃ can be readily converted to NH₄⁺ by protonolysis.^{13,14} A number of complexes employing Group 5-9 metals have been utilized for the catalytic silylation of dinitrogen, with the highest turnovers reported by Masuda and coworkers (270 N(SiMe₃)₃ equiv. per complex).^{9,15,16}

We have previously shown that halide-bridged Fe₃ clusters are competent for the stoichiometric reduction of dinitrogen. However, we were unable to release the bound dinitrogen-derived amide or imide ligands by protonolysis without complex decomposition,¹⁷ and we postulated that Me₃Si⁺ instead of H⁺ might be compatible with our complexes. Herein, we report that a family of triiron complexes housed within a tris(β-diketiminato) cyclophane effect the catalytic conversion of N₂ to N(SiMe₃)₃ using KC₈ and Me₃SiCl. Notably, the series of complexes span varying oxidation states and ancillary bridging ligands (Figure 1) allowing for the first systematic evaluation of the effect of nitrogenase-relevant ancillary ligands on dinitrogen activation.¹⁷⁻²⁶ Our results demonstrate that the non-cyclophane donors are labile under reducing conditions as a putative μ₃-nitridotriiron(II) complex is observed as a major and common product of most reactions.

Using previously reported protocols for catalytic silylation of N₂ with KC₈ and Me₃SiCl,²⁷⁻³⁰ reaction of 500 equiv. KC₈ and 500 equiv. Me₃SiCl in the presence of 0.2 mol% Fe₃Br₃L generated N(SiMe₃)₃, corresponding to 33 ± 3 equiv. of N(SiMe₃)₃ per cluster (N(SiMe₃)₃/Fe₃) and a 20% yield based on KC₈. The tris(trimethylsilyl)amine was confirmed as a product by GC and quantified indirectly as NH₄⁺ in acid digested product mixtures by ¹H-NMR spec-troscopy (Supporting Information, Figure S14). Encouraged by this result, we sought to evaluate the effect of time, solvent, and catalyst loading using the number of N(SiMe₃)₃/Fe₃ as the reporter.

Plots of equivalents of fixed nitrogen for reactions conducted in toluene and using 0.2 mol% catalyst versus time are logarithmic, and do not reach completion even after 120 h (Figure S16). As a means of standardizing our optimization protocol, we elected to evaluate product yields after 24 h. We probed the relationship between N(SiMe₃)₃ production compared to molar equivalents of KC₈ and Me₃SiCl used in the reaction. In all cases, we maintained an equimolar ratio of reductant to silyl reagent, and observed a positive correlation between the N(SiMe₃)₃ yield and KC₈/Me₃SiCl equivalents (Figure 2). However, the efficiency of converting electrons from KC₈ into N(SiMe₃)₃ decreases with increasing KC₈ and Me₃SiCl

equivalents from 28% for 125 equiv. KC_8 to 16% for 1000 equiv. KC_8 . This decreased efficacy remains under investigation but could arise from accelerated catalyst decomposition or an increased rate of disilane formation from transient $\text{Me}_3\text{Si}^\bullet$ radicals. To investigate the possibility of catalyst decomposition under catalytic conditions, we compared the yield from portionwise additions of KC_8 and Me_3SiCl to the catalyst with that for a single addition; 125 equiv. KC_8 and Me_3SiCl were added at 6 h intervals, and the reaction quenched after 24 h. Following this approach, the yield was 32 equiv. $\text{N}(\text{SiMe}_3)_3$ per complex after quenching. This value is comparable to that obtained from a single-addition of 500 equiv. $\text{KC}_8/\text{Me}_3\text{SiCl}$, suggesting a catalyst fidelity up to 500 equiv. of reductant. We also evaluated how the concentration of $\text{Fe}_3\text{Br}_3\text{L}$ effected the yield of $\text{N}(\text{SiMe}_3)_3$ (see Figure S17). The concentration of the catalyst has little or no influence on the obtained yields; more detailed mechanistic studies will be required and are the focus of ongoing work. Taken together, these results support that catalysts decomposition is unlikely responsible for the reduced efficiency with respect to KC_8 .

With respect to the effect of solvent on catalysis, $\text{N}(\text{SiMe}_3)_3$ yields were determined after 24 h for reactions under analogous conditions, utilizing toluene, THF, and Et_2O . Given the poor solubility of $\text{Fe}_3\text{Br}_3\text{L}$ in Et_2O , a standard approach was applied in which an aliquot of a toluene stock solution of $\text{Fe}_3\text{Br}_3\text{L}$ was diluted ten-fold in the appropriate solvent (for a final 9:1 mixture). Reactions employing Et_2O afforded higher yields than those with exclusively toluene for all tested triiron complexes (vide infra) with yield enhancements of two- or three-fold in some cases whereas the lowest yields were obtained with THF (15 equiv. $\text{N}(\text{SiMe}_3)_3$ for $\text{Fe}_3\text{Br}_3\text{L}$). We, therefore, provide only data for PhMe and 9:1 $\text{Et}_2\text{O}:\text{PhMe}$ in Table 1. This improvement using Et_2O can be rationalized as a combination of possible factors, such as an increased solubility of N_2 in Et_2O and solubility differences for triiron intermediates.^{31–33} Whereas the yields obtained in the 9:1 $\text{Et}_2\text{O}:\text{PhMe}$ mixture are comparable to other iron-based catalysts for this reaction under ambient conditions,^{11,27,29,30,34–36} the yield based on KC_8 – that is, the efficiency with which reducing equivalents are converted into $\text{N}(\text{SiMe}_3)_3$ – is the highest of any reported system (Table S2). Lowering the reaction temperature to -34°C results in only 33 ± 3 equiv. of $\text{N}(\text{SiMe}_3)_3$ per complex – a 20% yield based on KC_8 – in 9:1 $\text{Et}_2\text{O}:\text{PhMe}$ after 24 h. Extending the reaction time to 96 h at -34°C , however, affords 83 ± 6 $\text{N}(\text{SiMe}_3)_3/\text{Fe}_3\text{N}(\text{SiMe}_3)_3$, which correlates with a 50% yield based on reducing equivalents (Figure S18). This temperature effect on dinitrogen silylation is similar to that reported by Masuda and coworkers for a Co complex.¹⁶ To our knowledge, these triiron compounds are the most effective reported catalytic systems for this reaction, independent of metal ion type or complex nu-clearity (Table S3).^{9,16,28,37}

Consistent with homogeneous catalysis, reaction filtrates retain catalytic activity whereas residues are comparatively ineffective (see Supporting Information). However, one proposed complication of utilizing Me_3Si^+ in lieu of H^+ as an electrophile in this system is that silyl radicals – generated from one-electron reduction of Me_3Si^+ – may react directly with N_2 to generate $\text{N}(\text{SiMe}_3)_3$.^{13,14} Control experiments using no Fe catalyst or an equimolar amount of iron as FeBr_2 evidence minimal or no activity under the conditions employed for catalytic turnover (Entry 13, Table 1). The importance of our multinucleating system is evident by the

comparison of our observed turnovers to that a dimeric β -diketiminato iron(II) complex, $[\text{FeCIL}']_2$ ($\text{L}' = \text{DIPP-nacnac}$).³⁸ Employing an equimolar in iron amount of $[\text{FeCIL}']_2$ results in lower yields (ca. 33%) as compared to our complexes (Entry 14, Table 1), along with a likely greater contribution from heterogeneous species in catalysis (Supporting Information).

Given the family of triiron compounds at our disposal, we then explored the effect of the bridging ligand identity on yield of $\text{N}(\text{SiMe}_3)_3$ (Table 1). First, the halide-bridged complexes afford similar yields, with the order being $\text{Br} \approx \text{F} > \text{Cl}$. We postulate that this ordering may reflect the relative stabilities of transient μ_3 -halide or $\text{di}(\mu\text{-halide})$ complexes; access to these types of complexes to test this hypothesis remains elusive. Second, the trihydride species, $\text{Fe}_3\text{H}_3\text{L}$, affords ~50% less $\text{N}(\text{SiMe}_3)_3$ than the bromide congener whereas that of the dihydride-formate, $\text{Fe}_3(\text{H})_2(\text{HCOO})\text{L}$ is comparable to $\text{Fe}_3\text{Br}_3\text{L}$ (cf. entries 5 and 7 with 1, Table 1). This observation is noteworthy given the proposed importance of hydrides in N_2 reduction for the nitrogenase cofactors and contrasts reports of di-nitrogen reduction by reported iron hydride model compounds.^{39–41} Third, there is no apparent correlation between metal formal oxidation states of the starting complexes and yield of amine. For example, the $\text{tri}(\mu\text{-sulfido})\text{triiron(III)}$ and $\text{tribromotriiron(II)}$ complexes provide similar yields, whereas the triiron(I/II) species is statistically lower (cf. entries 11, 1, and 7, Table 1). The ligand field differences across the three compounds tempers any general conclusions as reduction and loss of halide donors from $\text{Fe}_3\text{Br}_3\text{L}$ would generate Fe(I) centers in weaker ligand field as compared to the $\text{di}(\mu\text{-carbonyl})(\mu_3\text{-hydride})$ compound.

$^1\text{H-NMR}$ spectra recorded on products from reduction reactions with varying equivalents of KC_8 and Me_3SiCl indicated formation of a D_{3h} symmetric species, which we tentatively assign to a μ_3 -nitridotriiron(II) complex (Figures S19–S24, *vide infra*). The extent of accumulation of this compound is sensitive to solvent and bridging ligands in the initial triiron complex. For example, reaction of 3 equiv. KC_8 and Me_3SiCl with $\text{Fe}_3\text{Br}_3\text{L}$ in Et_2O generates predominantly the μ_3 -nitridotriiron(II) complex, whereas the analogous reaction with 6 equiv. KC_8 and Me_3SiCl affords predominantly the previously reported $\text{tri}(\mu\text{-amido})\text{triiron(II)}$ compound, $\text{Fe}_3(\text{NH}_2)_3\text{L}$ (Figure S19–S20).¹⁷ There was also minimal formation of the μ_3 -nitridotriiron(II) species upon reduction of $\text{Fe}_3\text{H}_3\text{L}$, $\text{Fe}_3\text{H}_2(\text{O}_2\text{CH})\text{L}$, or $(\text{FeCO})_2\text{Fe}(\mu_3\text{-H})\text{L}$ in the presence of Me_3SiCl .

This μ_3 -nitridotriiron(II) complex could be independently synthesized by reduction of the reported $\text{Fe}_3\text{Br}_2(\mu_3\text{-N})\text{L}$ using two equivalents of KC_8 or KHBR_3 ($\text{R} = \text{Et}$ or *sec*-But).^{22,42} Attempts to obtain single crystals of sufficient quality for structural characterization have been as yet unsuccessful; crystals obtained hitherto are typically twinned, which we were unable to resolve in the data analysis.⁴³ The formulation, Fe_3NL , is consistent with ESI-MS data collected on THF solutions of this compound, although the data evidence adventitious oxidation of complexes during analysis. $^1\text{H-NMR}$ spectra of $\text{Fe}_3(\mu_3\text{-N})\text{L}$ are consistent with D_{3h} symmetry and the resonances agree with those of the common species observed in the catalytic silylation product mixtures mentioned above. Taken together, our data support a structure in which a nitride ligand is present in a μ_3 -bridging mode and a structure analogous to our previously reported chalcogenide-bridged tricopper complexes.²¹

Our data indicates, surprisingly, that bridging ligand identity has minimal influence on fixed-nitrogen yield. This result implies that, under reducing conditions, the initial bridging ligands may undergo silylation for formate, sulfide, nitride, or oxide and dissociation leading to compounds with single atom μ_3 -donors (e.g., sulfide) or one μ_3 - and one μ -donor. These species are likely reactive towards dinitrogen to install nitride donors; however, silylation of the remaining donors (e.g., sulfide) instead of the dinitrogen-derived nitride provides a pathway towards $\text{Fe}_3(\mu_3\text{-N})\text{L}$ (Figure 3). Subjecting $\text{Fe}_3(\mu_3\text{-N})\text{L}$ to the same reaction conditions as described above results in comparable albeit lower $\text{N}(\text{SiMe}_3)_3$ yields (Table 1). In addition, treatment of $\text{Fe}_3(\mu_3\text{-N})\text{L}$ with up to 20 equiv. of KC_8 and Me_3SiCl results in recovery of the nitride complex, suggesting stability of this complex under the reaction conditions (Figure S25–S27). We postulate, then, that the starting bridging ligands can be diluted from a catalytically-active species as the reaction proceeds, and ultimately funnel towards the μ_3 -nitride species. Indeed, we can correlate the greater accumulation of the $\text{Fe}_3(\mu_3\text{-N})\text{L}$ in those systems with less covalent metal-ligand interactions (e.g., $\text{Fe}_3\text{Br}_3\text{L}$) as compared to those with greater covalency (e.g., $\text{Fe}_3\text{S}_3\text{L}$). Therefore, we do not have definitive evidence for any specific benefit for supporting ligands on reaction yield. Our data do not suggest substitution of our ancillary ligands by chloride as $\text{Fe}_3\text{Cl}_3\text{L}$ or C_{2v} -symmetric species containing chlorides were not identified in our studies; we cannot rigorously exclude an additive effect by halide ions, although precipitation of potassium halides is expected to be highly favored. Another possible explanation relies on the fact that these ligands may influence recyclability and the reaction kinetics, but the predicted diverse speciation of the metal complexes during early turnover likely complicate this analysis (i.e., speciation changes as bridging ligands are exchanged for nitride). To validate the specific consequence of a particular bridging ligand, single turnover reactivity studies of the dinitrogen-reactive triiron complexes will be required rather than the precatalysts reported here. Candidate compounds include $\text{Fe}_3(\mu_3\text{-X})\text{L}$ and $\text{Fe}_3(\mu\text{-Y})(\mu_3\text{-X})\text{L}$ in which X and Y are varied systematically. Our results agree with previous reports by Nishibayashi and collaborators that showed minimal dependence of carbonyl or cyclo-pentadienyl ligands on the catalytic activity of iron(0) compounds attributed to ligand release under cycling conditions.³⁴ In addition, our results are surprisingly complementary to recent work on the nitrogenase cofactors that evidence ligand dissociation – specifically, sulfide – upon reductive activation of the cluster.⁴⁴ Release of bridging ligands to generate open coordination sites in weak-field ligated multiiron species is likely a common theme, and suggests new opportunities in the design of such catalysts.

In summary, a series of triiron clusters are competent for the catalytic fixation of dinitrogen to produce $\text{N}(\text{SiMe}_3)_3$ from Me_3SiCl and KC_8 under a dinitrogen atmosphere. Turnovers ranged from 20 to 83 ± 7 $\text{N}(\text{SiMe}_3)_3/\text{catalyst}$, with higher yields obtained in a mixture of $\text{Et}_2\text{O}/\text{PhMe}$ 9:1. To date, members of this triiron series exhibit the highest yields of $\text{N}(\text{SiMe}_3)_3$ based on KC_8 for this reaction.

Detailed mechanistic studies employing the nitridotriiron(II) complex as well as the targeted synthesis of possible intermediates are ongoing.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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ABBREVIATIONS

DIPP 2,6-diisopropylphenyl.

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- 43). Data reported in prior publications suggest the cyclophane ligand typically dominates crystal packing, which leads to co-crystallization of multiple compounds in a single crystal as well as a likelihood of twinning and poor crystal quality.
- 44). Sippel D; Rohde M; Netzer J; Trncik C; Gies J; Grunau K; Djurdjevic I; Decamps L; Andrade SLA; Einsle O A Bound Reaction Intermediate Sheds Light on the Mechanism of Nitrogenase. *Science* 2018, 359, 1484–1489. [PubMed: 29599235]

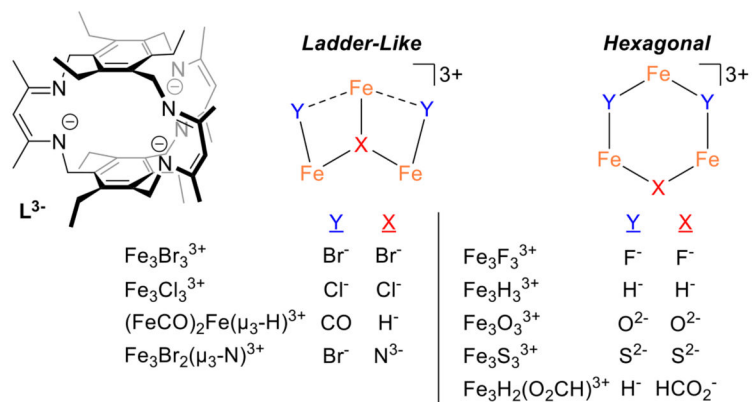
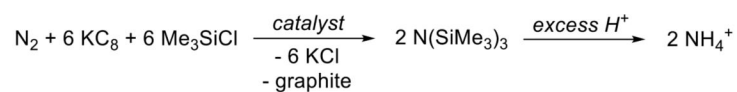


Figure 1. Catalytic silylation of N_2 (top) for the formation of $\text{N}(\text{SiMe}_3)_3$ and a series of planar triiron clusters (bottom) supported by L^{3-} employed here.

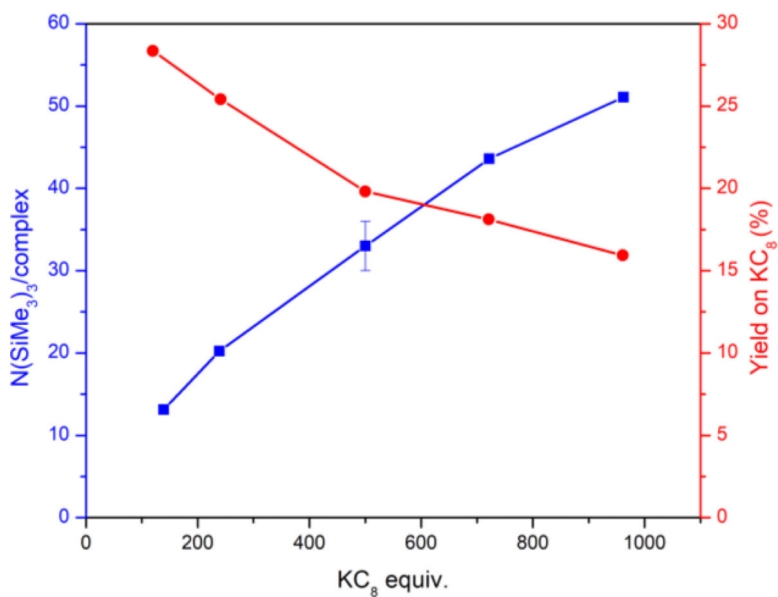


Figure 2. Effect of KC₈/ Me₃SiCl equivalents on N(SiMe₃)₃ production (blue squares) using Fe₃Br₃L catalytic system and corresponding yields based on KC₈ (red circles). Solid lines are included as visual guides for the general trend. Reaction conditions: equimolar amounts of KC₈ and Me₃SiCl in toluene at room temperature for 24 h.

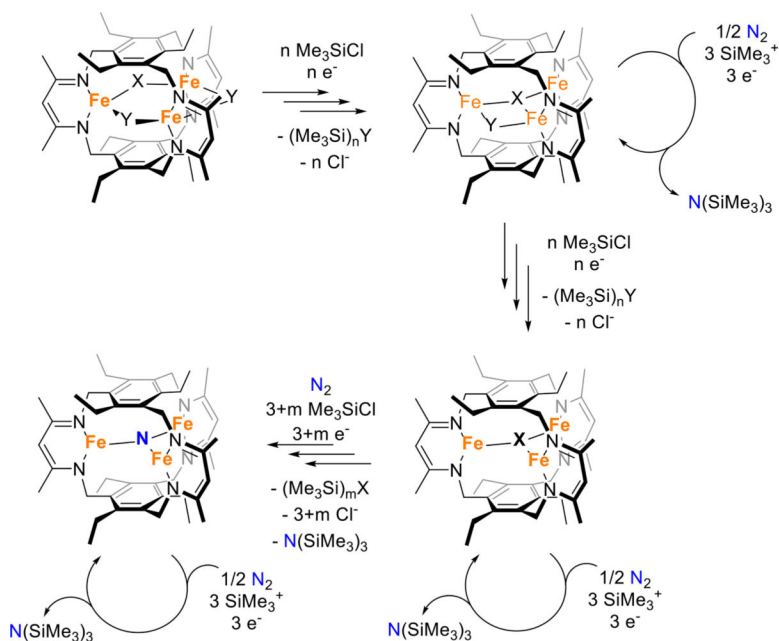


Figure 3.
Proposed reaction pathways during the catalytic cycle of a generic $\text{Fe}_3\text{XY}_2\text{L}$ complex.

Table 1.Catalytic dinitrogen silylation by triiron complexes ^(a)

Entry	Triiron Complex ^(b)	N(SiMe ₃) ₃ /Fe ₃ (yield in %)	
		Solvent A	Solvent B
1	Fe ₃ Br ₃ L	33 ± 3 (20)	57 ± 7 (34) 83 ± 7 (50) ^(c)
2	Fe ₃ Br ₃ L ^(d)	32 (19)	63 (38)
3	Fe ₃ F ₃ L	18 ± 2 (11)	64 ± 6 (38)
4	Fe ₃ Cl ₃ L	22 ± 2 (13)	45 ± 7 (27)
5	Fe ₃ H ₃ L	21 ± 3 (13)	34 ± 5 (20)
6	Fe ₃ H ₂ (O ₂ CH)L	27 ± 5 (16)	60 ± 7 (36)
7	(FeCO) ₂ Fe(μ ₃ H)L	21 ± 3 (13)	35 ± 3 (21)
8	Fe ₃ Br ₂ (μ ₃ -N)L	29 ± 3 (17)	51 ± 4 (31)
9	Fe ₃ (μ ₃ -N)L	31 ± 6 (19)	43 ± 3 (26)
10	Fe ₃ O ₃ L	25 ± 4 (15)	46 ± 4 (28)
11	Fe ₃ S ₃ L	31 (19)	58 ± 1 (35)
12	1.5 [FeClL'] ₂ ^(e)	17 ± 2 (10)	46 ± 8 (28) 56 (38) ^(c)
13	No Catalyst	0.7 (0)	<0.1 (0)
14	FeBr ₂	0.9 (0)	-----

^(a) Reaction conditions unless stated otherwise: 500 equiv. of K₂C₈ and 500 equiv. of TMSCl after 24 h at room temperature in triplicate. Solvents A and B are PhMe and Et₂O:PhMe 9:1, respectively. N(SiMe₃)₃ was quantified by acidolysis followed by ¹H-NMR

^(b) the synthesis of triiron complexes are reported or referenced in the supporting information;

^(c) result after 96 h at -34 °C;

^(d) portionwise method;

^(e) L' = DIPP-nacnac.