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Copolymer-Incarcerated Nickel Nanoparticles with *N*-Heterocyclic Carbene Precursors as Active Cross-Linking Agents for Corriu–Kumada–Tamao Reaction

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Supporting Information

ABSTRACT: We have developed heterogeneous polymer-incarcerated nickel nanoparticles (NPs), which catalyze cross-coupling reactions. The matrix structure of these catalysts incorporates both *N*-heterocyclic carbenes (NHCs) as ligands and Ni-NPs, thanks to a new design of cross-linking agents in polymer supports. These embedded NHCs were detected by field gradient swollen-resin magic angle spinning NMR analysis. They were successfully applied to Corriu–Kumada–Tamao reactions with a broad substrate scope including functional group tolerance, and the catalyst could be recovered and reused several times without loss of activity.

Carbon–carbon bond cross-coupling reactions catalyzed by transition metals are among the most fundamental organic reactions and have appeared in recent years as a powerful synthetic tool for the elaboration of complex organic molecules (e.g., natural products, pharmaceutical and agricultural compounds, electronic devices).[1] Surface-catalyzing C–C bond formation on supported transition metal nanoparticles (NPs) has emerged as a suitable chemical method because of the decreased metal contamination of products and the development of "greener" routes in organic synthesis by simplifying workup and using recyclable catalysts.[2] However, the development of heterogeneous metallic NPs effective in cross-coupling reactions has been limited mostly to Pd chemistry.[3] Since the pioneering work on the Corriu–Kumada–Tamao (CKT) reaction,[4] nickel has appeared as an appropriate alternative. Among the many contributions on homogeneous Ni systems dedicated to cross-coupling reactions,[5] only a few have focused on Ni immobilization[6] or on the development of surface chemistry by using Ni-NPs. In fact, Ni-NPs have been limited to hydrogen-transfer reactions;[7] and only Ni immobilized on charcoal (Ni/C) developed by Lipshutz's group has been applied to C–C bond formation.[6b−e,8] Despite the high activity of Ni/C, limitations were observed, such as pregeneration of active species by adding external ligands (phosphine) and *in situ* reduction of Ni(II), and in some cases leaching of metal was observed. Here we survey the development of highly active and useful heterogeneous Ni-NPs by incarcerating them with embedded *N*-heterocyclic carbenes (NHCs) that have the dual roles of ligand and cross-linking agent, and we look at their application in the CKT reaction.

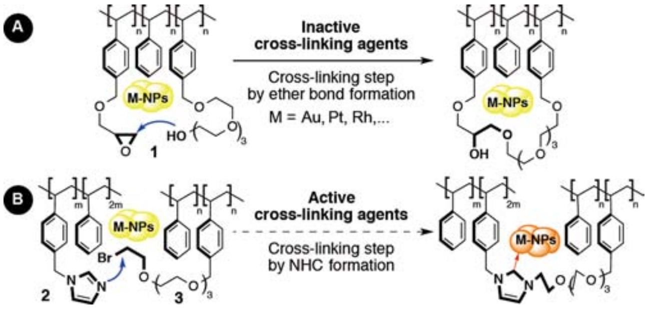

Figure 1. Concept of PI M-NPs using active cross-linking agents.

We have developed polymer-incarcerated (PI) metal catalysts with polystyrene-based copolymers containing alcohol and epoxide moieties as cross-linking agents like copolymer **1** (Figure 1A).[9] Copolymer **1** has been successfully applied to the stabilization and incarceration of different metal NPs,[10] such as Au-NPs,[11] the combination of Au-NPs with Fe, Co, or Ni (Au/M-NPs),[12] and Pt-NPs.[13] These catalysts exhibit high activity for organic transformations, and they can be recovered and reused several times without leaching of metals or loss of activity. Recently, we reported PICB-Rh/Ag-catalyzed 1,4-additions of boronic acids and found that a combination of NPs with external ligands (e.g., diene or phosphine) could tune the catalyst activity and/or selectivity.[14] One of the most successful recent classes of ligands in organometallic chemistry are NHCs.[15] There are, however, few reports on the use of NHC ligands for stabilizing or modifying NPs (Au-NPs,[16] Ru-NPs,[17] and Pd-NPs[18]). Although some homogeneous, efficient NHC-Ni systems for CKT reaction have been disclosed,[19] there are no reports on combinations of NHC and Ni-NPs. Turning our attention to this reaction catalyzed by Ni-NPs—with which it is probably necessary to use ligands to increase the activity—we decided to develop new copolymers with active cross-link moieties consisting of an imidazole part (**2**) and an alkyl bromide part (**3**) (Figure 1B). We envisioned that the cross-linking between these two copolymers could lead to the formation of embedded NHCs in one matrix and, by this protocol, a directly usable heterogeneous Ni-NPs catalyst without external addition of ligands could be afforded.

We began our studies by preparing various Ni-NP catalysts using the PI method, following our previously reported procedures with small adjustments (Table 1). As a modification, lithium triethylborohydride ($LiEt_3BH$) was used as a stronger reducing agent to give full reduction of Ni.[20] $NiBr_2(PPh_3)_2$ was selected as a nickel source, and different copolymers were tried as

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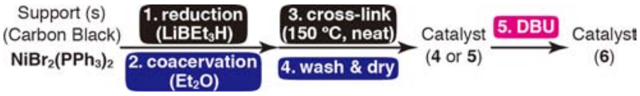
Table 1. Catalyst Preparations



Entry	Support(s)	Catalyst	Ni (mmol/g)[a]	Surface area (m^2/g)[b]
1	**1** + CB	PICB–Ni **4**	0.212	38.5
2	**2** + **3**	PI–IL–Ni **5a**	0.074	< 0.5
3	**2** + **3**	PI–NHC–Ni **6a**	0.074	< 0.5
4	**2** + **3** + CB	PICB–NHC–Ni **6b**	0.086	27.9
5[c]	**2** + **3** + CB	PICB–NHC–Ni **6c**	0.099	–
6	**2** + **3** + CB	PICB–NHC–Ni **6d**	0.148	–

[a] Determined by ICP-AES analysis. [b] Evaluated from Brunauer−Emmett−Teller analysis. [c] Catalyst prepared without reducing agent.

supports. First, we prepared PICB-Ni (**4**) using the previous copolymer **1** and carbon black (CB) as a second support to expanded the surface area (entry 1). Next, we synthesized two new polymers: (i) copolymer **2** was synthesized by copolymerization between styrene and 1-(4-vinylbenzyl)imidazole, and (ii) copolymer **3** was also synthesized by copolymerization between styrene and a monomer with an alkyl bromide function.[21] Unfortunately, the copolymerization of three monomers gave only insoluble materials, probably because of *in situ* cross-linking. Nevertheless, using a molar equivalent of mixed **2** and **3** instead of **1**, we synthesized PI-IL-Ni (**5a**) with the expected weight and Ni loading (entry 2).

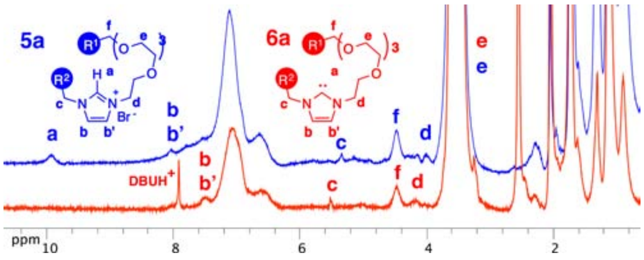


Figure 2. FGSR-MAS cpmg spectra of **5a** and **6a** in d_8-THF.

To probe our concept—embedded imidazolium salt and/or NHC formation using active cross-linkers—we conducted field gradient swollen-resin magic angle spinning (FGSR-MAS) NMR experiments with the catalyst **5a** using d_8-THF as the swelling solvent (Figure 2, blue signal).[22] The cpmg-NMR spectrum of **5a** shows three broad signals at 7.5, 8.0, and 9.9 ppm attributed respectively to the *CH*═*CH* and −N-*CH*-N groups of the imidazolium salt. This cpmg-NMR spectrum confirmed that the formation of the imidazolium salts resulted from the reaction of copolymers **2** and **3** in the cross-linking step.[23] It is also known that imidazolium salts can easily be converted to NHCs by a base treatment. Therefore, **5a** was treated with large excess (25 equiv) of 1,8-diazabicycloundec-7-ene (DBU), and after filtration and washing with organic solvents to remove the excess of the base, PI-NHC-Ni (**6a**) was obtained (Table 1, entry 3). Next, FGSR-MAS cpmg-NMR analysis was conducted (Figure 2, red signal). As expected, the previous signals at 9.9 ppm, attributed to −N-*CH*-N of the imidazolium salt structure, have completely disappeared, and only the broad signals at 7.5 and 8.0 ppm, assigned this time to *CH*═*CH* of the NHC structure, were observed. Two new sharp signals at 7.9 and 3.2 ppm were detected and assigned to the protonated DBU (DBUH$^+$), which might be partially retained in the polymeric structure. At this stage, these FGSR-MAS NMR spectra provided strong evidence that copolymer **2** reacted with copolymer **3** with the formation of the corresponding NHC after the base treatment to form a new composite material that has incarcerated Ni-NPs with embedded NHC ligands. The same procedure could be applied to the preparation of PICB-NHC-Ni (**6b**) containing CB as a second support (entry 4).

Next, we conducted high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) to characterize the newly prepared Ni-NPs catalysts (Figure 3 and SI). These analyses have shown that all these catalysts have similar morphology with formation of Ni-NPs (∼1−4 nm) with the exception of PICB-NHC-Ni (**6c**) (prepared without reducing agent), which showed only dispersed metals.[21]

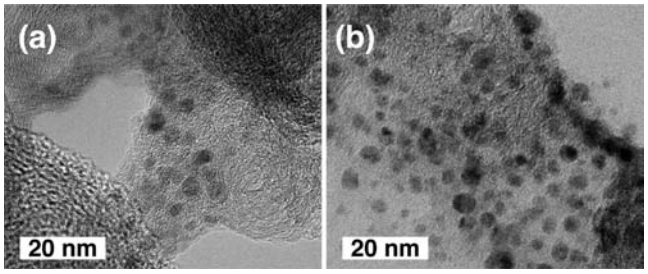
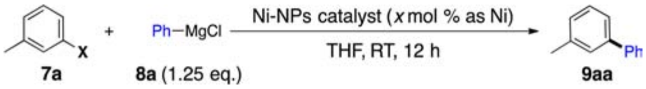


Figure 3. (a) HRTEM of catalyst **6b**. (b) STEM of catalyst **6b**.

We tried the CKT reaction with these different catalysts (Table 2). 3-Bromotoluene (**7a**) and phenylmagnesium chloride (**8a**) were selected as model substrates. A slight excess of Grignard reagent (GR) (1.25 equiv) was necessary because of the homocoupling of **8a** as a side reaction. We initially investigated the activity of **4**. With only 1 mol% loading, high temperature (65 °C) was required to obtain 41% yield of the coupling product **9aa** because of poor aryl bromide conversion (entry 1). In addition, inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements detected leaching of Ni to the solution phase following the reaction. Under milder conditions at room temperature (RT) using catalyst **4** with no additive, no reaction occurred (entry 2). Next, using 1 mol% of catalyst **5a** at RT, moderate activity without metal leaching was observed (entry 3). This higher catalyst activity of **5a** compared with **4** might be explained by the effect of the ionic liquid-like structure as stabilizer or by the formation of NHC ligand by deprotonation with basic aryl GRs. Encouraged by these results, we next tried catalyst **6a**—with which we have observed embedded NHC ligands in the polymeric structure by FGSR-MAS NMR analysis—at RT. Under these conditions, an excellent yield in favor of the cross-coupling product **9aa** was observed (entry 4). Catalyst **6b**, which was prepared by adding CB as a second support, showed even higher activity with 98% yield due to the larger surface area (27.9 m^2/g for **6b**; < 0.5 m^2/g for **6a**) (entry 5). Catalyst **6c**, prepared without the reduction step, had comparable activity; however, nickel leaching was observed (entry 6).[24] Next, we tried to decrease the catalyst loading. We found that 0.25 mol% of catalyst **6b** was enough to obtain full conversion with the high turnover number (TON) of 392 (entry 7). This TON can be increased to 950 using only 0.1 mol% of catalyst **6b** (entry 8). Catalyst **6d**, prepared with higher Ni loading, showed lower activity, which can be explain by a lower ratio between NHC and Ni (entry 9). Having succeeded in the CKT reaction using aryl bromide as the electrophile, we focused on other aryl halides. Under the same conditions, 3-iodotoluene showed similar reactivity (entry 10). With 3-

chlorotoluene the yield dropped to 33% (entry 11). To improve the reactivity, the temperature was increased to 65 °C (entry 12); at RT, higher catalyst loading (0.5 mol%) and additional LiBr (1 equiv) were necessary to obtain a similar yield of **9aa** (entry 13).[25] Even C−F bonds could be activated to give the product **9aa** in 71% yield at 65 °C (entry 15).[26] Finally, using dimethoxyethane (DME) as a solvent at 100 °C, **9aa** could also be obtained in excellent yield from aryl fluoride (entry 16).

Table 2. Optimization of the Reaction Conditions

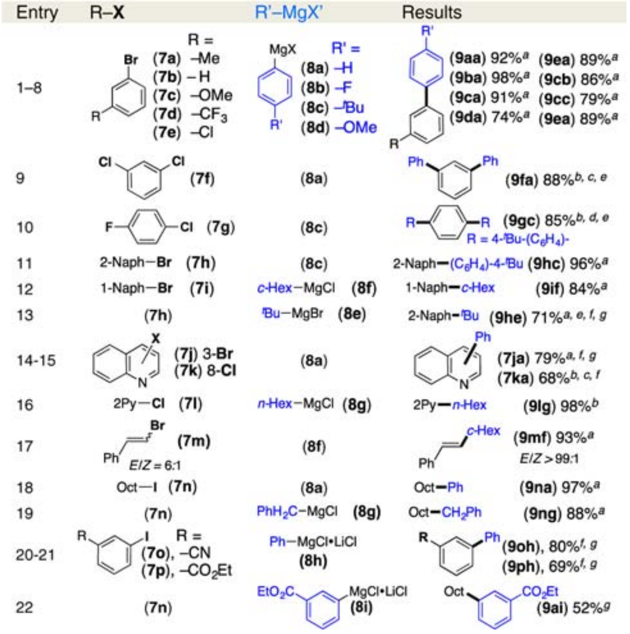


Entry	Catalyst (*x* mol % as Ni)	X	**9aa** (%)[a]	Leaching (%)[b]
1[c]	PICB–Ni **4** (1)	Br	41	0.12
2	PICB–Ni **4** (1)	Br	0	ND
3	PI–IL–Ni **5a** (1)	Br	52	ND
4	PI–NHC–Ni **6a** (1)	Br	91	ND
5	PICB–NHC–Ni **6b** (1)	Br	98	ND
6	PICB–NHC–Ni **6c** (1)	Br	98	0.32
7	PICB–NHC–Ni **6b** (0.25)	Br	98	ND
8	PICB–NHC–Ni **6b** (0.10)	Br	95	ND
9	PICB–NHC–Ni **6d** (0.10)	Br	78	ND
10	PICB–NHC–Ni **6b** (0.25)	I	98	ND
11	PICB–NHC–Ni **6b** (0.25)	Cl	33	ND
12[c]	PICB–NHC–Ni **6b** (0.25)	Cl	94	ND
13[d]	PICB–NHC–Ni **6b** (0.5)	Cl	84	ND
14	PICB–NHC–Ni **6b** (0.25)	F	0	ND
15[c, d]	PICB–NHC–Ni **6b** (0.25)	F	71	ND
16[d, e]	PICB–NHC–Ni **6b** (0.25)	F	98	ND
17-20	Run 2nd, 3rd, 4th, 5th	Br	96[f]	–
21	Run 6th	Br	76	–
22-25	Run 7th,[g] 8th, 9th, 10th	Br	92[f]	–

[a]Determined by gas chromatography analysis using dodecane as an internal standard. [b]Determined by ICP-MS analysis. [c]The reaction was performed at 65 °C. [d]LiBr (1 equiv) was used as an additive. [e]The reaction was performed in DME at 100 °C. [f]Average yield. [g]The catalyst was reactivated by treatment with DBU. ND = Below the detection limit of the ICP equipment (<0.003−0.005 ppm).

The viability of recycling catalyst **6b** was examined in the CKT reaction of aryl bromide **7a** with **8a** (entries 17−25). Initially, the catalysts were easily recovered by simple filtration and could be reused for the next cycle after washing with THF and CH_2Cl_2 and then drying; however, significant loss of activity was observed with only 48% yield for the second use. STEM and energy-dispersive spectroscopy analysis of the recovered catalyst showed no change of morphology, but a large amount of magnesium species derived from the GRs remained. To remove the magnesium salts, we investigated different washing solvent systems and finally found that washing with an aqueous ammonia solution followed by washing with THF and CH_2Cl_2 could help to revive the catalytic activity completely.[27] For the next three cycles, using the same washing procedure, no significant loss of activity was observed. The yield dropped to 76% for the sixth use, since this catalyst had been stored for 2 months without any precaution (i.e., in bench/open-air conditions) (entry 21). Nevertheless, the activity could be recovered using a similar washing method followed by treatment with DBU (in order to regenerate NHC ligands). The high activity was successfully restored and remained for a further five uses. These recovery and reuse experiments demonstrate the recyclability of **6b** and in particular the robustness of the embedded NHC ligands.

Table 3. Substrate Generality



Entry	R–X	R'–MgX'	Results
1–8	Br R = (7a) –Me (7b) –H (7c) –OMe (7d) –CF_3 (7e) –Cl	MgX R' = (8a) –H (8b) –F (8c) –^{t}Bu (8d) –OMe	R' R (9aa) 92%[a] (9ea) 89%[a] (9ba) 98%[a] (9cb) 86%[a] (9ca) 91%[a] (9cc) 79%[a] (9da) 74%[a] (9ea) 89%[a]
9	Cl Cl (7f)	(8a)	Ph Ph (9fa) 88%[b, c, e]
10	F–Cl (7g)	(8c)	R–R (9gc) 85%[b, d, e] R = 4-^{t}Bu-(C_6H_4)-
11	2-Naph−Br (7h)	(8c)	2-Naph−(C_6H_4)-4-^{t}Bu (9hc) 96%[a]
12	1-Naph−Br (7i)	c-Hex−MgCl (8f)	1-Naph−c-Hex (9if) 84%[a]
13	(7h)	^{t}Bu−MgBr (8e)	2-Naph−^{t}Bu (9he) 71%[a, e, f, g]
14-15	X N (7j) 3-Br (7k) 8-Cl	(8a)	Ph N (7ja) 79%[a, f, g] (7ka) 68%[b, c, f]
16	2Py−Cl (7l)	n-Hex−MgCl (8g)	2Py−n-Hex (9lg) 98%[b]
17	Br Ph (7m) E/Z = 6:1	(8f)	c-Hex Ph (9mf) 93%[a] E/Z > 99:1
18	Oct−I (7n)	(8a)	Oct−Ph (9na) 97%[a]
19	(7n)	PhH_2C−MgCl (8g)	Oct−CH_2Ph (9ng) 88%[a]
20-21	R I R = (7o), –CN (7p), –CO_2Et	Ph−MgCl•LiCl (8h)	R Ph (9oh), 80%[f, g] (9ph), 69%[f, g]
22	(7n)	EtO_2C MgCl•LiCl (8i)	Oct CO_2Et (9ai) 52%[g]

[a]R-X (1 equiv), GR (1.25 equiv), **6b** (0.25 mol% as Ni), THF, RT, 12 h. [b]R-X (1 equiv), GR (1.25 equiv), LiBr (1 equiv), **6b** (0.5 mol% as Ni), THF, RT, 12 h. [c]The reaction was performed at 65 °C. [d]The reaction was performed in DME at 100 °C. [e]2.5 equiv of GRs was used. [f]GR was slowly added. [g]Isolated with contaminating reductive dehalogenated (RH) product (~5−10%). [g]R-X (1 equiv), R-MgCl·LiCl (0. 1.25 equiv), **6b** (2.5 mol% as Ni), THF, 0 °C, 12 h.

With optimized conditions in hand, we next studied the scope and limitation of the CKT reaction (Table 3). First, we focused on sp^2−sp^2 bond formation using aryl bromide at RT and 0.25 mol% of **6b**. Both electron-rich and electron-deficient aryl substrates for both aryl halide and/or GRs worked well in this reaction (entries 1−7). Under these conditions, 1-bromo-3-chlorobenzene (**7e**) reacted only via the bromide part to lead exclusively to product **9ea** in high yield (entry 8). 1,3-Dichlorobenzene was converted under reflux conditions to *m*-terphenyl (**9fa**) in 8% yield (entry 9). Similar reactivity was observed with *p*-chloro-fluorobenzene (**7g**), and the reaction was performed at 100 °C in DME to give **9gc** in 85% yield (entry 10). The naphthyl group was also tolerated, and a high yield with *tert*-butyl-phenylmagnesium bromide (**8c**) was obtained (entry 11). Next, sp^2−sp^3 bond formation was investigated using alkyl GRs. Cyclohexylmagnesium chloride (**8f**) reacted with **7i** to afford **9if** in 84% yield, and **9he** was also obtained with the more difficult *tert*-butylmagnesium bromide (**8e**) (entries 12 and 13).[19b] We then turned our attention to heteroaromatic halides. 3-Bromoquinoline (**7j**) reacted with **8a** to afford **9ja** in 79% yield under standard conditions, while 8-chloroquinoline (**7k**) required higher reaction temperatures (reflux conditions) to form the cross-coupling product **9ka** in 68% yield, whereas 2-chloropyridine (**7l**) reacted with hexylmagnesium chloride (**8g**) at RT to give **9lg** in excellent yield (entries 13−16). Next, a mixture of (*E*) and (*Z*) isomers of *β*-bromostyrene (**7m**) was tested with **8f**, and the product **9mf** was obtained with only (*E*)-configuration in excellent yield (entry 17). With alkyl iodine compounds **7n** and **8a**, the cross-coupling product **9na** was obtained in excellent yield (entry 18). With sp^3−sp^3 cross-coupling, using **7n** and benzylmagnesium chloride (**8g**), the corresponding coupling product **9ng** was obtained in high yield (entry 19). Next, we investigated the functional group tolerance using GR prepared from Knochel's method.[28] The coupling products **9oh** and **9ph** were obtained in good yields with complete integrity of ester and cyano groups using lower temperature (0 °C) and 2.5 mol% of catalyst **6b** (entries 20 and 21).[29] Finally, even functionalized Knochel-type GR such as **8i** proved to be competent under these conditions (entry 22). To our best of knowledge, the direct use of Knochel-type GRs with Ni catalysts is unprecedented in the literature.

In summary, we have developed Ni-NPs catalysts with NHC precursor moieties, which play dual roles: cross-linking parts in the PI method and access to NHC ligands to activate Ni-NPs. These NHCs embedded in the polymer matrix were characterized by FGSR-MAS NMR analysis. Using this novel immobilization method, we demonstrate that ligands and Ni-NPs could be immobilized together to offer a direct, usable heterogeneous catalyst for which no external ligands are necessary. This heterogeneous catalyst was successfully applied to CKT reactions with quite wide substrate generality (e.g., aryl, vinyl, and alkyl halides with aryl or alkyl, Knochel-type GRs) in high yields including functional group tolerance. As for heterogeneous reactions in general, the simplicity in workup is especially attractive. Importantly, retention of nickel on the solid support without leaching allows products without metal contamination and results in recovery and reuse to decrease waste and to develop greener synthetic methods. We believe that the direct comparison of catalytic activities between PI Ni-NPs with embedded NHCs and PI Ni-NPs prepared from copolymer **1** could explain the positive effect of NHC ligands on the Ni-NPs. Further applications of these Ni-NPs catalysts to other reactions and more investigations to understand the surface interaction between Ni-NPs and NHC moieties in polymer are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Reaction procedure and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Table 1 graphic was replaced on July 10, 2013.