

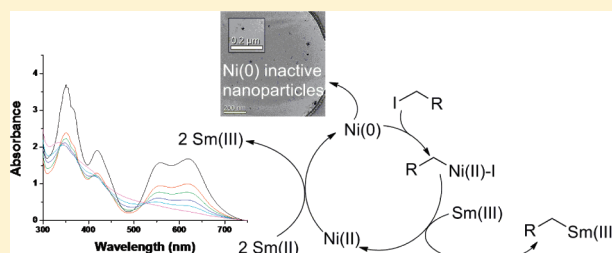
Catalytic Ni(II) in Reactions of SmI₂: Sm(II)- or Ni(0)-Based Chemistry?

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Supporting Information

ABSTRACT: The addition of catalytic amounts of Ni(II) salts provide enhanced reactivity and selectivity in numerous reactions of SmI₂, but the mechanistic basis for their effect is unknown. We report spectroscopic and kinetic studies on the mechanistic role of catalytic Ni(II) in the samarium Barbier reaction. The mechanistic studies presented herein show that the samarium Barbier reaction containing catalytic amounts of Ni(II) salts is driven solely by the reduction of Ni(II) to Ni(0) in a rate-limiting step. Once formed, Ni(0) inserts into the alkyl halide bond through oxidative addition to produce an organonickel species. During the reaction, the formation of colloidal Ni(0) occurs concomitantly with Ni(0) oxidative addition as an unproductive process. Overall, this study shows that a reaction thought to be driven by the unique features of SmI₂ is in fact a result of known Ni(0) chemistry.



INTRODUCTION

Transition metal salts and complexes are important components of many reactions involving samarium diiodide (SmI₂).¹ In fact, even the seminal paper of Kagan introducing SmI₂ to the chemistry community described the use of catalytic amounts of ferric chloride to accelerate several coupling reactions between alkyl iodides and ketones.² During the past several decades, a series of transition metal salts or complexes have been utilized in catalytic amounts in a range of important reactions including the coupling of alkyl iodides with carbonyls,³ conjugate addition reactions of alkyl iodides with α,β -unsaturated esters, amides, and lactones,⁴ coupling of acid chlorides and esters,⁵ intramolecular cyclizations and Grob fragmentations,⁶ and the coupling of alkyl halides with nitriles.⁷ The most commonly utilized salts are based on Fe(III) or Ni(II), and Kagan showed that NiI₂ was superior to other transition metal salts in many of these reactions.³ As a result, Ni(II)-based additives have become the additive of choice in most reactions requiring a transition metal-based catalyst.^{8a} Although the addition of catalytic amounts of Ni(II) salts provides enhanced reactivity and increased selectivity in many SmI₂-based reactions, the mechanistic basis for their effect is unknown. Several reports have suggested that Ni(II) species are reduced to Ni(0) by SmI₂;⁸ however, no detailed mechanistic studies on these suppositions have been initiated.

Nickel complexes in both the (0) and (II) oxidation states are extremely useful in a range of synthetically important carbon–carbon bond forming reactions.⁹ Activation of catalytic systems employing Ni can be initiated by the reduction of Ni(II) to Ni(0) with a stoichiometric reductant.¹⁰ Evaluation of the E° value of the Ni(II)/Ni(0) redox couple clearly shows that SmI₂ is capable of readily reducing Ni(II) to Ni(0).¹¹ Recent work by Ogoshi et al. demonstrated that facile reduction of Ni(II) by SmI₂ in the presence of *trans,trans,trans*-1,5,9-cyclododecatriene (CDT)

provides good yields of the Ni(0) complex, Ni(CDT).¹² Additionally, an examination of methods employed to produce Ni(0) nanoparticles shows that they are typically formed through reductions of Ni(II) starting materials.¹³ On the basis of the known chemistry of Sm and Ni, could Ni(0) and Ni(II) intermediates be responsible for the unique chemistry initiated by the addition of catalytic amounts of NiI₂ to SmI₂? Furthermore, is the process driven by homogeneous chemistry or colloidal Ni(0)? Herein we show that SmI₂ does in fact reduce the Ni(II) catalyst to Ni(0), and that a Ni(0) species is then responsible for carrying out the subsequent chemical reaction.

RESULTS AND DISCUSSION

The goal of this work was to determine the mechanistic role of catalytic amounts of Ni(II) in SmI₂-initiated reactions. Careful examination of the experimental procedures utilizing Ni(II) shows that, in most cases, the Ni(II) salt and SmI₂ are premixed before the addition of substrate.^{3–7,14} To initially study the SmI₂–Ni(II) system, SmI₂ in tetrahydrofuran (THF) was slowly titrated into solutions of NiI₂, Ni(II) acetylacetonate (Ni(acac)₂), and 1,2-bis(diphenylphosphino)ethane Ni(II) chloride (Ni(DPPE)₂Cl₂). In each case the blue color of the SmI₂ dissipated immediately producing a brown solution. Over time, a precipitate gradually formed from the solution. To study the system in more detail, the UV–vis spectra of a series of solutions of SmI₂ containing increasing amounts of Ni(II) salts were recorded as shown in Figure 1. As increasing amounts of NiI₂ were added to the solution of SmI₂ in THF, the UV–vis bands corresponding to SmI₂ decreased, and a broad absorbance from 400 to 500 nm consistent with colloidal Ni(0) began to

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Table 1. Reaction of **1** and **2** with SmI₂ and/or Various Ni Additives^a

entry	Ni additive	reaction time	3 yield ^b
1	none	72 h	69% ^c
2	NiI ₂ (1 mol %)	5 m	98%
3	Ni(acac) ₂ (1 mol %)	15 m	93%
4	Ni(DPPE)Cl ₂ (1 mol %)	10 m	95%
5	Ni(0) nanoparticles ^d	15 h	NR
6	SmI ₂ –NiI ₂ centrifuged solid ^e	15 h	NR
7	SmI ₂ –NiI ₂ centrifuged supernant ^f	5 m	96%

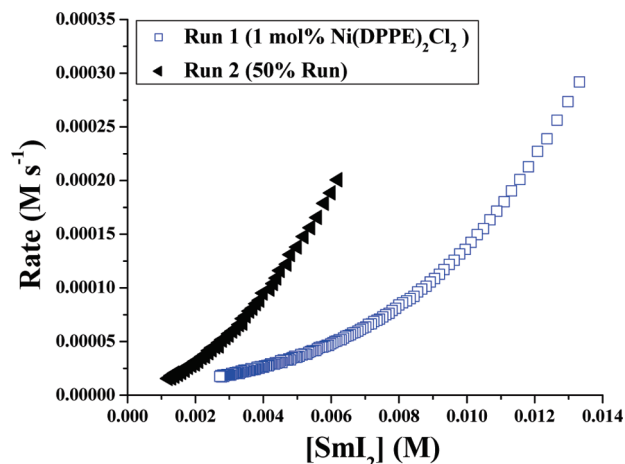
^a Ni(II) additive. ^b Yields based on NMR ratio between Barbier product and reduced dodecane. No starting material remained. ^c Isolated yield of Barbier product. ^d Commercial Ni(0) 20 nm powder. ^e SmI₂ (0.96 mmol) was added to a solution of NiI₂ (0.48 mmol) dropwise to form brown solution. After 5 min of stirring the solution was centrifuged for 5 min at 5000 rpm. The solid obtained in the reaction was separated and washed with THF before being subjected to the substrates (0.4 mmol). ^f Supernatant obtained from procedure (e) was isolated and reacted with the substrates. NR = no reaction.

to study the impact of Ni(II) salts and colloidal Ni(0) since the rates of reduction of both substrates by SmI₂ are well-established.¹⁶ For both substrates, the rate constant for reduction by SmI₂ is 5 orders of magnitude slower than the rate constant for Ni(II) reduction by SmI₂ determined above. Initial experiments were conducted for the Barbier reaction employing 1 mol % of Ni(II) salts as described by Kagan et al.³ The results of these experiments are shown in Table 1. In the absence of Ni(II), the reaction was sluggish resulting in a 69% yield of product after 72 h with the remainder of the reaction mixture consisting of unreacted starting material (Table 1, entry 1). The use of 1 mol % NiI₂, Ni(acac)₂, or Ni(DPPE)₂Cl₂ led to nearly quantitative yields of product in 5–15 min (Table 1, entries 2–4). To test whether Ni(0) nanoparticles are capable of initiating the reaction, commercially available Ni(0) nanoparticles (20 nm average particle size) were reacted with **1** and **2** in THF (Table 1, entry 5). No reaction occurred over a range of Ni(0) concentrations. Since the nanoparticles obtained from the mixture of SmI₂ and NiI₂ were smaller in diameter (as determined by TEM), another experiment was initiated in which the SmI₂ and NiI₂ were premixed, the solution centrifuged, and a solid precipitate obtained. These particles were then washed with THF in an inert atmosphere and mixed with **1** and **2**. No reaction occurred showing that, although Ni(0) nanoparticles are clearly formed during the course of the reaction, they do not initiate the Barbier reaction, which raises the question: is it possible that soluble Ni(0) is capable of initiating the reaction? To test this hypothesis, SmI₂ was mixed with a stoichiometric amount of Ni(II). The colloidal suspension was filtered, and **1** and **2** were added to the supernatant. Interestingly, a nearly quantitative yield of **3** was obtained after 5 min (Table 1, entry 7).

On the basis of the information obtained thus far, it is clear that Ni(II) salts are acting as catalysts in the samarium Barbier reaction. To investigate the mechanism by which the catalyst functions, reaction progress kinetic analysis (RPKA) experiments were employed.¹⁷ This method allows kinetic analyses to be performed on a system under synthetically relevant conditions. The “same excess” experiment of RPKA enables one to determine if the catalyst is being deactivated during the course of the reaction. To run the same excess experiment, the

Table 2. Same Excess RPKA Reaction Conditions

run	SmI ₂ (M)	1 (M)	1 excess (M)	2 (M)	2 excess (M)	Ni(II) (M)
1	0.02	0.040	0.030	0.040	0.030	2.0 × 10 ^{−4}
2	0.01	0.035	0.030	0.035	0.030	2.0 × 10 ^{−4}

**Figure 4.** Rate vs [SmI₂] for same excess experiments. (□, blue) Run 1 and (◄, black) Run 2. Reaction conditions listed in Table 2.

rates of two reactions are monitored: one run set at initial conditions, and the second run (50% run) set at one-half of the initial reaction concentrations, with every other reagent in excess as shown in Table 2.

The Barbier reaction was carried out using this method with a catalytic amount of Ni(DPPE)₂Cl₂. The reactions were followed by stopped-flow spectrophotometry, monitoring the decay of SmI₂ at 555 nm. Run 1 was performed with a 0.03 M excess of the substrates (with respect to SmI₂ at 0.02 M) and the catalyst set at 1 mol % (2.0 × 10^{−4} M) with respect to SmI₂ (Table 2, Run 1). In Run 2, [SmI₂] was 0.01 M, one-half of the SmI₂ concentration in Run 1. The reagent concentrations were decreased in an equivalent amount with respect to [SmI₂] to maintain the same excess concentrations. Identical to Run 1, the [Ni(II)] was maintained at 2.0 × 10^{−4} M (Table 2, Run 2). Under these conditions, Run 2 mimics the reaction concentrations that would be present at the midpoint of Run 1.

Ideally in a catalytic reaction system, the concentration of catalyst remains constant through the course of the reaction. As a result, if the catalyst is active and constant, the concentration of Ni should be the same halfway through the reaction. If the catalyst is *not* being deactivated during the course of the reaction, the plots of Runs 1 and 2 will overlay. If catalyst is deactivated through decreasing [Ni(DPPE)₂Cl₂], then the plots of the two runs will not overlay. Runs 1 and 2 were plotted as rate as a function of concentration, and no overlay was observed (Figure 4). This observation indicates that the [Ni] decreases over the course of the reaction and therefore is being deactivated.

As described from the experiments in Table 1, both the purchased Ni(0) nanoparticles (Table 1, entry 5) as well as the solid Ni(0) obtained from the SmI₂/NiI₂ mixture (Table 1, entry 5) did not initiate the Barbier reaction; however, when the substrates were reacted with the supernatant (Table 1, entry 7),

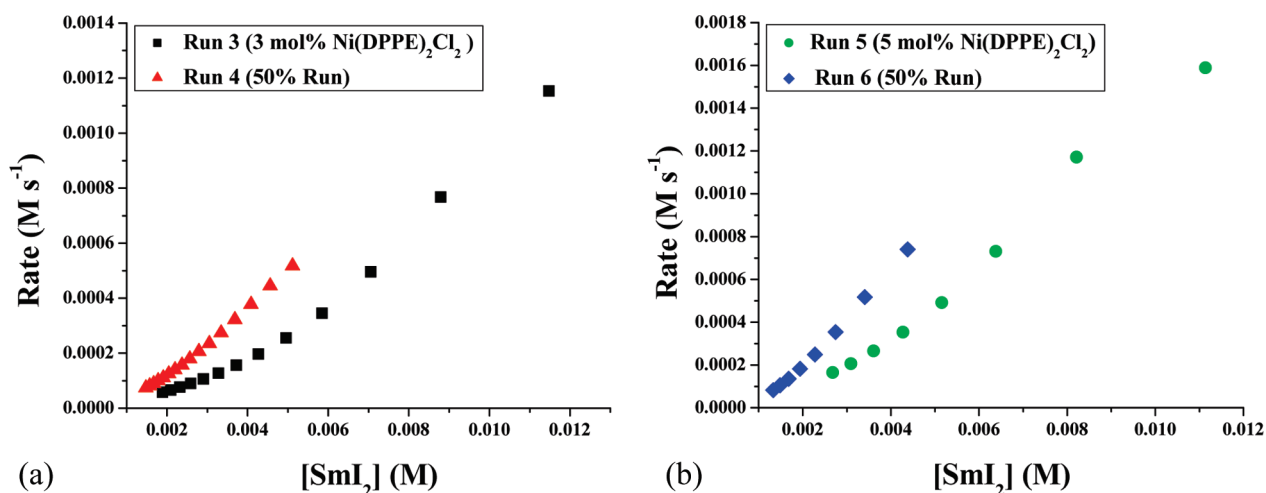


Figure 5. Rate vs $[\text{SmI}_2]$ for same excess experiments. (a) (■, black) Run 3 and (▲, red) Run 4. Reaction conditions similar to those listed in Table 2, with 3 mol % catalyst loading. (b) (●, green) Run 5 and (◆, blue) Run 6. Reaction conditions similar to those listed in Table 2, with 5 mol % catalyst loading.

Table 3. Conditions for Different Excess Experiments to Determine the Reaction Orders of the Substrates

run	SmI_2 (M)	1 (M)	1 excess (M)	2 (M)	2 excess (M)	Ni(II) (M)
7	0.02	0.04	0.03	0.04	0.03	2.0×10^{-4}
8	0.02	0.07	0.06	0.04	0.03	2.0×10^{-4}
9	0.02	0.04	0.03	0.07	0.06	2.0×10^{-4}

the reaction proceeded. Taking this information together with the fact that the catalyst is being deactivated with 1 mol % Ni(II), it is plausible that the deactivation pathway of the catalyst is the formation of aggregated colloidal Ni(0). As Ni(II) is rapidly reduced to Ni(0) by SmI₂, some Ni(0) species could aggregate and precipitate out of solution, while some concentration of Ni(0) remains suspended and soluble. The remaining soluble Ni(0) is responsible for catalyzing the reaction.

Even though the Barbier reaction is synthetically successful with 1 mol % Ni(II), deactivation of the catalyst occurs. To determine if an optimal environment for the catalyst could be created, thereby enhancing the efficiency of the samarium Barbier reaction, the $[\text{Ni(II)}]$ was increased. Figure 5 displays data resulting from the new concentrations of Ni(DPPE)₂Cl₂ added to the system: 3 mol % (Runs 3 and 4) and 5 mol % (Runs 5 and 6). As indicated by the same excess experiments, deactivation is decreased but not prevented with the addition of higher concentrations of Ni(II). From these results, 3 mol % catalyst loading was deemed most ideal to employ in further experiments since the least amount of deactivation was observed at this concentration.

Moreover, using different excess experiments with respect to $[\text{Ni}]$, the order of Ni can be determined. The turnover frequency of the catalyst is determined by normalizing the rate by $[\text{Ni}]$. A range of 3–5 mol % catalyst was examined. The overlay of the plots indicates that the reaction is first order in the Ni catalyst (Figure 6).

To determine the rate orders of 1 and 2, the effect of the concentration of each reagent on the rate of reaction was determined. Table 3 displays the concentrations of each reaction component. When the decays of Runs 7 and 8 were plotted, overlay was observed (Figure 7), indicating that an increase in

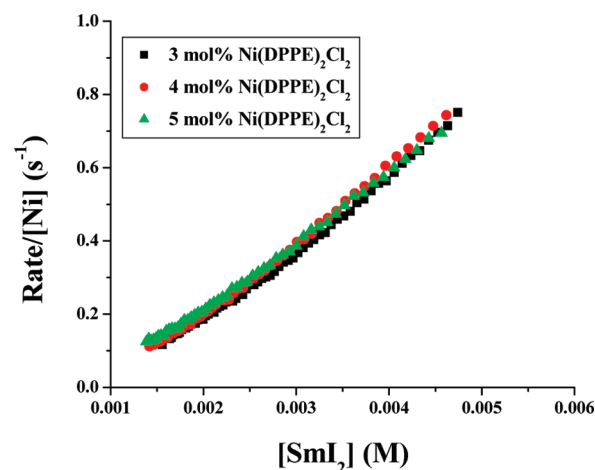


Figure 6. Turnover frequency of Ni(II) in the samarium Barbier reaction. $[\text{SmI}_2] = 0.01$ M; $[1] = 0.035$ M; $[2] = 0.035$ M; $[\text{Ni(DPPE)}_2\text{Cl}_2] =$ (■, black) 6.0×10^{-4} M; (●, red) 8.0×10^{-4} M; (▲, green) 1.0×10^{-3} M.

$[1]$ does not change the reaction rate, a finding consistent with a zero order dependence of 1. A similar overlay is observed when Runs 7 and 9 are plotted (Figure 8), again indicating a zero order for 2. These orders were also verified under pseudofirst-order conditions (see Supporting Information).

Further, the rate constant of the Barbier reaction with Ni(II) catalyst was examined using the initial rate method, with increasing amounts of Ni(DPPE)₂Cl₂ added to the system. A rate constant of $16.6 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$ was obtained from these data (Figure 9). This value is in good agreement with the rate constant found for the reduction of Ni(DPPE)₂Cl₂ by SmI₂ in the absence of substrates (Figure 3b), further indicating that the rate-determining step in the cycle is the initial reduction of Ni(II).

The order of SmI₂ in the reaction was determined by pseudo first-order kinetic methods. Rates were determined by stopped-flow spectroscopy with an increasing amount of SmI₂. $[\text{Ni(DPPE)}_2]$ was kept consistent at 3 mol % with respect to SmI₂, while both 1 and 2 were set at a 10 equivalent excess. As the

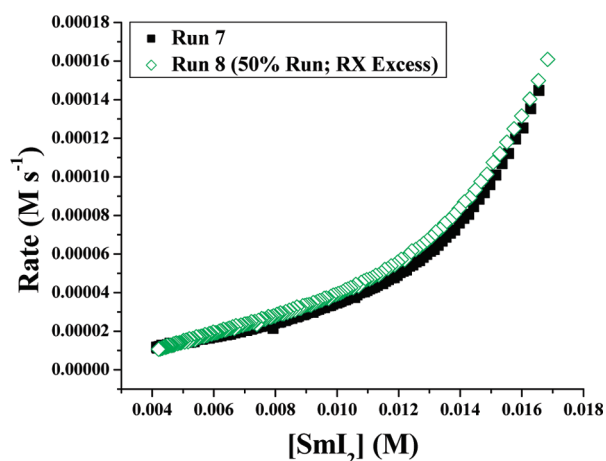


Figure 7. Plot of rate vs $[\text{SmI}_2]$ for different excess experiments; (■, black) Run 7 and (◇, green) Run 8 to determine 1 reaction order. Reaction conditions are listed in Table 3. The overlay indicates that the reaction is zero order in 1.

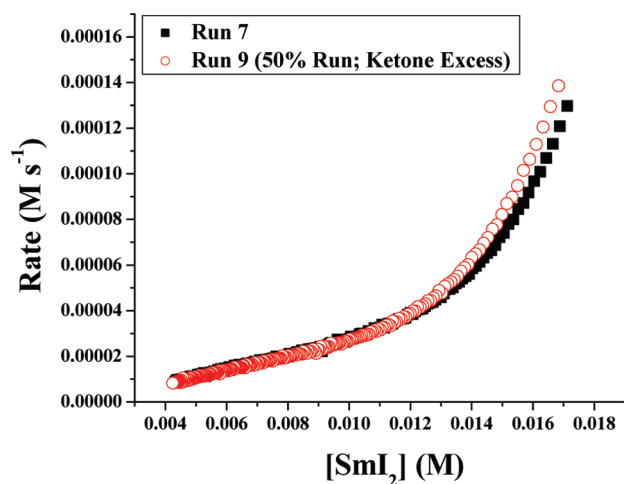


Figure 8. Plot of rate vs $[\text{SmI}_2]$ for different excess experiments; (■, black) Run 7 and (○, red) Run 9 to determine 2 reaction order. Reaction conditions are listed in Table 3. The overlay indicates that the reaction is zero order in 2.

concentration of $[\text{SmI}_2]$ increased, the rates increased linearly, indicating a first-order dependence of SmI_2 (Figure 10). The experimentally determined rate orders for each of the components of the Barbier reaction are included in Table 4. Rate orders of zero were observed for both 1 and 2, while first-order rates were seen for Ni(II) and SmI_2 . These data suggest the initial reduction of Ni(II) by SmI_2 being the rate-determining step in the reaction.

The data compiled on the $\text{SmI}_2/\text{Ni(II)}$ -initiated Barbier reaction show the following: (1) SmI_2 reduces Ni(II) salts; (2) Ni(0) nanoparticles are formed upon reduction; (3) Ni(II) salts catalyze the reaction; however, (4) colloidal Ni(0) does not initiate the Barbier reaction; (5) Ni(II) salts are reduced significantly faster than alkyl iodides or dialkyl ketones by SmI_2 ; and (6) the reaction is zero order in substrates and first order in SmI_2 and Ni . Given these findings, the mechanism in Scheme 2 is proposed. Ni(II) is initially reduced to Ni(0) through two single electron transfers from two equivalents of SmI_2 . Ni(0) either

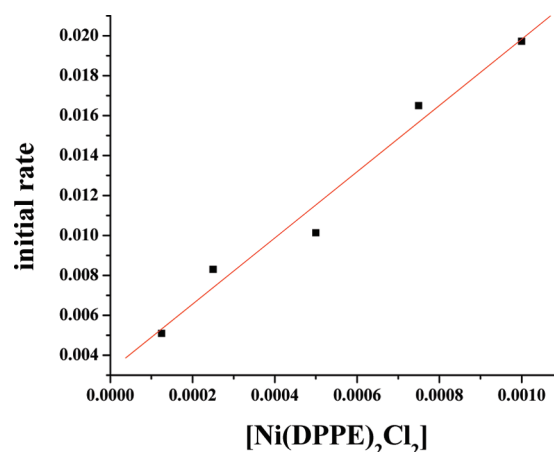


Figure 9. Rate constant of $\text{Ni(DPPE)}_2\text{Cl}_2$ in the samarium Barbier reaction. $[\text{SmI}_2] = 5 \text{ mM}$; $[\text{Ni(DPPE)}_2\text{Cl}_2] = 0.5\text{--}4 \text{ mol \%}$; $[\text{1}] = 50 \text{ mM}$; $[\text{2}] = 50 \text{ mM}$. Rate constant = $16 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$.

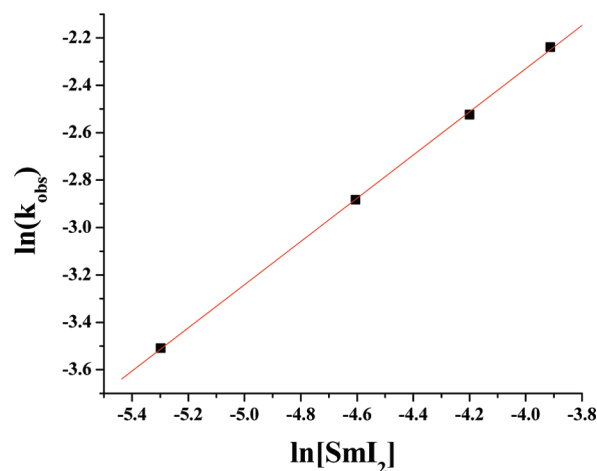


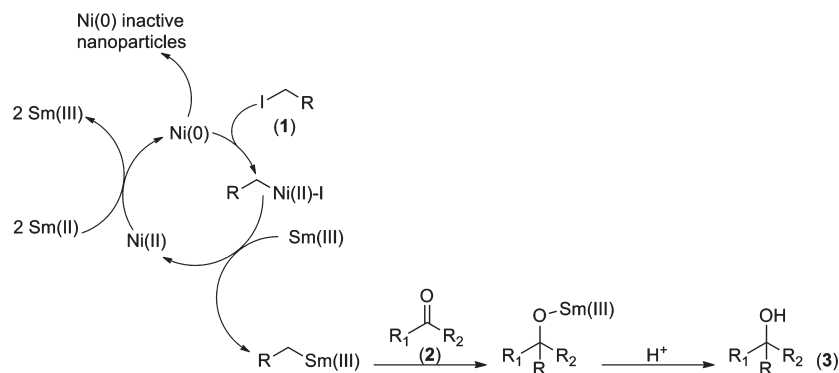
Figure 10. Rate order of SmI_2 in the Ni(II) catalyzed samarium Barbier reaction. $[\text{SmI}_2] = 5\text{--}20 \text{ mM}$; $[\text{Ni(DPPE)}_2\text{Cl}_2] = 0.15\text{--}0.60 \text{ mM}$ (3 mol % with respect to $[\text{SmI}_2]$); $[\text{1}] = 0.2 \text{ M}$; $[\text{2}] = 0.2 \text{ M}$. Rate order = 0.91 ± 0.01 .

Table 4. Reaction Orders for the Reagents in the Ni(II) -Catalyzed Barbier Reaction

SmI_2	$\text{Ni(DPPE)}_2\text{Cl}_2$	1	2
0.91 ± 0.01	1.0 ± 0.1	0	0

inserts into the alkyl halide bond through a facile oxidative addition or aggregates to form colloidal Ni(0) , a pathway which deactivates the catalyst. After oxidative addition, transmetalation occurs in which Sm(III) releases Ni(II) for reentry into the catalytic cycle and a more stable organosamarium intermediate is formed.¹⁸ The organosamarium adds to the ketone, and final protonation of the Sm(III) alkoxide provides the final carbinol product. It is important to note that transmetalation may occur at an alternative stage. For instance, after oxidative addition the organonickel species may directly add to the ketone forming a nickel alkoxide. Due to the high oxophilicity of Sm ,

Scheme 2. Catalytic Cycle of Ni(0)-Mediated Barbier Coupling



transmetalation might occur releasing Ni(II) and forming a Sm alkoxide, followed by protonation.

CONCLUSIONS

The mechanistic studies presented herein show that the samarium Barbier reaction containing catalytic amounts of Ni(II) salts is driven by reduction of Ni(II) to Ni(0). Once reduced, Ni(0) inserts into the alkyl halide bond through oxidative addition to produce an organonickel species. Transmetalation by Sm(III) forms the organosamarium species to couple with the dialkyl ketone and releases Ni(II) which can be reduced by stoichiometric SmI₂ reductant. The formation of colloidal Ni(0) occurs concomitantly with Ni(0) oxidative addition as an unproductive process.

Catalytic amounts of Ni(II) salts are routinely used in a variety of SmI₂ reductions, improving the reaction time or product ratio, without a clear understanding of the mechanistic role of the Ni(II) catalyst. This is the first instance where it has been shown that the reaction thought to be driven by the unique features of SmI₂ is in fact a result of known Ni(0) chemistry.¹⁹ Given the use of Ni(II) and other transition metal salts in many reactions initiated by SmI₂, it is likely that this facet of the reaction chemistry and mechanism is more prevalent than recognized. We are currently examining the mechanism of other SmI₂-based reactions containing transition metal salts to determine the intermediacy of transition metal-based intermediates and the use of this knowledge to develop alternative methods for the organic chemists' toolbox. The results of these studies will be reported in due course.

EXPERIMENTAL SECTION

Materials and General Procedures. THF was purified after purging with argon gas and passing over a column of activated alumina by a Solvent Purification System (Innovative Technology Inc.; MA). Dried solvents and reagents were stored in an Innovative Technology, Inc. drybox containing an argon atmosphere and a platinum catalyst for drying. SmI₂ was prepared by stirring Sm metal and iodine in THF until the characteristic blue color of Sm²⁺ appeared. The concentration of the Sm complex (0.10 M in THF) was determined by iodometric titration. 3-Pentanone (2) was purchased from Aldrich and distilled under vacuum from CaO before use. Iodododecane (1), Sm metal, and Ni(acac)₂ were purchased from Acros and used with no further purification. NiI₂ and Ni(DPPE)₂Cl₂ were purchased from Aldrich

and used with no further purification. Ni nanoparticles (aps 20 nm) were purchased from Sun Innovations Inc.

The Barbier reaction was carried out in a drybox with degassed reagents. SmI₂ was prepared as described above. Ni(II) species (0.004 mmol) was added to 2 mL of THF and stirred to dissolve. SmI₂ (4.0 mL, 0.1 M) was added dropwise to the Ni(II) solution, and with the slow addition the solution turned brown. Separately, iodododecane (1) (49.3 μ L, 0.2 mmol) and 3-pentanone (2) (21.2 μ L, 0.2 mmol) were added to 5 mL of THF. The substrate solution was added dropwise to the SmI₂–Ni solution. This reaction was left to stir for 5–15 min (depending on the Ni(II) additive). The reaction was quenched by exposing to air and adding 0.1 M HCl. The reaction mixture was then washed with water and extracted twice with ether. The organic layer was washed individually with H₂O, Na₂S₂O₃, and brine, dried over MgSO₄, and then concentrated to obtain the pure Barbier product.

Stopped-Flow Rate Studies. Kinetic experiments in THF were performed with a computer-controlled SX.18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd. Surrey, UK). The SmI₂ and substrates with Ni(II) were taken separately in airtight Hamilton syringes from a drybox and injected into the stopped-flow system. The cell block and the drive syringes of the stopped flow reaction analyzer were flushed a minimum of three times with dry, degassed THF to make the system anaerobic. Using reaction progress kinetic analysis, the concentration of SmI₂ used for the study was 20 mM. The concentrations of the substrates were kept at synthetically relevant conditions with only slight excess (as indicated in text). When using pseudofirst-order conditions the [SmI₂] was 5 mM, and the concentration of the substrates was kept high relative to [SmI₂] (125 mM). In all cases the mole fraction of Ni(II) species were determined with respect to [SmI₂]. The reaction rates were determined from the decay of SmI₂ absorbance at 555 nm. Under reaction progress kinetic analysis conditions, the rate was determined from the decay of the SmI₂ absorbance at 555 nm: rate = (Δ [SmI₂]/ Δ time, s). The pseudofirst-order rate constants were determined by using standard methods.²⁰ The decay of the SmI₂ displayed first-order behavior over >3 half-lives.

UV–vis spectroscopy experiments were performed on a Shimadzu UV-1601 UV–vis spectrophotometer controlled by UV Probe (version 1.11) software. NMR experiments were carried out on a Bruker 500 MHz instrument using CDCl₃ as the solvent.

ASSOCIATED CONTENT

S Supporting Information. General experimental methods and spectroscopic and rate data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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