Homoleptic Iron Complexes

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TMEDA in Iron-Catalyzed Kumada Coupling: Amine Adduct versus Homoleptic “ate” Complex Formation**

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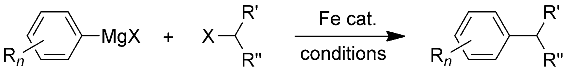
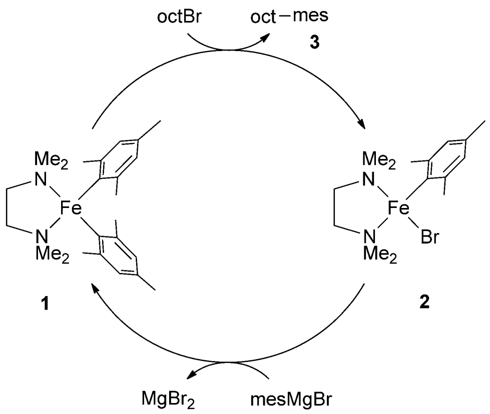
Abstract: *The reactions of iron chlorides with mesityl Grignard reagents and tetramethylethylenediamine (TMEDA) under catalytically relevant conditions tend to yield the homoleptic “ate” complex $[Fe(mes)_3]^-$ (mes = mesityl) rather than adducts of the diamine, and it is this ate complex that accounts for the catalytic activity. Both $[Fe(mes)_3]^-$ and the related complex $[Fe(Bn)_3]^-$ (Bn = benzyl) react faster with representative electrophiles than the equivalent neutral $[FeR_2(TMEDA)]$ complexes. Fe^I species are observed under catalytically relevant conditions with both benzyl and smaller aryl Grignard reagents. The X-ray structures of $[Fe(Bn)_3]^-$ and $[Fe(Bn)_4]^-$ were determined; $[Fe(Bn)_4]^-$ is the first homoleptic σ-hydrocarbyl Fe^{III} complex that has been structurally characterized.*

Iron-catalyzed couplings of aryl Grignard reagents and alkyl halides (Scheme 1)[1] are run under a wide variety of conditions, although chelating diamines, such as TMEDA (tetramethylethylenediamine), are used in many instances.[2,3] Herein, we report our preliminary studies to elucidate the possible role(s) of TMEDA under various catalytic conditions. Specifically, we address three questions: 1) What is the role of TMEDA in catalytic reactions with model compounds that are derived from bulky aryl Grignard reagents? 2) How representative are these models for reactions with less bulky Grignard reagents? 3) Can oxidation states below Fe^{II} be accessed in the presence of TMEDA and Grignard reagents?



Scheme 1. Iron-catalyzed coupling of aryl Grignard reagents with alkyl halides.



Scheme 2. Previously proposed catalytic cycle.[4]

The catalytic cycle shown in Scheme 2 has been proposed as a model for the Fe/TMEDA-catalyzed coupling of aryl Grignard reagents with alkyl halides, based on the reactions of isolated intermediates **1** and **2**.[4] Formation of **1** under catalytic conditions was supported by ^{1}H NMR spectroscopy of a single reaction mixture similar to that used for catalysis, though in the absence of the electrophile and without an excess of the nucleophile.

Species **1** was formed as the principal paramagnetic iron-containing species from a mixture of $FeCl_3$, mesMgBr (mes = mesityl), and TMEDA in a 1:3:8 ratio. One equivalent of the Grignard reagent presumably serves to reduce the Fe^{III} to Fe^{II} (with concomitant formation of bimesityl), leaving two equivalents to furnish complex **1**. However, under catalytic conditions, the amount of Grignard reagent relative to iron is much higher. We found that using this mixture of $FeCl_3$, Grignard reagent, and TMEDA (1:3:8) in THF, complex **1** is generated along with at least two other paramagnetic species,[5] the major one of which is the previously reported Fe^{II} ate complex $[Fe(mes)_3]^-$ (**4**).[6,7] Upon addition of more equivalents of the Grignard reagent, the proportion of **4** increases until, after the addition of four extra equivalents, **4** was the sole paramagnetic species that could be observed by ^{1}H NMR spectroscopy.

Scheme 3 illustrates that complex **4** could also be produced by the reactions of mesMgBr with complex **1**, or with $[\{Fe(mes)\}_2(\mu\text{-}mes)_2]$ (**5**), or with either $FeCl_2$ or $FeCl_3$ in the presence or absence of TMEDA. The ^{1}H NMR spectrum of a 1:1 mixture of **4** and TMEDA shows only signals of **4**; increasing the amount of TMEDA (in the absence of mesMgBr) leads to the formation of small amounts of complex **1** until at 10 equivalents the ratio of **4**/**1** is approximately 1:1.3.[5]

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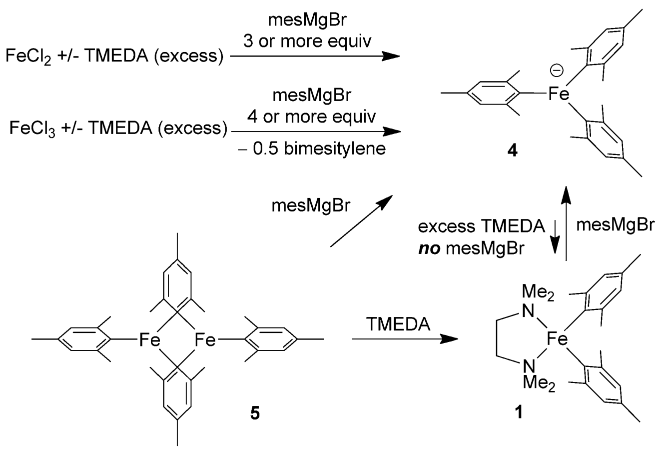
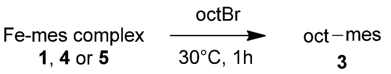


Scheme 3.

Complex **4** was also found to be the only paramagnetic species that can be observed by ^{1}H NMR analysis of the reaction mixture of a representative catalytic cross-coupling.[8] This does not preclude the presence of **1** at a concentration below the NMR detection limit, and if **1** were able to react much more rapidly with the electrophile than **4** does, then it could still be responsible for catalytic turnover despite its very low concentration. However, both the data in Scheme 4 and reaction profiles (Supporting Information, Figures S5 and S6)[9] show that complex **4** reacts significantly faster with bromooctane than **1** does. Furthermore, the reaction with **1** displays a pronounced induction time of at least five minutes, which demonstrates conclusively that it cannot be part of the catalytic cycle.



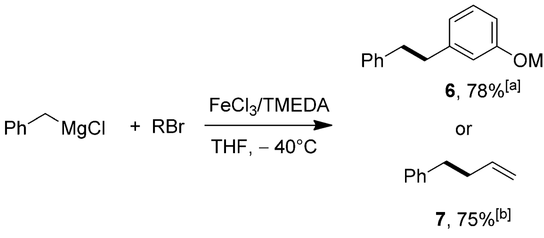
$$\underset{\mathbf{1},\ \mathbf{4}\text{ or }\mathbf{5}}{\text{Fe-mes complex}} \xrightarrow[30°\text{C, 1h}]{\text{octBr}} \underset{\mathbf{3}}{\text{oct}-\text{mes}}$$

25% from **1** (75% octBr; < 1% octane; < 1% octene; reaction stays yellow)
50% from **4** (0% octBr; 1% octane; 49% octene; reaction turns black)
24% from **5** (48% octBr; 1% octane; 21% octene; reaction turns black)

Scheme 4.

Taken together, the data above indicate that TMEDA is not coordinated to the complexes that are observed under catalytic conditions, and that TMEDA is unlikely to play a role in the primary catalytic cycle. Therefore, homoleptic complex **4** should be considered in place of complex **1** in the catalytic cycle shown in Scheme 2.[10,11] What then is the role of TMEDA?[12] We found that the yield of cross-coupled product in a representative catalytic reaction was not influenced by the presence or absence of TMEDA.[13] However, in the latter case, a smaller amount of starting material was recovered, and greater amounts of octene and octane were formed, which suggests that TMEDA must play a role in suppressing competing, unselective pathways.[14] It seems likely that TMEDA traps intermediates that are formed off-cycle and would otherwise lead to less selective manifolds being populated.

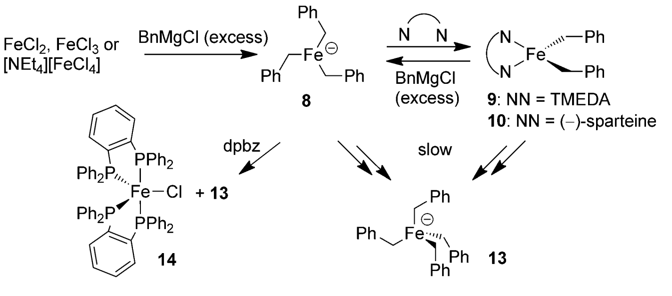
Sterically demanding ligands often kinetically stabilize organometallic complexes with respect to reductive elimination. Hence, the behavior of mesityl iron species may not reflect that of other Grignard reagents. Indeed, aryl Grignard reagents with 2,6-dimethyl groups perform poorly in cross-coupling reactions, giving either low yields after many hours,[4] or no reaction.[3a,15] Therefore, we also investigated the reactivity of sterically less demanding Grignard reagents, including BnMgCl. This species undergoes cross-coupling in the presence of iron(III) chloride and TMEDA, albeit accompanied by some homo-coupling (Scheme 5).



Scheme 5. Iron-catalyzed cross-couplings of benzyl Grignard reagents. Yields were determined by ^{1}H NMR spectroscopy. [a] 1,2-Diphenylethane and 1,2-di-(3-methoxyphenyl)ethane were produced in 35% and 14% yield, respectively. R = 3-methoxybenzyl. [b] 1,2-diphenylethane (8%) and traces of hexadiene were formed. R = allyl.

The reaction of FeCl$_2$ with BnMgCl (4 equiv) gave the new 12-electron ate complex [FeBn$_3$]$^-$ (**8**), which is stable at room temperature. Complex **8** could also be produced from FeCl$_3$ or [NEt$_4$][FeCl$_4$] with BnMgCl ($\geq$4 equiv; Scheme 6).[16] Whereas TMEDA could not efficiently displace the mesityl group in **4** to yield **1**, excess TMEDA reacted with **8** to yield [FeBn$_2$(TMEDA)] (**9**)[17] and the reaction with (−)-sparteine gave **10** (Scheme 6).[18] In both cases the reaction was reversed by the addition of excess BnMgCl. Complex **8** reacted with an excess of 3-methoxybenzyl bromide to give **6** and the homocoupled products at −40 °C, as seen for the catalytic reaction.[9] By contrast, the TMEDA complex **9** did not react under the same conditions, which indicates that this TMEDA adduct cannot be part of the catalytic cycle.

The X-ray structure of **8** with a mixed magnesium halide/triflate counterion is shown in Figure 1.[19] Structurally characterized mononuclear homoleptic σ-organometallic iron(II) complexes are rare and, unlike **8**, either rely on



Scheme 6.

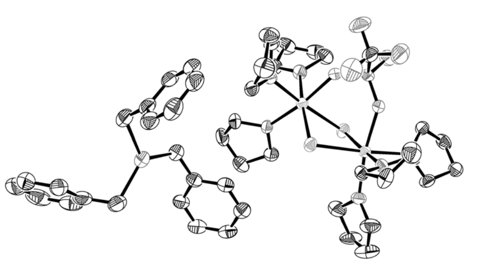


Figure 1. Structure of $[\{(thf)_3Mg\}_2(\mu\text{-}Cl)_2(\mu\text{-}OTf)][FeBn_3]$, $[\{(thf)_3Mg\}_2(\mu\text{-}Cl)_2(\mu\text{-}OTf)]$[**8**]. Ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity.

bulky ligands, such as $[Fe(mes^*)_2]$ ($mes^* = C_6H_2\text{-}2,4,6\text{-}t Bu_3$) and $[Fe\{C(SiMe)_3\}_2]$,[20,21] or they are ate complexes with stabilizing Li⋯C interactions, such as $[Li(Et_2O)_2][Li(dioxane)][FePh_4]$ (**11**), $[Li_3(Me)(Et_2O)_2][FeMe_4]$ (**12**), and $[Li(Et_2O)]_2[Fe(1\text{-naphthyl})_4]$.[22,23]

The geometry at the iron center of **8** is approximately trigonal planar with C-Fe-C angles ranging from 116.1(3) to 124.3(2)°. The Fe−C bond lengths range from 2.088(5) to 2.115(6) Å, and are longer than those in $[FeMes^*_2]$ and $[Fe\{C(SiMe)_3\}_2]$, but similar to those for the anionic complex **11**.

When samples of complex **8** were left to crystallize, we reproducibly obtained crystals of a second species: the 13-electron homoleptic iron(III) tetrabenzyl ate complex **13** with a $[MgCl(thf)_5]^+$ counterion (**13a**; Figure 2). To the best of our knowledge, the only structurally characterized homoleptic σ-organometallic iron(III) complex that has been reported previously is the approximately square planar $[Li(thf)_4][Fe(C_6Cl_5)_4]$.[24] By contrast, the iron center in complex **13a** is essentially tetrahedral with C-Fe-C angles in the range of 106.05(7)–112.54(7)°. The Fe−C bond lengths in **13a** range from 2.081(2) to 2.101(2) Å and are comparable to the Fe−C bond length of the terminal $Fe{-}CH_3$ moiety in the tetrahedral Fe^{II} complex **12** (2.095(4) Å) despite the difference in oxidation state, but are significantly shorter than the other Fe−C bonds in **12** (average 2.185(4) Å), which feature secondary C⋯Li interactions.[22] A second crystal structure for the anion **13** was obtained after reaction of complex **8** and TMEDA (**13b**; Figure 2). In this case, the counter-cation is $[Mg_3Cl_5(TMEDA)_3]^+$, indicating a pronounced preference for coordination of the TMEDA to magnesium rather than to the Fe^{III} center. Therefore, although TMEDA can (reversibly) coordinate to Fe^{II} benzyl intermediates, it does not appear to coordinate to Fe^{III} in the presence of magnesium salts.

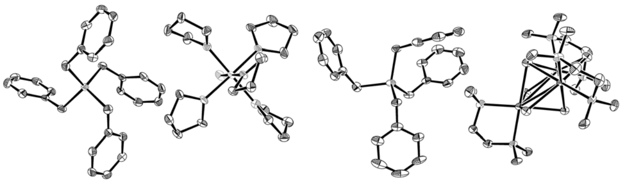


Figure 2. Structures of **13**, with $[MgCl(thf)_5]^+$ (left; **13a**) and $[Mg_3Cl_5(TMEDA)_3]^+$ (right; **13b**) as the counterions. Ellipsoids set at 50% probability; hydrogen atoms and toluene solvate (**13b**) are omitted for clarity.

The formation of the Fe^{III} species **13** from **8** presumably occurs through disproportionation, which implies that iron species with oxidation states below Fe^{II} must also have been formed. Although we did not observe these reduced species directly, the reaction of **8** with the chelating diphosphine 1,2-bis(diphenylphosphino)benzene (dpbz) that was followed by EPR spectroscopy[9] revealed the formation of the previously reported Fe^{I} complex **14**,[25] whereas crystals isolated from the reaction mixture were confirmed to be **13a** by X-ray crystallography).

Finally, we turned our attention to the Fe/TMEDA-catalyzed coupling reactions of smaller *aryl* Grignard reagents. Unlike with the mesityl Grignard reagent, which gives yellow homogeneous solutions throughout the course of the reaction, the appearance of the reaction mixtures for coupling reactions of less sterically encumbered aryl Grignard reagents is highly dependent on the reaction conditions. Rapid addition of the Grignard reagent results in black suspensions of catalytically active zero-valent iron nanoparticles;[15] dropwise addition typically gives red transient intermediates in otherwise yellow solutions.[26] The facile reduction to Fe^0 nanoparticles[27,28] contrasts profoundly with the stability of the Fe^{II} mesityl complexes described above, reflecting the stability of the latter with respect to reductive elimination.[29]

In an attempt to study the transient red intermediates that were observed in catalytic reactions with dropwise addition of the Grignard reagent,[30] we reacted 4-TolylMgBr with $FeCl_3$ in THF in the presence or absence of TMEDA at −30 °C. This gave red solutions with decomposition of the iron-containing species above −20 °C. Definitive structural information on the nature of the various species that are present in these solutions has so far been elusive,[31] but EPR spectra of the solutions (with and without TMEDA) revealed the presence of an $S = \frac{1}{2}$ species, which is consistent with the formation of an Fe^{I} complex.[5] Furthermore, addition of dpbz led to the formation of the previously reported iron(I) phosphine complex $[Fe(4\text{-tolyl})(dpbz)_2]$.[25]

In summary, we have shown that the reactions of iron chlorides with bulky aryl Grignard reagents and TMEDA under catalytically relevant conditions tend to yield homoleptic organoiron complexes rather than adducts of the diamine. Whereas TMEDA does (reversibly) react with a homoleptic tribenzyl Fe^{II} ate complex, it does not react with a tetrabenzyl Fe^{III} ate species, but prefers to coordinate to the magnesium-based counterion instead. Both $[Fe(mes)_3]^-$ and $[Fe(Bn)_3]^-$ react faster with electrophiles than the equivalent neutral $[FeR_2(TMEDA)]$ complexes.

In light of the organoiron complexes that were observed in this study, catalytic pathways for which the lowest oxidation state is Fe^{II} appear plausible with bulky aryl groups (such as mesityl) that resist reductive elimination. However, the facile formation of zero-valent nanoparticles with smaller aryl Grignard reagents and the observed formation of Fe^{I} species with both benzyl and tolyl Grignard reagents all strongly suggest the involvement of catalytically relevant species with oxidation states *below* Fe^{II} when Grignard reagents with substituents that are smaller than the mesityl moiety are exploited.[32]

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[7] The spectrum is comparable to that of a genuine sample of **4** that was prepared according to Ref. [6a].

[8] Cross-coupling of OctBr and mesMgBr catalyzed by $FeCl_3$/TMEDA as described in Ref. [4]. ^{1}H NMR spectrum recorded at room temperature after 70 min (ca. 10% conversion into **3**).

[9] See the Supporting Information.

[10] ^{1}H NMR spectroscopy of the reaction of **4** with OctBr (0.8 equiv) indicated the presence of residual amounts of **4** along with peaks at δ 131, 106, and 30 ppm, tentatively assigned to the complex $[FeBr(mes)_2]^-$, as a very similar spectrum is obtained on reacting **5** with $[NBu_4]Br$. We therefore suggest that complexes **1** and **2** should be replaced with **4** and $[FeBr(mes)_2]^-$, respectively, in the highly simplified cycle in Scheme 2.

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[13] The cross-coupling of OctBr and mesMgBr catalyzed by $FeCl_3$/TMEDA as described in Ref. [4] gave **3** in 35% yield. Repeating the reaction without TMEDA gave **3** in a yield of 36%. The former reaction gave 64% of recovered bromooctane, <1% octane, and <1% octene, the latter gave these compounds in 57%, 2%, and 5% yield, respectively.

[14] This is reflected in both the lower selectivities of **4** and **5** in the reactions described in Scheme 4 and in the different appearances of the reaction mixtures, with the less selective reactions yielding black suspensions of reduced iron. Early in the reaction of OctBr with **4**, the selectivity for **3** is high, but rapidly decreases as the reaction proceeds (Figure S6). This implies that the iron species that are formed while **4** is consumed account for the competing side-reactions.

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[26] See the Supporting Information for a video.

[27] It has been suggested that an Fe^0 complex can be produced under catalytically relevant conditions (see Ref. [22]), but this was based on an erroneous crystal structure determination. The structure is better modelled as an Fe^{II} dihydride. For the incorrect structure determination, see: T. A. Bazhenova, R. M. Lobkovskaya, R. P. Shibaeva, A. E. Shilov, A. K. Shilova, M. Gruselle, G. Leny, B. Tchoubar, *J. Organomet. Chem.* **1983**, *244*, 265. For the corrected structure, see: J. M. Jefferis, G. S. Girolami, *Organometallics* **1998**, *17*, 3630.

[28] An Fe^{-II}/Fe^0 pathway has been proposed because stoichiometric and catalytic reactions of $[Li(TMEDA)]_2[Fe(\eta^2\text{-}C_2H_4)_4]$ are much faster than those of model complexes in oxidation states 0, I, or II (see Ref. [22]). As these models contain a cyclopentadienyl (Cp) or a pentamethylcyclopentadienyl (Cp*) ligand, a simpler explanation may be that these ligands, and not the oxidation state of the pre-catalysts, are responsible for the observed rate retardation. The Fe^{-II}/Fe^0 hypothesis suggests that the tested model Fe^0 complex, namely $[Li(TMEDA)][CpFe(C_2H_4)_2]$, should be as effective as the Fe^{-II} complex if the Cp ligand did not hamper productivity; however, it displayed the lowest catalytic activity.

[29] The nanoparticles may simply act as a resting-state reservoir for active homogeneous species in higher oxidation states. Indeed, they react rapidly when added dropwise to a large excess of the electrophile (see the Supporting Information for a video), which suggests that at least a part of, if not the entire catalytic cycle may occur in solution.

[30] A previous study focused on the isolation of model complexes using ArLi rather than ArMgX reagents under similar conditions (Ref. [22]); however, it cannot be assumed that the same species are formed. Indeed, lithium reagents give significantly poorer performance in iron-catalyzed cross-coupling reactions. For instance, the reaction of CyBr (Cy = cyclohexyl) with PhMgBr catalyzed by $FeCl_2$ (5 mol%) and TMEDA (10 mol%) at RT gives CyPh in 76% yield, the equivalent reaction with PhLi provides CyPh in only 38%; also see example in Ref. [22].

[31] $FeCl_2$ and 3 or 5 equivalents of 4-tolylMgCl (THF, −30 °C) gave a red solution with paramagnetically shifted peaks in the ^1H NMR spectrum at δ 292.3, 117.9, and 99.2 ppm. The stoichiometry is consistent with the formation of the ate complex $[Fe(4\text{-}tol)_3]^-$, analogous to **4**. Repeating the reaction with 1–10 equivalents of TMEDA gave increasing amounts of a second species (δ 221.7, 95.3, and 89.4 ppm), possibly owing to the formation of $[Fe(4\text{-}tol)_4]^{2-}$, an analogue of $[Fe(Ph)_4]^{2-}$ (Ref. [22]), or $[FeCl(4\text{-}tol)_3]^-$. No peaks for TMEDA coordinated to a paramagnetic iron center were observed, but we cannot rule out the possibility that TMEDA coordinates to an NMR-silent Fe center.

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