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On the oxidation state of iron in iron-mediated C-C couplings

Anna Hedström, Erik Lindstedt, Per-Ola Norrby*

University of Gothenburg, Department of Chemistry and Molecular Biology, Kemigården 4, SE-412 96 Göteborg, Sweden

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ABSTRACT

The nature of the active catalyst in iron-catalyzed C–C couplings has been under debate. In here, we study the couplings with aryl Grignard reagents, and clearly show that the active catalyst is an Fe(I) species. The Grignard alone can reduce the pre-catalyst to the Fe(I) state, and no further, as shown by quantification of product formation. Addition of the electrophile results in complete cross-coupling, validating the nature of the active catalyst. A computational study reveals that the active iron catalyst has a spin state of S = 3/2, high spin for Fe(I) but intermediate spin for Fe(III) complexes, even though the Fe(III) precatalyst salts have a high spin state (S = 5/2). The spin change occurs after the first transmetallation, when the strong ligand field of the aryl group raises the energy of one d-orbital, inducing an electron pairing event. All steps in the formation of an active cross-coupling catalyst are facile and strongly exergonic.

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1. Introduction

The interest in iron catalyzed coupling reactions is continuously growing; iron salts are environmentally benign, cheap, and with relatively low toxicity. Iron can exist in various oxidation states, from Fe(-II) to Fe(+VIII) [1], allowing the metal to participate in electron transfer and redox processes, including C-C coupling processes [2]. Several groups have proposed catalytic cycles for the iron catalyzed coupling reaction between an alkyl Grignard reagent and an aryl halide, based on the well-established mechanisms for Ni- and Pd-catalyzed cross-couplings [3] (Scheme 1).

Kochi originally favored a cycle where initially formed Fe(I) undergoes oxidative addition yielding an Fe(III) species, with subsequent transmetallation and reductive elimination returning to the catalytically active Fe(I) species [4–8]. However, Kochi could not clearly distinguish between this process and one where iron cycles between oxidation states 0 and II [8,9]. In the 1990's, the observation that isolated Fe(–II) complexes are very efficient precatalysts for the coupling reaction led to the proposal of an Fe(–II)/ Fe(0) cycle [10–15]. Other catalyst states, like Fe(–I), have also been proposed [16]. Our own mechanistic investigations (a combination of experimental and computational studies) [17,18] indicate that the most likely catalyst is an Fe(I) complex, in good agreement with the Kochi proposal [9]. However, in our case, as well as in Kochi's

E-mail address: pon@chem.gu.se (P.-O. Norrby).

studies, it is hard to distinguish between full conversion of into Fe(I) complexes, and partial conversion into Fe in lower oxidation states. Fe(I) complexes are rare [19], but a few well-characterized examples are reported in the literature [20–24], and in particular recent work by Bedford and coworkers support the involvement of their isolated Fe(I)-phosphine complexes in the catalytic C–C coupling [25]. However, the most common protocols for iron-catalyzed couplings include only ligands with weaker ligand fields, like halides and N-methyl-2-pyrrolidone (NMP) [26]. Since the nature of the active catalyst under these more weakly coordinating conditions is still in doubt, we have here undertaken a study of the oxidation state of the active catalyst under these conditions.

Two major versions of the iron-catalyzed C–C coupling are in common use: coupling of alkyl Grignard reagents with aryl chlorides or triflates [27,28], and coupling of aryl Grignards with alkyl bromides [29,30], primarily secondary bromides. The former reaction requires the presence of stabilizers like NMP for optimum performance [26], and frequently leads to extensive catalyst breakdown near the end of the reaction due to the strong reducing power of the alkyl Grignard [17]. The latter reaction, due to the lower reducing power of aryl Grignard reagents, can be performed in diethyl ether without added stabilizers [29]. In fact, we have recently shown that this system generates a live catalyst that stays active even after full consumption of the electrophile [31]. Thus, the active catalyst can be generated separately by reaction of aryl Grignard with simple iron salts with concomitant formation of biaryl [32], and will enter the coupling cycle on subsequent addition of alkyl bromides. The isolated reaction of aryl Grignard reagents with iron salts thus forms a

 $[\]ast\,$ Corresponding author. Tel.: +46 31 7869034.

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Scheme 1. Generic metal-catalyzed C-C coupling with Grignard reagents.

pleasingly simple test system for elucidating the nature of the active catalyst in the iron-catalyzed C–C coupling.

2. Results and discussion

2.1. Stoichiometric iron reduction

The stoichiometry of the reduction of iron using aryl Grignard (Scheme 2) was investigated in a titration experiment under inert conditions. An iron salt was dissolved in tetrahydrofuran (THF), and added in batches to a solution of phenyl magnesium bromide in diethyl ether (DEE) with an internal standard (dodecane), at constant intervals of 5–15 min. Before each addition, a sample was withdrawn, subjected to an inert workup, and then analyzed by GC. The inert workup was crucial to reproducibility. In non-inert workup, the reaction mixture was oxidized by oxygen in the air, possibly through reaction with low-valent aryl iron species, so-called "Kharasch"-complexes [32]. However, under inert conditions, the concentration of biphenyl increased smoothly, as illustrated in Fig. 1.

The mass balance in the titration experiment was checked by also monitoring the formation of benzene. No other phenylcontaining species were detected. As can be seen in Fig. 1, the reaction was followed until the Grignard reagent was fully consumed, at which point the concentration of biphenyl no longer increases. The slope, corresponding to the stoichiometry of the reaction, was measured on the initial linear region, determined by comparative F-test analysis.

The titration experiment was performed with standard FeBr₃ and FeCl₃ of at least 98% purity, as well as with highly purified FeCl₃ (99.99%). FeBr₂ was selected as a representative Fe(II) salt. We attempted to use FeCl₂, but solubility became an issue. The convenient non-hygroscopic Fe(acac)₃ (acac = acetylacetonate) was tested, but was found to yield multiple products due to addition of Grignard to the acac moiety, and was therefore excluded from the current study. The results are shown in Table 1.

The data for Fe(III) complexes in Table 1 clearly show a reproducible stoichiometry very close to 1. Since formation of biphenyl from Grignard reagents is a two-electron process, this gives strong indication that iron is reduced to Fe(I), but not further, even in the presence of excess aryl Grignard reagent.

Since our lab has recently found that apparent iron-catalyzed processes were instead due to trace metal contaminants [33], we



Scheme 2. Reaction of phenyl magnesium bromide with iron salts yields biphenyl while forming a reduced iron species.



Fig. 1. Biphenyl formation on titration with iron salts.

tested the importance of contaminant by including a sample of high purity FeCl₃. The results were virtually the same as with the standard quality salt, indicating that trace metals are not responsible for the homocoupling. In the current case, this was expected, since iron has been shown to perform C–C couplings at dry ice temperatures [18], where no other metal is a competent catalyst.

The Fe(II) complex shows lower reproducibility (Table 1). This is not entirely unexpected, since Fe(II) salts can suffer from rapid oxidation upon air contact, resulting in a higher slope. Still, the data gives slopes close to the expected 0.5 eq. biphenyl formation, consistent with one-electron reduction of Fe(II). We note that diaryl-Fe(II) complexes cannot yield Fe(I) by the normal reductive elimination, since that must necessarily reduce the metal by two electrons. However, we have earlier shown that diaryl-Fe(II) in a bimetallic complex with another Fe(II) unit can undergo a variant of the reductive elimination with a reasonable, albeit slightly higher barrier, yielding two Fe(I) moieties [17].

There is a possibility that our titration experiment does not yield a single Fe(I) species, but instead a mixture of iron complexes with an *average* oxidation state of +1. However, the linearity of the plots, as well as the close correspondence between the Fe(III) and Fe(II) precatalysts makes this scenario unlikely. An equilibrating mixture should demonstrate a dependence on concentration, and therefore induce noticeable curvature in the Fig. 1 plots. A stable bimetallic Fe(0)-Fe(II) complex cannot be excluded, but in the absence of specific supporting ligands, we find it unlikely that such a mixed-valence complex would be favored in all concentration regimes. In the presence of the more strongly reducing alkyl Grignard reagents, we have previously found strong concentration effects and have argued that these are due to the formation of iron oligomers [18], but even then, our computational study indicated that reductive elimination was limited to forming Fe(I), and that the role of bimetallic complexes primarily is to allow the aforementioned bimetallic reduction of two Fe(II) moieties to two Fe(I) complexes [17].

able	1				
lope	and linear	ity of biphenyl	l formation	for different ire	on salts, Scheme

Iron salt	Purity	Slope	r^2
FeBr ₃	98%	0.95	0.999
FeCl ₃	98%	0.997	0.996
	99.99%	1.0	0.977
FeBr ₂	99.99%	0.596	0.993
		0.603	1.00
		0.492	0.987

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2.2. Active catalyst

To verify that the Fe(I) complex produced in the titration experiment is indeed an active, live catalyst for the cross-coupling reaction, we performed a variation of the titration experiment described in Section 2.1. Iron additions were alternated with additions of a model electrophile, cyclohexyl bromide, with sample aliquots withdrawn before addition of each reagent (Scheme 3). In the GC analysis, we now also monitored appearance of the cross-coupling product, phenyl cyclohexane. The results of the monitoring seen in Fig. 2; even-numbered points correspond to sampling after FeCl₃ addition, odd-numbered points to cyclohexyl bromide addition.

As can be seen in Fig. 2, the reaction is very reliable; iron addition gives clean production of biphenyl, whereas cyclohexyl bromide addition only increases the yield of cross-coupling product. The addition before sample 10 consumes the last of the Grignard reagent, and no further product formation is seen after this point. From this point onwards, we can also detect unreacted cyclohexyl bromide in the reaction mixture.

2.3. Proposed reaction mechanism

Starting from Fe(III), the following reaction mechanism is suggested for the homocoupling: two consecutive transmetallations (TM) give a diarylated Fe(III) complex which can either undergo a third TM to a poly-arylated species followed by a reductive elimination (RE) to yield biphenyl and aryl-Fe(I) (path i) or a RE to yield biphenyl and Fe(I)-bromide (path ii). The FeBr can then be transmetallated to PhFe. The complexes in Scheme 4 are stabilized by solvent molecules (omitted for clarity). To verify the plausibility of the proposed mechanism, and to elucidate details about the degree of solvation and spin states, the proposed mechanism in Scheme 4 was further investigated by DFT calculations (Section 2.4).

2.4. Computational studies

To check the postulated reaction mechanism, and to differentiate between the two suggested paths, we investigated the mechanisms in Scheme 4 using dispersion-corrected DFT methods. All energies used here are free energies in solvent, calculated as detailed in Section 5. For transmetallation steps, we assumed that association of Grignard reagents to iron complexes, and dissociation of MgBr₂ from the aryl iron products, would have negligible barriers [17], and therefore only calculated the structures and energies of the bimetallic Fe $-\mu$ -Ph-Mg complexes. In all cases, the association to a bimetallic complex required dissociation of one solvent molecule from each metal, at a slight enthalpic cost but entropic gain. As can be seen in Fig. 3, the first transmetallation occurs on the high spin energy surface, but the strong ligand field of the aryl is sufficient to favor an intermediate spin (S = 3/2) of all aryl Fe(III) species.

The intermediate spin is very rarely seen [34]. Classical solutions in ligand field theory are generally based on symmetric ligand fields, yielding degenerate d-orbital energies, and thus will



Scheme 3. Alternating catalyst production and cross-coupling.



Fig. 2. Product monitoring upon alternating additions, Scheme 3.

generally only allow low or high spin solution. However, in a nonsymmetric field with only one strong ligand, only one orbital is increased in energy. With exactly one d-orbital empty, two delectrons will pair, yielding 3 unpaired electrons and thus S = 3/2(Fig. 4).

The first transmetallation can occur entirely on the high spin surface, delivering a mono-aryl in a spin-excited state from a strongly exergonic reaction. In a case like this, there is no need to calculate spin surface crossing points. The spin crossing does not have to be part of a barrier, but can occur in a stable species through collisions with surrounding molecules. The calculated energy difference between the spin states may not be very reliable with a DFT method, but should be in the range of molecular vibrations, that is, less than ca. 50 kJ/mol.

The second transmetallation would be expected to occur on the intermediate spin surface. The two first transmetallations are both strongly exergonic. The diaryl Fe(III) species can choose between two paths; either association of a Grignard reagent resulting in a third transmetallation (path i), or reductive elimination yielding the observed biphenyl product (path ii). The latter reaction has a potential energy barrier of only ca. 1 kI/mol, with a free energy of the transition state that is actually lower than that of the reactant. This is of course a computational artifact, a result of the fact that one normal mode less contributes to the ZPE correction in the TS. However, with such a low potential energy barrier, a single molecular vibration is sufficient to bring the reactant across the barrier, with the result that no possible diffusion process can compete. As discussed by Harvey et al. [35], a bimolecular reaction will always have a free energy barrier of at least ca. 20 kJ/mol at ambient temperature, even when no barrier can be found on the potential energy surface, that is, when the reaction is under diffusion control. We can therefore state with confidence that the third transmetallation cannot occur before reductive elimination. The resulting high spin (S = 3/2) Fe(I) complex can undergo a virtually isoergic transmetallation, in good agreement with earlier studies using alkyl Grignard species [17]. Neither FeBr nor FePh prefers a



Scheme 4. Suggested reaction mechanisms for the homocoupling of aryl Grignard reagent.

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Fig. 3. Free energies surface (FES) of the homocoupling reaction. Vertical lines connect different spin states of the same complex. Curves represent associations with barriers of at least 20 kJ/mol, dashed lines correspond to dissociations. The number of explicit solvent molecules (s) has been optimized for each complex.

low spin state, irrespective of the number of explicit solvents coordinated to iron. However, Bedford has shown that addition of bidentate phosphines with strong ligand fields can result in formation of low spin Fe(I) complexes [25].

3. Conclusions

Reaction monitoring of iron-mediated coupling of aryl Grignard with iron salts clearly indicates that the lowest oxidation state of an iron that can be reached under these conditions is Fe(I). The experimental result is in good agreement with our earlier computational studies, where we showed that reductive elimination to Fe(0) has a prohibitively high barrier [18], and that lower oxidation states are strongly disfavored not only kinetically but also thermodynamically [17]. The resulting Fe(I) complex is stable in diethyl ether without additives, and is shown to be a living catalyst for the C–C coupling of phenyl magnesium bromide and cyclohexyl bromide.

Computational studies indicate that the homo-coupling followed in the monitoring studies is a facile process, with the first



Fig. 4. Ligand field analysis of Fe(III), a d5-metal, giving the two classical solutions based on octahedral geometries, and an expected perturbation from a single strong field ligand.

transmetallation occurring on the high spin surface, whereas subsequent steps where the iron is aryl-substituted prefers an intermediate spin. After the second transmetallation, a reductive elimination occurs virtually without a barrier, yielding biphenyl and Fe(I)Br. The latter is in equilibrium with Fe(I)Ph through reversible transmetallation with the Grignard reagent. It has earlier been shown that both types of Fe(I) species are competent intermediates in the cross-coupling reaction [17].

4. Experimental

4.1. Typical procedure for monitoring of aryl homocoupling

THF and DEE were distilled from benzophenone and sodium, dodecane was distilled from calcium hydride, pentane was degassed prior to use, phenyl magnesium bromide was bought from Sigma–Aldrich and titrated [36] before use.

An oven-dried 100 ml round bottomed flask was sealed with a rubber septum, then evacuated and refilled with nitrogen three times. The flask was charged with DEE (60 ml), dodecane (225 ul. 1 mmol) and phenyl magnesium bromide (1.2 mmol, in DEE solution). An aliquot (0.5 ml) was taken from the mixture and quenched by filtering it through a pentane-saturated short silica plug under nitrogen. The silica plug consisted of a Pasteur pipette with a glass wool plug, a short layer of silica and top-sealed with a rubber septum with a nitrogen inlet. The silica was pre-flushed with degassed pentane before the addition of any sample. The sample was eluted through the silica plug with pentane into a degassed sat. NH₄Cl solution. The organic phase was diluted with DEE and analyzed by GC (dodecane was used as internal standard, 40-100 °C, 18 °C/min, 100-300 °C, 20 °C/min). A solution of FeCl₃ (0.06 mmol, 0.05 M in THF) was added to the reaction vessel. After stirring for 5 min, an aliquot (0.5 ml) was collected and analyzed as described above. The procedure was repeated with addition of FeCl₃ (0.05 M in THF) in portions of 0.06 mmol (a total of ten portions).

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4.2. Addition of cyclohexyl bromide

An oven-dried dry 100 mL round-bottomed flask was equipped with a rubber septum and a stirrer bar, then evacuated and refilled with nitrogen three times. The flask was charged with DEE (60 ml), dodecane (225 µl, 1 mmol) and phenyl magnesium bromide (1.2 mmol, 1.97 M in DEE). An aliquot (0.5 ml) was taken from the mixture and guenched by filtering it through a wet short silica plug with a pentane layer above the silica under nitrogen (see Section 4.1). The sample was eluted with pentane into a degassed sat. NH₄Cl solution. The organic phase was diluted with DEE and analyzed by GC (dodecane was used as internal standard, 40-100 °C 18 °C/min, 100-300 °C, 20 °C/min). A solution of FeCl₃ (0.06 mmol, 0.05 M in THF) was added to the reaction vessel. After stirring for 5 min, an aliquot (0.5 ml) was collected and analyzed as described above. A solution of cyclohexyl bromide (0.03 mmol, 0.5 M in THF) was added to the reaction vessel. After stirring for 5 min, an aliquot (0.5 ml) was collected and analyzed as described above. The procedure was repeated with alternating addition of FeCl₃ (0.05 M in THF) and cyclohexyl bromide (0.5 M in THF).

5. Computational details

All DFT calculations were performed in Jaguar 8.0 from Schrödinger [37]. We utilized the B3LYP-D3 method, which combines the recent dispersion correction developed by Grimme and coworkers [38] in conjunction with the B3LYP functional [39-41]. The basis set was LACVP*, a combination of 6-31G* for light elements together with the Hay-Wadt ECP basis for Fe and Br [42]. Geometries were optimized in gas phase, with explicit solvent molecules modeled by dimethyl ether (DME). Thermodynamic corrections to the free energy were obtained from frequency calculations at the optimized geometries. Energies in solvent were calculated using the PBF implicit solvation model at the optimized gas phase geometries [43,44]. All reported energies are final free energies obtained by addition of the thermodynamic correction (including zero point energy correction) from the frequency calculation to the energies in solvent calculated using PBF. The number of explicit solvent models was optimized for each species, as judged by the calculated free energies. We note that the use of gas phase vibrational entropies will slightly favor dissociation of the explicit solvents; no attempt was made to correct for this systematic error.

For all iron-containing complexes, we used the unrestricted method to converge the open-shell wavefunctions. The $\langle S^2 \rangle$ values were inspected after each calculation and, if the value was more than a few percent above the theoretical expectation, a restricted open shell wavefunction was calculated and used as an initial guess in the unrestricted calculation. In all cases, this procedure yielded acceptable values of $\langle S^2 \rangle$. All possible spin states (S = 1/2, 3/2, and for Fe(III) also 5/2) were calculated.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.04.024.

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