Nickel-catalyzed Homo-coupling of Aryl Ethers with Magnesium Anthracene Reductant

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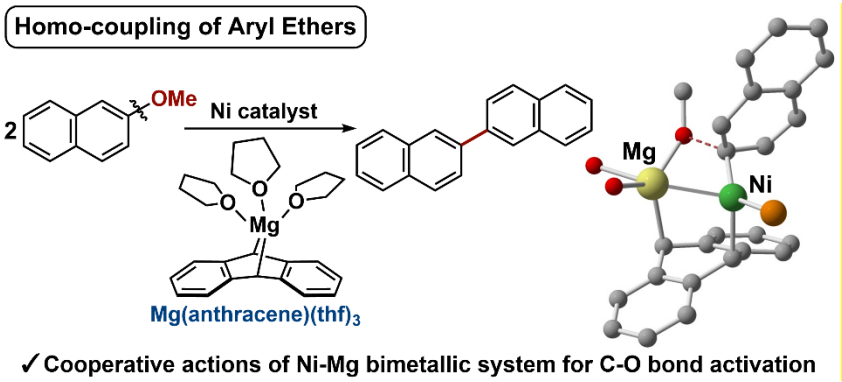

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Abstract Nickel-catalyzed reductive homo-coupling of aryl ethers has been achieved with Mg(anthracene)(thf)$_3$ as a readily available low-cost reductant. DFT calculations provided a rationale for the specific efficiency of the diorganomagnesium-type two-electron reducing agent. The calculations showed that the dianionic anthracene-9,10-diyl ligand reduces the two aryl ether substrates resulting in the homo-coupling reaction through supplying the electrons to the Ni-Mg bimetallic system to form organomagnesium nickel(0)-ate complexes, which cause two sequential C–O bond cleavage reactions. The calculations also showed cooperative actions of Lewis-acidic magnesium atoms and electron-rich nickel atoms in the C–O cleavage reactions.

Key words Homo-coupling, C–O Bond Activation, Nickel Catalyst, Magnesium Anthracene, DFT Calculation

Homo-coupling of aryl halides is a straightforward method for preparing symmetrical biaryls as key building blocks of electronic materials, dyes, and biologically active compounds.[1] This reaction was first demonstrated by Ullmann in 1901 using copper as a stoichiometric reductant.[2] In the pursuit of better selectivity and reaction efficiency, a number of protocols using transition metal catalysts in addition to stoichiometric reductants has since been developed.[3,4] While aryl halides and aryl sulfonates are common substrates for the homo-coupling reactions, extension of the scope of homo-coupling toward using aryl ethers, which are attractive substrates in terms of their ready availability from nature, is a formidable challenge at this moment. In this regard, Chatani and Tobisu reported the nickel-catalyzed homo-coupling of methoxyarenes using bis(neopentyl glycolato)diborane [B$_2$(nep)$_2$] as a reductant.[5] This homo-coupling reaction consisted of two nickel-catalyzed reactions. One is the borylation of the methoxyarene substrate (ArOMe) to form the corresponding arylboronate [ArB(nep)], and the other is the subsequent Suzuki–Miyaura-type cross-coupling between the arylboronate and a second molecule of methoxyarene. A major issue for this transformation is the use of the expensive boron reagent B$_2$(nep)$_2$ as a stoichiometric reductant, generating costly waste.

Considering the potential of nickel catalysis in the development of efficient homo-coupling of aryl ethers and the well-demonstrated importance of Lewis-acidic cooperative participation of organometallic reagents in C–O bond cleavage by a nickel(0) species,[6,7] we focused on Mg(anthracene)(thf)$_3$ (**1**)[8–11] as a potentially suitable reducing agent. Mg(anthracene)(thf)$_3$ is easily prepared from inexpensive magnesium powder and anthracene in THF (Figure 1).[12] Here, we report nickel-catalyzed homo-coupling of aryl ethers using Mg(anthracene)(thf)$_3$ (**1**) as a stoichiometric reductant. The use of reductant **1** was crucial for the homo-coupling. Density functional theory (DFT) calculations suggested the occurrence of cooperative Ni-Mg bimetallic C–O bond activation through the formation of organomagnesium nickel(0)-ate complexes and Lewis acidic activation of the alkoxy leaving groups by ionized magnesium atoms.

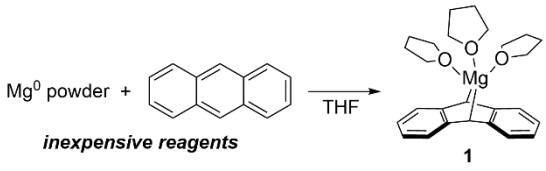


Figure 1. Preparation and a chemical structure of Mg(anthracene)(thf)$_3$ (**1**).

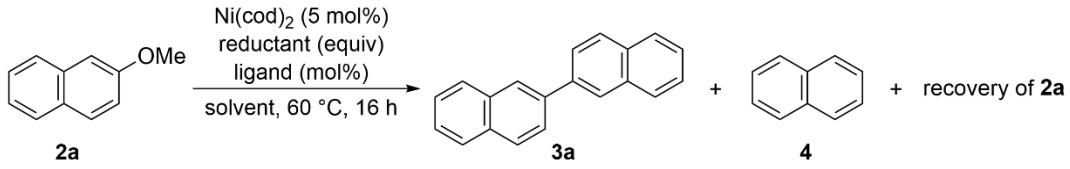
Specifically, the reaction of 2-methoxynaphthalene (**2a**) with an equimolar amount of Mg(anthracene)(thf)$_3$ (**1**) (**2a**/1=1/1) in the presence of a nickel-phosphine catalyst prepared *in situ* from Ni(cod)$_2$ (5 mol%) and tricyclohexylphosphine (20 mol%) in THF at 60 °C for 16 hours gave the desired homo-coupling product 2,2'-binaphthalene (**3a**) in 79% yield (Table 1, entry 1). This reaction formed a small amount of naphthalene (**4**, 5 %) as detected by ^{1}H NMR analysis of a crude mixture. The use of **1** was essential since **3a** was not obtained when other metal powder reductants such as magnesium, zinc, and manganese were used

(entries 2-4). The reaction in the presence of a stoichiometric amount of $Ni(cod)_2$ without using an additional reductant did not cause the reaction of **2a** (entry 5). The use of a catalytic amount (10 mol%) of **1** with a stoichiometric amount of magnesium powder resulted in only 9% yield of **3a** (entry 6), indicating that the use of pre-formed Mg(anthracene)$(thf)_3$ (**1**) is essential.

Next, ligand effects were examined. When triphenylphosphine was employed as a ligand, **3a** was not obtained at all (entry 7). The use of 1,2-bis(dicyclohexylphosphino)ethane (dcype) as a peralkylbisphosphine ligand also caused no reaction (entry 8). While 1,3-dimesitylimidazol-2-ylidene (IMes) as a *N*-heterocyclic carbene ligand caused moderate catalytic activity to afford **3a** in 68% yield (entry 9), only a trace amount of **3a** was obtained with the more sterically demanding ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (entry 10). Thus, tricyclohexylphosphine was selected as the optimal ligand. When the amount of tricyclohexylphosphine was reduced to 10 mol% (Ni/P=1/2), the catalytic activity was maintained to give **3a** in 80% yield (entry 11). However, further reduction of the amount of the ligand to 5 mol% (Ni/P=1/1) resulted in a decreased yield (69%, entry 12). The homo-coupling reaction of **2a** also occurred even in the absence of the phosphine ligand albeit with a lower yield (49%) of **3a** (entry 13). Heating the solution of **2a** and Mg(anthracene)$(thf)_3$ (**1**) in THF at 60 °C for 16 h in the absence of a nickel catalyst resulted in complete recovery of **2a**, indicating that direct reduction of **2a** with **1** did not occur under the reaction conditions (entry 14). The use of nickel(II) complex $Ni(acac)_2$ instead of $Ni(cod)_2$ led to decreased yield (20%, entry 15).[13] Cyclopentyl methyl ether (CPME), 1,4-dioxane, dimethoxyethane (DME), and toluene as a reaction solvent also gave the homo-coupling product albeit with lower yields (entries 16-19).

The use of an equimolar amount of the reductant **1** relative to **2a** was optimal for the homo-coupling of **2a** (Table 1, entries 1 and 11). Either an increase or a decrease in the relative amount of **1** caused a slight decrease in the homo-coupling efficiency; the use of 1.5 and 0.75 equivalents of **1** gave **3a** in 72% and 71% yields, respectively (Table 1, entries 20 and 21). The variation of the optimal reaction conditions (entry 11) by adding varying amounts of anthracene caused a significant decrease in the yield of the homo-coupling product **3a**, with 20 mol% and 50 mol% of anthracene giving **3a** in only 61% and 44% yields, respectively (entries 22 and 23). These inhibitory effects of anthracene suggest that anthracene generated *in situ* from **1** as the reaction proceeds may suppress the efficiency of nickel catalysis through anthracene-nickel π-coordination. This unfavorable interaction may be the cause of incomplete conversion of the starting material under the optimal conditions (entries 1, 11).

Table 1. Screening of Reaction Conditions[a]



entry	reductant (equiv)	ligand (mol%)	solvent	yield of **3a** [%][b]	yield of **4** [%][b]	recovery of **2a** [%][b]
1	**1** (1.0 equiv)	PCy_3 (20 mol%)	THF	79	5	14
2	Mg^0 (1.0 equiv)	PCy_3 (20 mol%)	THF	0	1	97
3	Zn^0 (1.0 equiv)	PCy_3 (20 mol%)	THF	0	trace	>99
4	Mn^0 (1.0 equiv)	PCy_3 (20 mol%)	THF	0	trace	>99
5	$Ni(cod)_2$ (1.0 equiv)	PCy_3 (200 mol%)	THF	0	0	>99
6	**1** (0.1 equiv) Mg^0 (1.0 equiv)	PCy_3 (20 mol%)	THF	9	1	88
7	**1** (1.0 equiv)	PPh_3 (20 mol%)	THF	0	3	94
8	**1** (1.0 equiv)	dcype (10 mol%)	THF	0	0	>99
9	**1** (1.0 equiv)	IMes (20 mol%)	THF	68	15	13
10	**1** (1.0 equiv)	IPr (20 mol%)	THF	trace	2	95
11	**1** (1.0 equiv)	PCy_3 (10 mol%)	THF	80 (73)[c]	5	15
12	**1** (1.0 equiv)	PCy_3 (5 mol%)	THF	69	4	23
13	**1** (1.0 equiv)	none	THF	49	4	45
14[d]	**1** (1.0 equiv)	PCy_3 (20 mol%)	THF	0	0	>99
15[e]	**1** (1.0 equiv)	PCy_3 (10 mol%)	THF	20	6	68
16	**1** (1.0 equiv)	PCy_3 (10 mol%)	CPME	62	5	29

17	**1** (1.0 equiv)	PCy_3 (10 mol%)	1,4-dioxane	62	2	28
18	**1** (1.0 equiv)	PCy_3 (10 mol%)	DME	15	1	83
19	**1** (1.0 equiv)	PCy_3 (10 mol%)	toluene	48	3	45
20	**1** (1.5 equiv)	PCy_3 (10 mol%)	THF	72	4	19
21	**1** (0.75 equiv)	PCy_3 (10 mol%)	THF	71	4	23
22	**1** (1.0 equiv) anthracene (0.2 equiv)	PCy_3 (10 mol%)	THF	61	5	31
23	**1** (1.0 equiv) anthracene (0.5 equiv)	PCy_3 (10 mol%)	THF	44	4	49

[a] **2a** (0.1 mmol), reductant (xx equiv), $Ni(cod)_2$ (5 mol%), and ligand (yy mol%) in dry THF (0.5 mL) at 60 ˚C for 16 h. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield. [d] Without $Ni(cod)_2$. [e] Using $Ni(acac)_2$ instead of $Ni(cod)_2$.

With the optimized conditions (Table 1, entry 11) in hand, the reactivity of various ethers derived from 2-naphthol was investigated (Figure 2). The leaving group had a strong impact on the reactivity. The yield of the homo-coupling product **3a** decreased in the order of increasing bulkiness of the leaving group (ethyl ether **2b,** 36 %; butyl ether **2c**, 19 %; isopropyl ether **2d,** 3 %). Methoxyethoxyethyl ether **2e** gave product **3a** in moderate yield (56 %), suggesting that the chelation of the leaving group to the ionized magnesium atom may have enhanced the reactivity, while no chelation effect was observed with methoxymethyl (MOM) ether **2f**, which gave **3a** in only 20% yield. Interestingly, a symmetrical diaryl ether 2,2'-oxydinaphthalene (**2g**) gave **3a**, which corresponds to the deoxygenation product, in 33% yield based on the molar amount of the used **2g**. This appeared, however, not to be a deoxygenation reaction but the homo-coupling of two aryl ether molecules (66% yield as the product of homo-coupling reaction) since 2-naphthol was observed in the crude product mixture in 79% yield. 2-Phenoxynaphthalene (**2h**) underwent selective C(naphthyl)–O bond cleavage resulting in the homo-coupling of the 2-naphthyl group to afford **3a** in 43% yield with the formation of phenol in 53% yield. The attempted reaction of carbamate **2i** resulted in decomposition of the starting material.

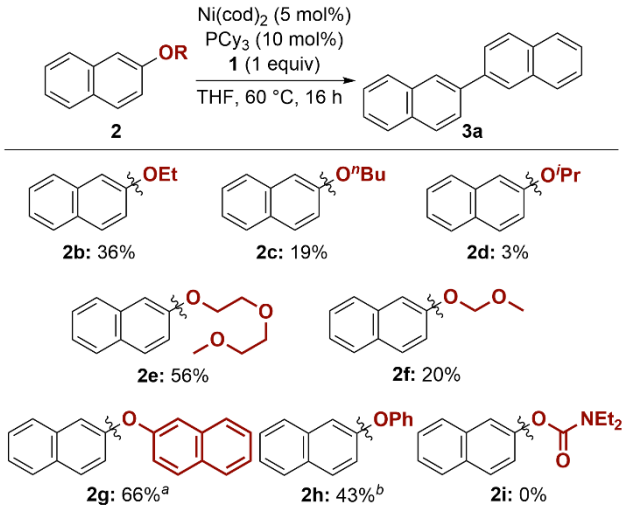


Figure 2. Effects of leaving groups. Substrate (0.1 mmol), **1** (0.1 mmol), $Ni(cod)_2$ (5 mol%), and PCy_3 (10 mol%) in dry THF (0.5 mL) at 60 ˚C for 16 h. Yield was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [a] 2-Naphthol was obtained in 79% yield. [b] Phenol was obtained in 53% yield.

Next, the scope and limitations of aryl methyl ethers were examined (Figure 3). 6-Hexyl-2-methoxynaphthalene (**2j**) and 1-(6-methoxynaphthalen-2-yl)piperidine (**2k**) gave the corresponding homo-coupling products in moderate yields (60% and 63%). Triarylamines **2l**,**m** and carbazole-substituted naphthyl ether **2n** served as substrates, and the desired products were obtained in 60%, 37%, and 35% yields, respectively. Interestingly, the methoxy groups on the aniline moieties of **2m** remained intact, resulting in a site-selective reaction at the naphthyl moiety. 2-Methoxy-9-methyl-9*H*-carbazole (**2o**) afforded the corresponding biscarbazole product in 19% yield. In the reaction of 2-methoxytriphenylene (**2p**), a non-negligible amount of triphenylene (22%) was produced as a reduction product, diminishing the yield of the desired homo-coupling product to 14%. 1-Methoxynaphthalene (**2q**) and 4-methoxybiphenyl (**2r**) were inert compounds for this protocol. The reaction of 6-methoxyquinoline (**2s**) and (*E*)-(3-methoxyprop-1-en-1-yl)benzene (**2t**) resulted in decomposition of the starting materials.

To test the applicability of this reaction to large-scale synthesis, the homo-coupling of **2a** was conducted on a 4.0 mmol scale. After the reaction, residual Mg(anthracene)$(thf)_3$ (**1**) was quenched with 1M HCl aqueous solution at 0 °C, and anthracene and residual **2a** were easily removed by Kugelrohr distillation at 150 °C (0.1 mmHg). The crude mixture was purified by silica-gel column chromatography to afford **3a** in 51% yield.

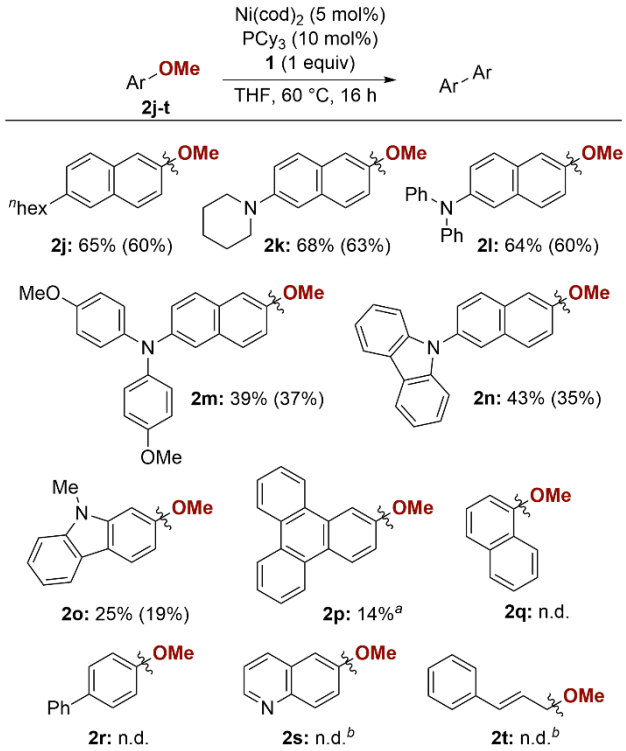


Figure 3. Scope and limitations. Substrate (0.1 mmol), **1** (0.1 mmol), $Ni(cod)_2$ (5 mol%), and PCy_3 (10 mol%) in dry THF (0.5 mL) at 60 °C for 16 h. Yield was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield is shown in parenthesis. n.d.: Homo-coupling product was not detected in the crude product. [a] Triphenylene was obtained in 22% yield. [b] Complex mixture was observed.

To gain insight into the reaction mechanism, DFT calculations were conducted. It was reported that C–O bond cleavage with a nickel(0) complex through conventional oxidative addition requires a high activation energy.[14] Harsh conditions are often required for nickel-catalyzed transformation of aryl ethers *via* C–O bond cleavage,[6] with exception of the Kumada-Tamao-Corriu-type coupling of aryl ethers using Grignard reagents as a coupling partner that occur under much milder conditions in many cases.[15,16] Regarding this issue, DFT calculation studies by Uchiyama and Wang suggested that *in situ* generation of nickel(0)-ate complexes from nickel(0) complexes and Grignard reagents would be the key for C–O bond cleavage.[17] Based on this knowledge and the analogy between Grignard reagents and $Mg(anthracene)(thf)_3$ (**1**),[9] we performed DFT calculations for nickel-catalyzed homo-coupling of 2-naphthyl methyl ether (**2a**) with **1** as a reductant, focusing on the nature of the nickel(0)-ate complexes and Lewis-acidic characters of the ionized magnesium atom.

The geometry optimization was carried out at the M06/lanl2dz (for Ni), 6-31G(d) (for others)/PCM(THF) level of theory, and additional single-point calculations were performed at the M06/SDD (for Ni), 6-311++G(d,p) (for others)/PCM(THF) level of theory.[18] The obtained energy diagram is shown in Figure 4. Replacement of a THF molecule on the magnesium atom of **1** with 2-methoxynaphthalene (**2a**, shown in red) gives **Int-1**. Subsequent η^2-coordination of 2-methoxynaphthalene at the C1–C2 unsaturated bond to $Ni(PCy_3)$ forms **Int-2**, which undergoes migration of the negatively charged 9-anthracenyl carbon atom from the magnesium atom to the nickel atom to form the more stable magnesium nickel(0)-ate complex **Int-3**. This key intermediate undergoes C–O bond cleavage with Lewis-acidic cooperative participation of the ionized magnesium atom with a reasonable energy barrier (**$TS_{3\text{-}4}$**, 12.1 kcal/mol) to give **Int-4**. As shown in Figure 5, this bimetallic C–O bond cleavage (**Int-3**-**$TS_{3\text{-}4}$**-**Int-4**) is accompanied by significant flattening of the anthracen-9,10-diyl ligand, which corresponds to electron release from the dianionic ligand to the nickel center. We propose that this electron release is the key for facile C–O cleavage. Moreover, we noticed that the nickel center of the C–O cleavage product (**Int-4**) remains electron-rich due to this electron-releasing effect of the anthracene-9,10-diyl ligand. Figure 5b shows that the methoxy ligand is bound solely to the magnesium atom and that the 2-naphthyl ligand is also σ-bonded to the magnesium atom with π-coordination to the nickel atom. Next, **Int-4** undergoes replacement of another THF molecule on the magnesium atom with the second 2-methoxynaphthalene molecule (**2a**, shown in blue) to form **Int-5**. Energetically favorable dissociation of a neutral anthracene molecule accompanied by π-coordination of the second 2-methoxynaphthalene molecule to the nickel atom produces a new magnesium nickel(0)-ate complex (**Int-6**) with the release of energy as high as 24.2 kcal/mol. The second C–O cleavage proceeds again in bimetallic mode with an energy barrier of 11.9 kcal/mol to afford diaryl nickel(II) complex **Int-7**. Note that after this C–O cleavage the 2-naphthyl ligand originating from the first 2-methoxynaphthalene molecule loses its interaction with the magnesium atom, consequently forming a complete σ-bond with the nickel atom. Finally, reductive elimination of **Int-7** gives the biaryl product (**3a**) and a nickel(0) species, which then enters the second catalytic cycle (see Supporting Information for details of the calculations on the reductive elimination step). Thus, this computationally obtained reaction pathway illustrates the characteristic features of the $Mg(anthracene)(thf)_3$ (**1**) reductant, which forms electron-rich organomagnesium nickel(0)-ate complexes as key intermediates for the two sequential aryl ether C–O bond cleavage reactions.

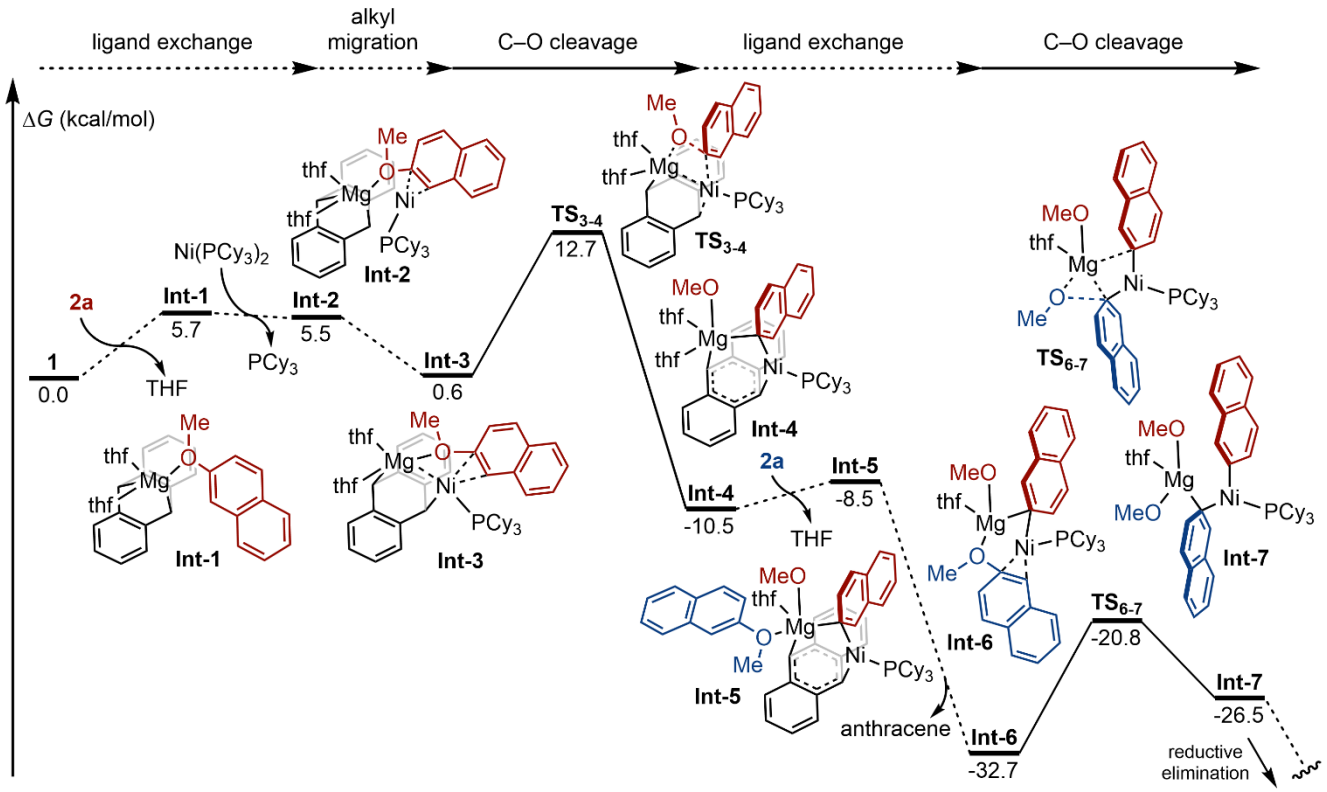


Figure 4. Energy diagram for homo-coupling of 2-methoxynaphthalene (**2a**) mediated by Mg(anthracene)(thf)$_3$ (**1**) and Ni(PCy$_3$)$_2$. Calculations were performed at M06/SDD (for Ni), 6-311++G(d,p) (for others)/PCM(THF)// M06/lanl2dz (for Ni), 6-31G(d) (for others)/PCM(THF) level of theory.

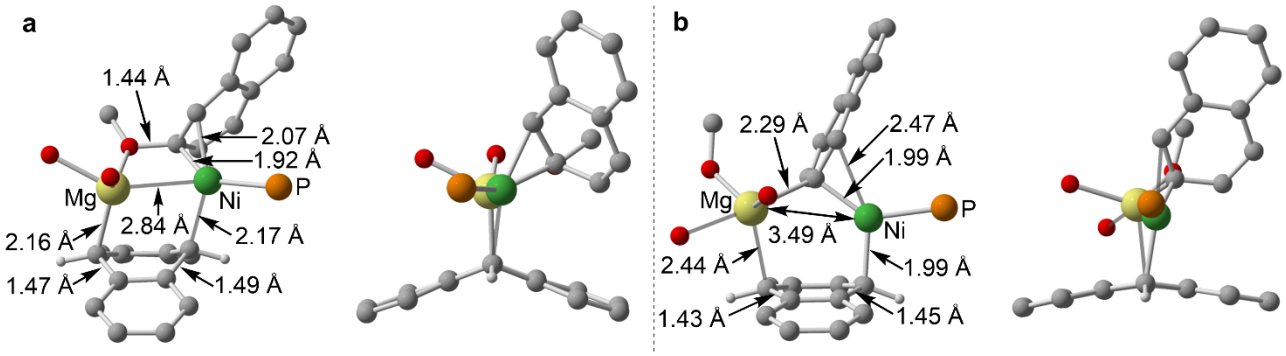


Figure 5. Structures of (a) **Int-3** and (b) **Int-4**. Hydrogen atoms, cyclohexyl groups on phosphorus atoms, and carbon frameworks of THF molecules are omitted for clarity.

In summary, we developed a nickel-catalyzed homo-coupling of aryl ethers with Mg(anthracene)(thf)$_3$ as a readily available low-cost reductant. DFT calculations provided the rationale for the specific efficiency of Mg(anthracene)(thf)$_3$ as a stoichiometric two-electron reductant. The dianionic anthracene-9,10-diyl ligand donates electrons to the Ni-Mg bimetallic system to form electron-rich magnesium nickel(0)-ate complexes. These cause two sequential aryl ether C–O bond cleavage reactions through cooperative actions of Lewis-acidic magnesium atoms and electron-rich nickel atoms.

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All air and moisture-sensitive reactions were performed using standard Schlenk techniques or a glove box under a nitrogen gas atmosphere. THF was dried and deoxygenated with a Grubbs column system (Glass Counter Solvent Dispensing System, Nikko Hansen & Co, Ltd.). Mg(anthracene)(thf)$_3$ was prepared according to the reported procedure,[12] and was stored and treated in the nitrogen-filled glove box. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were measured on a JEOL ECZ-400S spectrometer. High resolution mass spectra were obtained with Thermo Fisher Scientific Exactive and JEOL JMS-T100GCv spectrometers at the Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University. IR spectra were obtained on a JASCO FT-IR-4600 spectrometer. Flash column chromatography was performed using silica gel (Wakogel FC-40, 0.020-0.040 nm >70%).

Homo-coupling of Aryl Ethers

In a nitrogen-filled glove box, an aryl ether (0.1 mmol) was placed in a screw vial containing a stir bar. Ni(cod)$_2$ (1.4 mg, 0.005 mmol, 5 mol%), PCy$_3$ (2.8 mg, 0.01 mmol, 10 mol%), Mg(anthracene)(thf)$_3$ (41.9 mg, 0.1 mmol, 1 equiv), and dry THF (0.5 mL) were added into the vial. The vial was sealed with a screw cap and taken out from the glove box. After stirring at 60 °C for 16 hours, the resulting mixture was cooled to room temperature and quenched

with 1M HCl aq. In the case of amine compounds, the resulting mixture was neutralized with saturated $NaHCO_3$ aq. The organic layer was extracted with dichloromethane and passed through a short-pad of silica-gel. After addition of an internal standard, the yield was determined by ^1H NMR analysis. The products were isolated according to the following procedures.

Isolation and Characterization of the Homo-coupled Products

2,2'-Binaphthalene (3a)[5]

A crude mixture was distilled to remove anthracene and 2-methoxynaphthalene (150 °C, 0.1 mmHg). Then, residual compounds were purified by silica-gel column chromatography (only hexane). White solid (9.25 mg, 73% yield). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.18 (s, 2H), 7.98-7.93 (m, 4H), 7.92-7.88 (m, 4H), 7.56-7.49 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 138.4, 133.7, 132.7, 128.5, 128.2, 127.7, 126.3, 126.1, 126.0, 125.7. HRMS (EI) m/z calc. for $C_{20}H_{14}$ 254.10955 found 254.10891.

6,6'-Dihexyl-2,2'-binaphthalene[5]

A crude mixture was distilled to remove anthracene and 2-hexyl-6-methoxynaphthalene (150 °C, 0.1 mmHg). Then, residual compounds were purified by silica-gel column chromatography (only hexane). White solid (12.72 mg, 60% yield). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.12 (s, 2H),7.90- 7.83 (m, 6H), 7.65 (s, 2H), 7.38 (dd, *J* = 8.5, 1.6 Hz, 2H), 2.80 (t, *J* = 7.7 Hz, 4H), 1.77-1.69 (m, 4H), 1.41-1.30 (m, 12H), 0.90 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 140.7, 137.7, 132.8, 132.2, 128.04, 127.95, 126.1, 125.7, 36.2, 31.8, 31.3, 29.0, 22.6, 14.1. HRMS (EI) m/z calc. for $C_{32}H_{38}$ 422.29735 found 422.29680.

6,6'-Di(piperidin-1-yl)-2,2'-binaphthalene

A crude mixture was purified by silica-gel column chromatography (EtOAc/hexane=3/100 to 1/10). Light brown solid (13.25 mg, 63% yield). mp: 175°C (decomp.). IR (ATR, ν/cm^{-1}): 2931 m, 2854 w, 2806 w, 1626 w, 1591 s, 1448 w, 1387 w, 1202 s, 1112 m, 926 m, 871 s, 802 m, 666 m, 630 w. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.01 (s, 2H), 7.80-7.75 (m, 6H), 7.31 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.16 (d, *J* = 2.1 Hz, 2H), 3.29 (t, *J* = 5.4 Hz, 8H), 1.82-1.74 (m, 8H), 1.68-1.60 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 150.1, 135.9, 133.8, 128.8, 128.6, 127.1, 125.8, 125.1, 120.4, 110.1, 50.9, 25.9, 24.4. HRMS (ESI$^+$) m/z calc. for $C_{30}H_{33}N_2$ 421.26383 found 421.26361.

***N*^{6},*N*^{6},*N*$^{6'}$,*N*$^{6'}$-Tetraphenyl-[2,2'-binaphthalene]-6,6'-diamine**

A crude mixture was purified by washing with EtOH. Light green solid (17.60 mg, 60% yield). mp: 245-247 °C. IR (ATR, ν/cm^{-1}): 3026 w, 1628 w, 1585 m, 1485 m, 1377 w, 1265 m, 1171 w, 876 m, 750 s, 692 s, 661 m, 613 w. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.06 (s, 2H), 7.79 (d, *J* = 9.2 Hz, 2H), 7.78 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 2.0 Hz, 2H), 7.33-7.27 (m, 10H), 7.16 (dd, *J* = 7.6, 1.2 Hz, 8H), 7.06 (tt, *J* = 7.2, 1.2 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 147.7, 145.6, 137.0, 133.5, 130.2, 129.3, 129,1, 127.5, 126.0, 125.4, 124.8, 124.4, 123.0, 119.8. HRMS (APCI) m/z calc. for $C_{44}H_{33}N_2$ 589.26383 found 589.26422.

***N*^{6},*N*^{6},*N*$^{6'}$,*N*$^{6'}$-Tetrakis(4-methoxyphenyl)-[2,2'-binaphthalene]-6,6'-diamine**[19]

A crude mixture was purified by silica-gel column chromatography (Et_2O/hexane=1/20 to 1/5). Pale yellow solid (13.15 mg, 37% yield). ^1H NMR (DMSO-d_6, 400 MHz, 25 °C): δ 8.15 (s, 2H), 7.81-7.79 (m, 4H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.11-7.04 (m, 12H), 6.93 (d, *J* = 9.2 Hz, 8H), 3.75 (s, 12H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 25 °C): δ 155.8, 146.3, 140.2, 134.9, 133.3, 129.1, 128.8, 127.1, 126.6, 125.4, 124.6, 121.9, 115.0, 114.2, 55.2. HRMS (EI) m/z calc. for $C_{48}H_{40}N_2O_4$ 708.29881 found 708.29908.

6,6'-Di(9*H*-carbazol-9-yl)-2,2'-binaphthalene

A crude mixture was purified by washing with EtOH. Light brown solid (10.13 mg, 35% yield). mp: 270 °C (decomp.). IR (ATR, ν/cm^{-1}): 2920 w, 2852 w, 2224 w, 1749 m, 1657 m, 1599 w, 1331w, 1126 s, 1043 m, 849 m, 596 m, 548 s. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.36 (s, 2H), 8.21-8.19 (m, 6H), 8.13 (d, *J* = 2.0 Hz, 2H), 8.09-8.03 (m, 4H), 7.76 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.45 (dt, *J* = 7.0, 0.8 Hz, 4H), 7.33 (dt, *J* = 7.0, 0.8 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 141.0, 138.8, 135.5, 133.3, 132.7, 130.2, 128,6, 126.6, 126.2, 126.0, 125.9, 125.1, 123.5, 120.4, 120.1, 109.8. HRMS (ESI$^+$) m/z calc. for $C_{44}H_{29}N_2$ 585.23253 found 585.23249.

9,9'-Dimethyl-9*H*,9'*H*-2,2'-bicarbazole[5]

A crude mixture was purified by silica-gel column chromatography (Et_2O/hexane=1/20 to 1/5). White solid (3.51 mg, 19% yield). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.19 (dd, *J* = 8.0, 0.5 Hz, 2H), 8.14 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.73 (d, *J* = 1.1 Hz, 2H), 7.64 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.29-7.25 (m, 2H), 3.95 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 141.6, 141.5, 140.2, 125.6, 122.6, 121.9, 120.5, 120.3, 119.1, 119.0, 108.4, 107.4, 29.2. HRMS (EI) m/z calc. for $C_{26}H_{20}N_2$ 360.16265 found 360.16214.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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