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Salt-Free Reduction of Nonprecious Transition-Metal Compounds: Generation of Amorphous Ni Nanoparticles for Catalytic C–C Bond Formation

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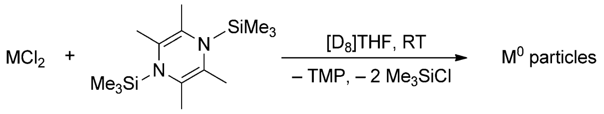
Abstract: *A salt-free procedure for the generation of a wide variety of metal(0) particles, including Fe, Co, Ni, and Cu, was achieved using 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1**), which reduced the corresponding metal precursors under mild conditions. Notably, Ni particles formed in situ from the treatment of Ni(acac)$_2$ (acac = acetylacetonate) with **1** in toluene exhibited significant catalytic activity for reductive C–C bond-forming reactions of aryl halides in the presence of excess amounts of **1**. By examination of high-magnification transmission electron microscopy images and electron diffraction patterns, we concluded that amorphous Ni nanoparticles (Ni aNPs) were essential for the high catalytic activity.*

Nanoparticles of transition metals are unique and versatile catalysts that have attracted particular interest because they show boundary and bilateral character between homo- and heterogeneous catalysts.[1,2] Nanocatalysts have a relatively wide reactive surface and a controlled nanoscale size and shape. In general, crystalline nanoparticles (*c*NPs) of noble metals, such as Pd and Au, exhibit high catalytic performances in several C–C bond-forming reactions.[3–8] The development of an approach to replace catalytic systems of noble metals with nonprecious metals such as Ni, Co, and Cu is currently in high demand. Although several *c*NPs of these nonprecious metals have been prepared, they exhibited poor catalytic activity toward C–C bond-forming reactions.[9–12] The relatively poor catalytic performance of these nonprecious transition-metal nanocatalysts is due mainly to their larger particle size and smaller reactive surface, as well as their sensitivity to oxidation damage. Herein, we report that 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**1**)[13] reduced halides, carboxylates, and acetylacetonates (acac) of some nonprecious metals to produce the corresponding metallic particles under mild conditions. Additionally, amorphous Ni^0 nanoparticles (Ni *a*NPs), derived from [Ni(acac)$_2$] and **1**, were effective catalysts for reductive C–C bond-forming reactions.

We began by examining the potential of **1** to act as a reductant for some typical nonprecious transition metals along with typical noble transition metals (Table 1). The addition of **1** (2 equiv) to a yellow suspension of CuCl$_2$ in [D$_8$]THF at room temperature induced a rapid reaction forming a reddish-brown dispersion of small Cu particles, which gradually precipitated completely over 24 h. Based on NMR spectroscopy of the filtrate, 1 equiv of **1** had been consumed to give 2,3,5,6-tetramethylpyrazine (TMP; 1 equiv) together with Me$_3$SiCl (2 equiv). These results indicated that the 2-electron reduction of CuCl$_2$ had generated Cu^0 particles, even though CuCl$_2$ was barely dissolved in the solvent (Table 1, entry 1).[14] We also successfully employed **1** as a reagent in the reduction of FeCl$_2$, CoCl$_2$, and NiCl$_2$ to form the corresponding ferromagnetic Fe, Co, and Ni black powders (entries 2–4).[15] Some noble metal salts, such as

Table 1: Reduction of transition-metal chlorides by organosilicon reductant **1**.[a]



1 (2.0 equiv)

Entry	Metal chloride	Conv. of **1** [%][b]	Product
1	CuCl$_2$(thf)$_{0.8}$	50	Cu^0 particles
2	FeCl$_2$(thf)$_2$	50	Fe^0 particles
3	CoCl$_2$(thf)$_{1.5}$	50	Co^0 particles
4	NiCl$_2$	50	Ni^0 particles
5	PdCl$_2$	50	Pd^0 particles
6	PtCl$_2$	50	Pt^0 particles
7	CrCl$_3$(thf)$_3$	25	CrCl$_2$(thf)$_2$
8	MnCl$_2$(thf)$_2$	0	No reaction

[a] Conditions: metal chloride (0.050 mmol), **1** (0.10 mmol) in [D$_8$]THF (0.50 mL) at room temperature. [b] Determined by ^{1}H NMR measurement of the ratio between 2,3,5,6-tetramethylpyrazine (TMP), Me$_3$SiCl, and **1**. For further application to other metal halides, see Table S1 in the Supporting Information.

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$PdCl_2$ and $PtCl_2$, were also reduced to give metallic Pd and Pt particles, respectively (entries 5 and 6), although a longer reaction time was required. $CrCl_3(thf)_3$ reacted with 0.5 equiv of **1** to generate green mixture containing $CrCl_2(thf)_2$ (entry 7), whereas $MnCl_2(thf)_2$ was inert due to its highly negative redox potential (entry 8).

As compound **1** could be employed in the salt-free reduction of some late-transition-metal chlorides to form the corresponding metal particles, we next examined the catalytic activities of the metal particles in Ullmann coupling reactions of 4-iodoanisole (see the Supporting Information, Table S3), which was recently applied to noble metal nanoparticle catalysts.[8,16] Upon combination with a slight excess of **1** (1.5 equiv), $NiCl_2$ and $CoCl_2(thf)_{1.5}$ in C_6D_6 at 80 °C showed strong catalytic activities, giving 4,4′-dimethoxybiphenyl in 68 % and 92 % yields, respectively. In sharp contrast, Pd^0 and Pt^0 particles generated in situ did not exhibit catalytic activity in Ullmann coupling reactions (22 % and 0 % yields, respectively), although they were superior to nonprecious catalysts for activating $C(sp^2)-I$ bonds. The other metal particles listed in Table 1 did not catalyze biaryl formation. Further screening of $Ni(acac)_2$ and $Co(acac)_2$ led us to determine that $Ni(acac)_2$ and **1** was the best catalytic system for the homocoupling reaction of 4-iodoanisole.

The optimized conditions established for the homocoupling of 4-iodoanisole using Ni catalysts were also applicable to 4-bromoanisole, converting it into 4,4′-dimethoxybiphenyl in 96 % yield (Table 2, entry 1). The catalyst loading could be decreased to 1 mol % and the reaction afforded the product in 94 % yield (entry 2). Addition of TMP, a product that formed from **1**, showed no accelerating effect on the reaction to improve the yield of the product (entries 3 versus 4). This result indicated that TMP did not act as a ligand for the Ni species, although *N*-heteroaromatic compounds, such as pyridine and 2,2′-bipyridine, were reported to work as ligands for some Ni-catalyzed reactions.[17] In fact, Ni nanoparticles, which had been generated before the homocoupling reaction from $Ni(acac)_2$/**1** in toluene at 80 °C, exhibited almost the same catalytic activity in this reaction (entry 5). To our surprise, no catalytic activity was observed for three different sets of Ni nanoparticles generated from known procedures using $NiCl_2$/Li/4,4′-di-*tert*-butylbiphenyl, $Ni(acac)_2/NaBH_4$, and $Ni(cod)_2/H_2$, all of which were typical experimental conditions used for the preparation of crystalline Ni nanoparticles (Ni *c*NPs; entries 6–8).[18,19] Additionally, when $NaBH_4$ was employed as a reductant in place of **1** (Table 2, entry 9), it was found that the reaction was unsuccessful (using Ni NPs generated by $Ni(acac)_2$/**1**), indicating that **1** was a superior reductant to $NaBH_4$ in this biaryl formation reaction.

To gain insight into the catalytically active Ni species, we characterized the Ni species generated in situ in the absence of any substrate and ligand by transmission electron microscopy (Figure 1). The observed image clearly showed the formation of Ni particles with an approximate size of 15 nm (Figure 1 a), and the corresponding electron diffraction pattern appeared as a halo, suggesting that the nanoparticles were amorphous in nature (*a*NPs; Figure 1 b).[20] The crystallinity and size of these Ni *a*NPs remained intact after the biaryl formation reaction (Figure S2). On the other hand, a clear electron diffraction ring pattern was obtained for Ni particles with an approximate size of 8 nm derived from $NiCl_2$/Li/4,4′-di-*tert*-butylbiphenyl, which were isolated as Ni *c*NPs (Figure 1 c and d). When $NaBH_4$ was used as reductant, Ni NPs approximately 9 nm in size with low crystallinity were generated (Figure S2). These results provided the first evidence that the catalytic activity of Ni NPs for reductive biaryl formation depended on the crystallinity of the Ni NPs, although it has been reported that Pd *a*NPs exhibit higher activity for Suzuki–Miyaura coupling reactions than the corresponding *c*NPs.[21]

We further characterized the Ni *a*NPs by X-ray photoelectron spectroscopy (XPS; Figure S3). In the XPS spectrum, a major sharp peak for Ni $2p_{3/2}$ (852.5 eV) was detected (and assigned to Ni^0) with a relatively weak peak for Ni $2p_{3/2}$ (854.7 eV; attributed to NiO). In contrast, the XPS spectrum of Ni *c*NPs generated from $NiCl_2$/Li/DTBB displayed one

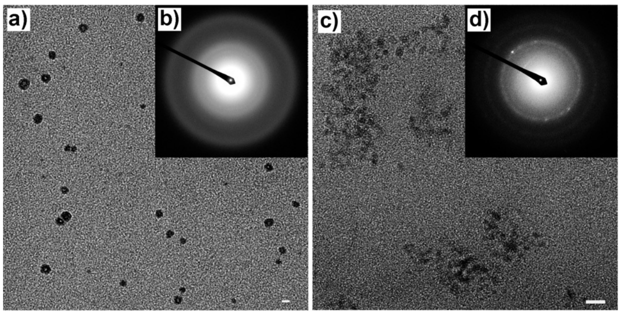
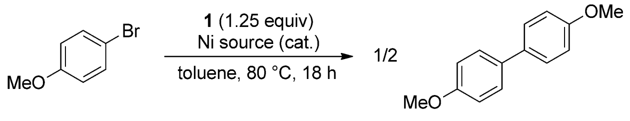


Figure 1. a) High-magnification TEM image and b) corresponding transmission electron diffraction (TED) pattern of Ni *a*NPs generated from $Ni(acac)_2$/**1** (entry 5 in Table 2). c) High-magnification TEM image and d) corresponding TED pattern of Ni *c*NPs generated from $NiCl_2$/Li/4,4′-di-*tert*-butylbiphenyl (entry 6 in Table 2). Scale bars in TEM images (bottom right) = 10 nm.

Table 2: Catalytic performances of different Ni sources for the Ullmann coupling reaction.



Entry	Ni source (mol %)	Yield (%)[a]
1	$Ni(acac)_2$ (5)	96
2	$Ni(acac)_2$ (1)	94
3[b]	$Ni(acac)_2$ (5)	34
4[b,c]	$Ni(acac)_2$ (5)	27
5	Ni particles from $Ni(acac)_2$/**1** (5)	94
6	Ni particles from $NiCl_2$/Li/DTBB[d] (5)[f]	0
7	Ni particles from $Ni(acac)_2/NaBH_4$ (5)[f]	0
8	Ni particles from $Ni(cod)_2/H_2$(3 atm) (5)	0
9[e]	Ni particles from $Ni(acac)_2$/**1** (5)	trace

[a] Yield of isolated product. [b] Reaction time was 9 h. [c] TMP (10 mol %) was added as additive. [d] DTBB = 4,4′-di-*tert*-butylbiphenyl. [e] $NaBH_4$ (1.25 equiv) was used as reductant instead of **1**. [f] In THF, instead of toluene.

sharp peak for Ni $2p_{3/2}$ (852.5 eV) for Ni^0. These experiments revealed that the catalytically active Ni *a*NPs contained not only Ni^0 but also NiO, resulting from partial oxidation of the surfaces of the Ni *a*NPs or partial decomposition of the $Ni(acac)_2$-derived species during the formation of the *a*NPs. We also performed XPS analysis of the Ni *a*NPs collected from the reaction mixture after the Ullmann coupling reaction. Similar to the spectrum recorded for the Ni *a*NPs before the catalytic reaction, two peaks were detected, one for Ni^0 (852.5 eV) and one for NiO (854.7 eV), corresponding to the Ni $2p_{3/2}$ levels. The relative quantity of NiO in the Ni *a*NPs increased after the Ullmann coupling reaction. It was also found that the Ni *a*NPs exhibited similar catalytic activity for the Ullmann coupling reaction after exposing the Ni *a*NPs to air, suggesting that the catalytically active Ni^0 species was generated in the presence of excess **1** in the reaction mixture (see below).

The different catalytic activities of Ni *a*NPs and *c*NPs were presumably because of differences in the rates of leaching of Ni^0 at the molecular level from the NPs. Ni^0 species released from the *a*NPs reacted immediately with 4-bromoanisole to produce the Ullmann coupling product. The amorphous nature of the NPs was maintained during the catalytic reaction (Figure S2), meaning that the high catalytic activity of the nanoparticles was maintained. When 4-chloroanisole was added as a substrate for the Ni *a*NPs, no Ullmann coupling product was observed. However, in the presence of 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), C−Cl bond cleavage proceeded to form the coupled product in 96% yield, indicating that oxidative addition of 4-chloroanisole to $(dtbpy)Ni^0$ generated in situ proceeded to give the biaryl product. In sharp contrast, Ni *c*NPs which were stable against leaching of Ni^0 species were not active for the Ullmann coupling of 4-chloroanisole under the reaction conditions employed (toluene, 80 °C), even in the presence of dtbpy. The advantages of *a*NPs over *c*NPs in terms of their catalytic application was also reported for a catalyst based on Pd NPs; Liu and Hu found that changing the morphology of the Pd NPs from amorphous to crystalline led to a corresponding decrease in their catalytic activity.[21] During this re-ordering process, a Pd^0 species was found to leach from the *a*NPs giving rise to the high catalytic activity of the Pd *a*NPs.[21]

Based on the above-mentioned results, we proposed the following reaction mechanism (Figure 2). Ni *a*NPs were initially generated in situ from $Ni(acac)_2$ and **1**. The Ni^0 species which leached from the Ni *a*NPs were oxidized by the aryl halide to generate NiX(Ar), which was converted into Ni^0, NiX_2, and the Ullmann coupling product.[22] In the presence of reductant **1**, NiX_2 was reduced to regenerate Ni^0. During this process, Ni *a*NPs acted as a Ni^0 reservoir for the release of Ni^0 into the reaction mixture, a strategy proposed by Dupont and de Vries based on their seminal study of C−C bond formation catalyzed by nanoparticles.[23,25] When $[NiO]_n$ was released from the *a*NPs, the Ni^{II} species might be reduced by **1** to afford Ni^0. In relation to the reaction shown in Scheme 1, the released Ni^0 species was coordinated by dtbpy to form $[(dtbpy)Ni^0]$ which subsequently activated the C−Cl bond of 4-chloroanisole.

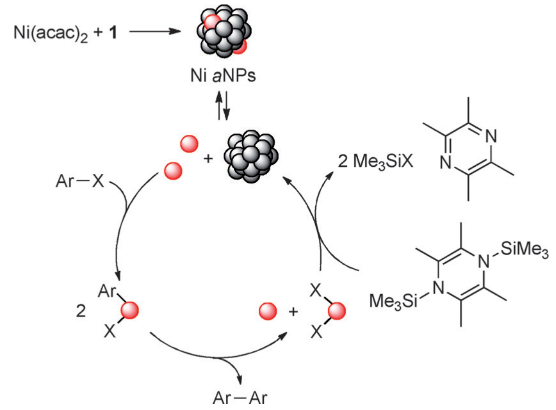
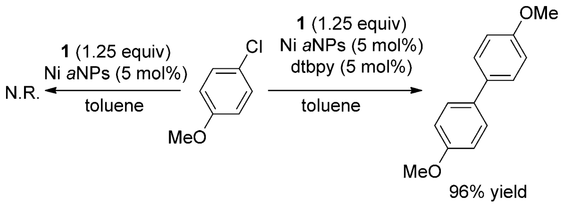


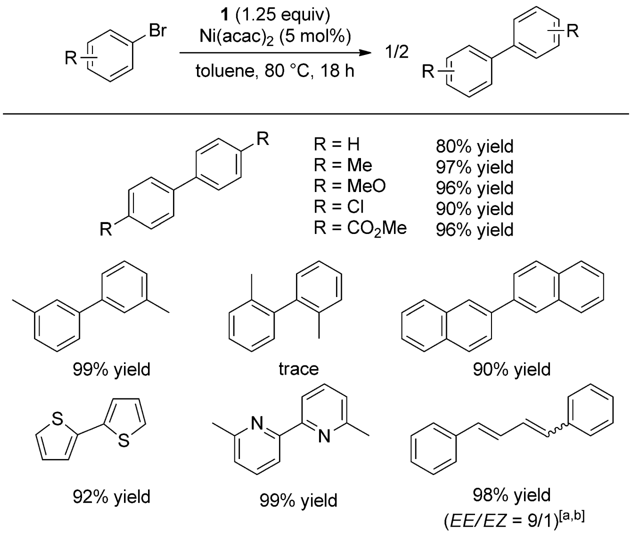
Figure 2. Possible reaction mechanism for reductive biaryl formation catalyzed by Ni *a*NPs.



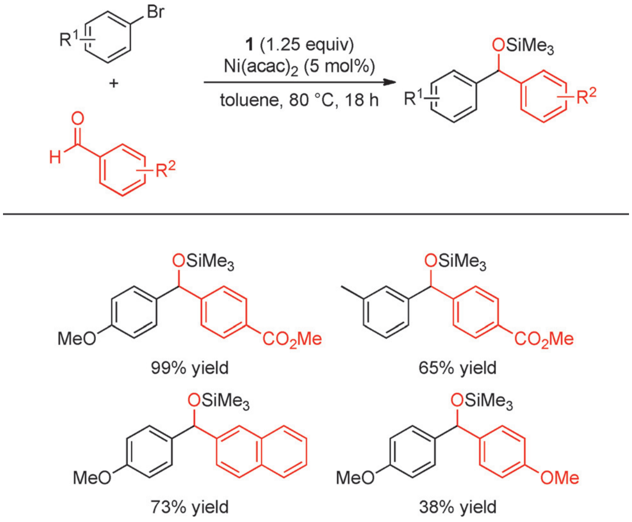
Scheme 1. Ullmann coupling reaction of 4-chloroanisole in the presence of Ni *a*NPs with or without the coligand dtbpy. N.R. = no reaction.

With the $Ni(acac)_2/\mathbf{1}$ catalytic system in hand, we examined the scope of aryl halides which could be employed in catalytic Ullmann coupling reactions (summarized in Scheme 2). A wide variety of aryl halides was applicable for the dimerization reaction, and both electron-donating and electron-withdrawing groups were tolerated. Notably, the C−Br bond of 4-chlorobromobenzene was selectively cleaved to give 4,4′-dichlorobiphenyl in 90% yield. Although having a substituent at the *ortho* position hampered the reaction, both *meta*- and *para*-substituted arylhalides could be applied as substrates. 2-Bromonaphthalene and heteroaromatic compounds, such as 2-bromopyridine and 2-bromothiophene, were also good substrates, with the reactions proceeding smoothly to afford the corresponding biaryls. When β-bromostyrene was used as a substrate, the *EE*/*EZ* mixture of the dimer diene (9/1) was obtained without incorporation of any Heck reaction product.

The inertness of **1** toward the carbonyl functionality led us to apply our catalytic system to a reductive arylation of arylaldehydes (Scheme 3).[26] We examined the reaction between 4-bromoanisole and methyl terephthalaldehyde to produce the corresponding silylated diaryl methanol derivative in quantitative yield. The more sterically hindered 3-methylbromobenzene could also be successfully applied in this reaction. Both electron-donating and electron-withdrawing aryl aldehydes were well tolerated in this reductive arylation, and target compounds were obtained in moderate to high yield. Accordingly, **1** worked as a concomitant reducing reagent for the Ni *a*NP catalyst without direct reduction of the aldehyde.



Scheme 2. Substrate scope for catalytic Ullmann coupling reactions. [a] An *E*/*Z* (93/7) mixture of β-bromostyrene was used as substrate. [b] Calculated from ^{1}H NMR spectroscopic analysis.



Scheme 3. The reductive arylation of arylaldehydes catalyzed by Ni *a*NPs.

In conclusion, we have developed a new strategy for using the organosilicon reducing reagent **1** to generate catalytically active metal(0) nanoparticles under homogeneous conditions. The most notable finding was that the amorphous nature of Ni NPs was responsible for the high catalytic activity in the Ullmann coupling reaction and the reductive arylation of arylaldehyde. Additionally, as a result of the inertness of **1** towards organic substrates, such as aryl halides and aldehydes, **1** could be applied as a concomitant reductant in catalytic C−C bond-forming reactions between these substrates. We also found that main-group metal chlorides, such as $GaCl_3$ and $InCl_3$, were reduced upon treatment with the reductant **1** to form the corresponding metal particles, further demonstrating the potential of the reductant.

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