EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402391

Efficient Synthesis and Versatile Reactivity of Porphyrinyl Grignard Reagents

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Keywords: Porphyrinoids / Iodine–magnesium exchange / Grignard reaction / Metalation

Iodine–magnesium exchange between iodoporphyrins and *i*PrMgCl·LiCl proceeded successfully without decomposition of the porphyrin core. The resulting porphyrinyl Grignard reagents are nucleophilic enough to react with various carbonyl compounds, such as aldehydes, ketones, and amides. Furthermore, the porphyrinyl Grignard reagents underwent transmetalation to afford porphyrinyl copper and zinc species of mild and unique reactivity. These could be engaged in 1,4-addition and Negishi coupling, respectively.

Introduction

Porphyrins are an important class of heteroaromatic compounds that play a wide variety of roles in nature, such as in oxygen transport and photosynthesis.[1] Significant attention has been paid to the development of new porphyrins that exhibit interesting and useful properties in catalysis, biological applications, and materials sciences. Peripheral functionalizations of porphyrin cores definitely represent an effective process for the synthesis of porphyrins that have altered properties.

Metalation of the peripheries of porphyrins is regarded as a key step for peripheral functionalization because the resulting carbon–metal bond should be reactive towards various transformations.[2] Direct mercuration is historically important as the first peripheral metalation.[3] Although the resulting carbon–mercury bonds were usefully convertible, the toxicity of mercury would impede practical applications. In contrast, borylated porphyrins are easily accessible and safely underwent useful transformations[4] such as Suzuki–Miyaura cross-coupling, oxidative hydroxylation, and halogenation.[5]

Considering the importance of these borylated porphyrins, we expected that peripherally magnesiated porphyrins should also be fascinating synthetic intermediates because of their higher nucleophilicity and hence their potential to participate in a wider variety of efficient bond-forming processes.[6] However, the synthesis and reactions of magnesiated porphyrins remained unexplored. Chen et al. had reported the only example of the generation of a porphyrinyl Grignard reagent from *meso*-bromoporphyrin,[7] but use of commercially available magnesium turnings had been unsuccessful, and preparation of active Rieke magnesium in situ from $MgCl_2$, KI, and extremely reactive metallic potassium was essential. The Grignard reagent reacted with aromatic aldehydes in only low yields and reacted anomalously with ketones to form α-porphyrinylated ketones, the scope of electrophiles thus being extremely limited and unusual. These results indicate that the formation of the Grignard reagent had been inefficient and accompanied by side reactions. In addition, the reactions had to be performed in a Barbier fashion to avoid decomposition of the Grignard reagent. We thus assumed that the efficient generation of the porphyrinyl Grignard reagent was difficult because a porphyrin skeleton is susceptible to nucleophilic attack,[8] single electron transfer,[9] and reductive demetalation[10] under Chen's conditions.

The preparation of functionalized Grignard reagents is rather difficult because insertion of magnesium metal into a carbon–halogen bond does not work under cryogenic conditions and many functional groups are incompatible under noncryogenic conditions. In 2004, Knochel et al. developed *i*PrMgCl·LiCl as a powerful tool for smooth halogen–magnesium exchange.[11] This breakthrough allowed the preparation of a variety of functionalized aryl and heteroaryl Grignard reagents at low temperatures, thereby considerably advancing organic synthesis. We envisioned that porphyrinyl Grignard reagents might be efficiently synthesizable at low temperatures through iodine–magnesium exchange with *i*PrMgCl·LiCl. This indeed proved to be the case, and here we wish to report the first efficient synthesis of porphyrinyl Grignard reagents and their versatile reactivity.

Results and Discussion

Firstly, we aimed to identify the formation of porphyrinyl Grignard reagent **2Ni**, prepared through the iodine–magnesium exchange reaction of Ni^{II} β-iodoporphyrin **1Ni**[5] (**1M**

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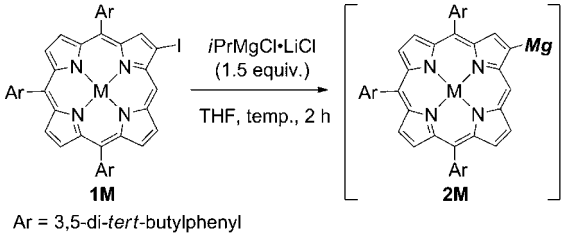
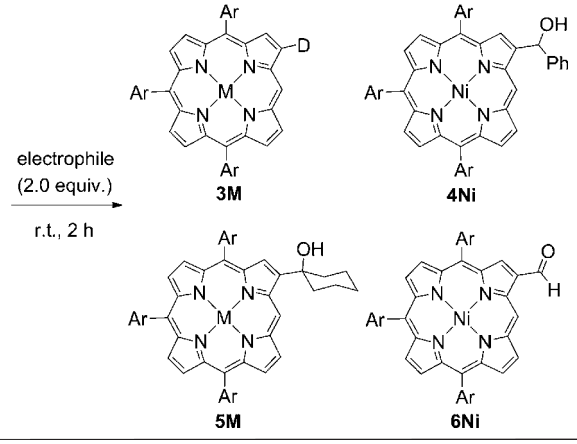
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402391.

with M = Ni, Table 1; throughout this manuscript Ar = 3,5-di-*tert*-butylphenyl and ***Mg*** located at the periphery denotes MgCl·LiCl.). After treatment of **1Ni** with *i*PrMgCl·LiCl in THF at –40 °C for 2 h, D_2O was added to the resulting reaction mixture to afford β-deuterioporphyrin **3Ni** in 95% yield. This result suggests that the iodine–magnesium exchange reaction provided **2Ni** without any significant side reactions. Indeed, **2Ni** showed typical Grignard behavior in reactions with carbonyl compounds, such as benzaldehyde, cyclohexanone, and dimethylformamide (DMF) to give **4Ni**, **5Ni**, and **6Ni**[12] in 78%, 71%, and 70% yields, respectively.

Table 1. Preparations and reactions of β-magnesiated porphyrins **2M**.





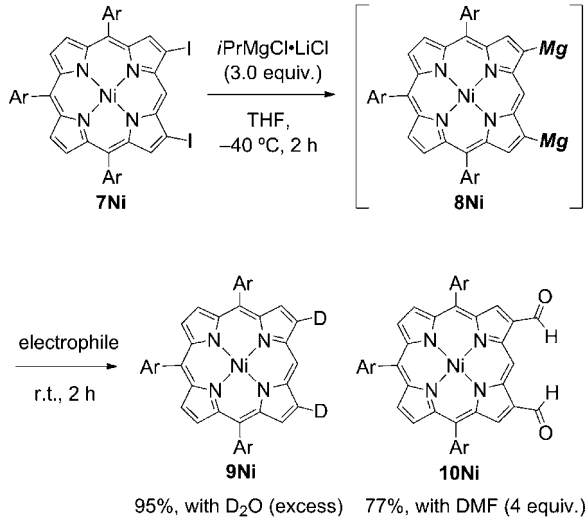
Entry	Substrate	Temp. [°C]	Electrophile	Product	Yield [%]
1	**1Ni**	–40	D_2O	**3Ni**	95[a]
2	**1Ni**	–40	PhCHO	**4Ni**	78
3	**1Ni**	–40	cyclohexanone	**5Ni**	70
4	**1Ni**	–40	DMF	**6Ni**	71
5	**1Zn**	–80	D_2O	**3Zn**	90[a]
6	**1Zn**	–80	cyclohexanone	**5Zn**	68

[a] With an excess amount of D_2O for 5 min.

Iodine–magnesium exchange with the zinc analogue **1Zn** was carried out at a lower temperature because zinc porphyrins were more labile under the reaction conditions. The formation of Zn^{II} porphyrinyl Grignard reagent **2Zn** was also confirmed by treatment with D_2O to give **3Zn** in 90% yield. Nucleophilic addition of **2Zn** to cyclohexanone also took place cleanly to provide **5Zn** in 68% yield.

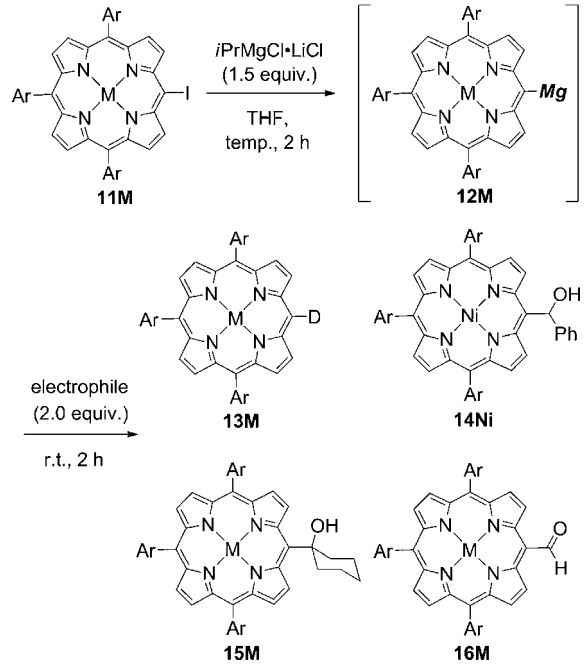
We also attempted twofold iodine–magnesium exchange of Ni^{II} β,β′-diiodoporphyrin **7Ni**[5l] with *i*PrMgCl·LiCl in THF at –40 °C (Scheme 1). The iodine–magnesium exchange was successful, and the resulting dimagnesiated complex **8Ni** was trapped with D_2O or DMF to furnish β,β′-dideuterio- or β,β′-diformylporphyrin **9Ni** or **10Ni** in 95% or 77% yields, respectively.

Encouraged by the success in these reactions of β-iodoporphyrins, we next tried to apply these procedures to *meso*-iodoporphyrins **11M**[13] (Table 2). Similar deuterium label-



Scheme 1. Dimagnesiation of β,β′-diiodoporphyrin **7Ni**.

Table 2. Preparations and reactions of *meso*-magnesiated porphyrins **12M**.



Entry	Substrate	Temp. [°C]	Electrophile	Product	Yield [%]
1	**11Ni**	–40	D_2O	**13Ni**	94[a]
2	**11Ni**	–40	PhCHO	**14Ni**	68
3	**11Ni**	–40	cyclohexanone	**15Ni**	39
4	**11Ni**	–40	DMF	**16Ni**	50[b]
5	**11Zn**	–80	D_2O	**13Zn**	92[a]
6	**11Zn**	–80	cyclohexanone	**15Zn**	18
7	**11Zn**	–80	DMF	**16Zn**	53[b]

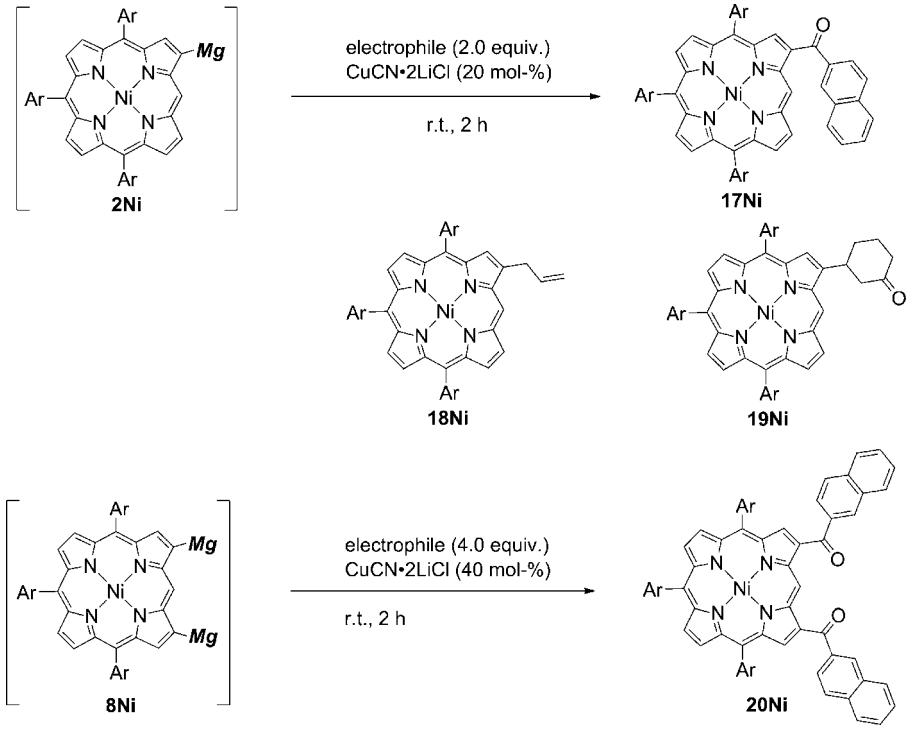
[a] With an excess amount of D_2O for 5 min. [b] For 24 h.

ing experiments strongly suggest quantitative formation of the corresponding Grignard reagent **12M** through iodine–magnesium exchange (Entries 1 and 5). *meso*-Magnesiated porphyrin **12Ni** also reacted with benzaldehyde to give **14Ni** in a reasonable yield of 68%. Unfortunately, however, the reactions with DMF required long times and furnished **16M** only in moderate yields, because of the low nucleophilicity of the sterically hindered *meso*-carbon. Treatment with cyclohexanone provided **15M**[12] only in low yields, due to competitive protonation of **12M** with the α-protons of cyclohexanone.

We then envisioned that the utility of the porphyrinyl Grignard reagents might be extended through transmetalation with other metal salts. Indeed, porphyrinyl copper species were generated from the corresponding porphyrinylmagnesium compounds and exhibited desired reactivities (Table 3). In the presence of a catalytic amount of CuCN·2 LiCl,[11a] porphyrinyl Grignard reagents **2Ni** and **8Ni** reacted with 2-naphthoyl chloride to give β-(2-naphthoyl)porphyrins **17Ni** and **20Ni**[12] in 72% and 62% yields, respectively. An S_N2' reaction with allyl bromide also proceeded to yield β-allylporphyrin **18Ni** efficiently. In the presence of chlorotrimethylsilane,[14] 1,4-addition to cyclohex-2-en-1-one occurred to provide the desired adduct **19Ni** in 68% yield. On the other hand, the reaction between porphyrinylmagnesium **2Ni** and cyclohex-2-en-1-one without CuCN·2 LiCl gave a rather complicated and inseparable mixture. APCI-TOF MS analysis of the mixture tentatively implied that the mixture included not only β-unsubstituted porphyrin and **19Ni** but also considerable amounts of β-phenylporphyrin and β-(cyclohexa-1,3-dienyl)porphyrin, which would result from 1,2-addition to cyclohex-2-en-1-one.

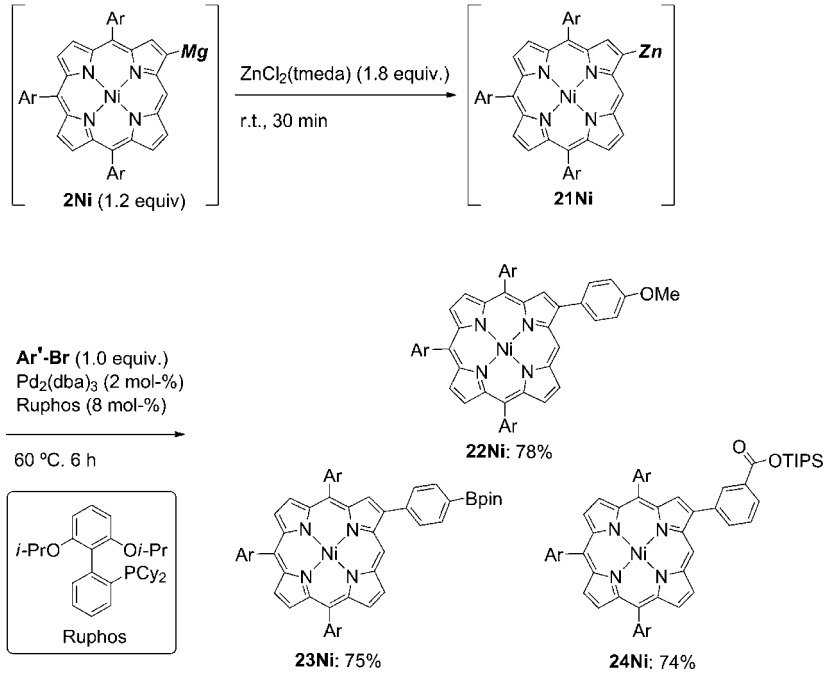
We finally examined Negishi cross-coupling of porphyrinylzinc species (Scheme 2). Porphyrinylzinc **21Ni** was prepared by transmetalation of porphyrinyl Grignard reagent **2Ni** with $ZnCl_2$(tmeda) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). In the presence of $Pd_2(dba)_3$/2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (Ruphos) catalyst,[15] Negishi cross-coupling between **21Ni** and 4-bromoanisole gave β-(4-anisyl)porphyrin **22Ni** in 78% yield. The high reactivity of organozinc reagents in transmetalation with aryl palladium halides allows activator-free cross-coupling. With this advantage, 4-bromophenylboronate reacted chemoselectively to yield **23Ni** with the boronate moiety remaining untouched. Furthermore, the low nucleophilicity of organozinc reagents toward carbonyl groups enabled cross-coupling between **21Ni** and triisopropylsilyl 3-bromobenzoate without any observable nucleophilic attack.

Table 3. Reactions of porphyrinyl copper.



Entry	Substrate	Electrophile	Product	Yield [%]
1	**2Ni**	2-naphthoyl chloride	**17Ni**	72
2	**2Ni**	allyl bromide	**18Ni**	80
3	**2Ni**	cyclohex-2-en-1-one	**19Ni**	68[a]
4	**8Ni**	2-naphthoyl chloride	**20Ni**	62

[a] With Me_3SiCl (2 equiv.).



Scheme 2. Negishi cross-coupling reactions of **21Ni**.

Conclusions

We have successfully achieved the efficient synthesis of peripherally magnesiated porphyrins through iodine–magnesium exchange between iodoporphyrins and *i*PrMgCl·LiCl under mild conditions. The porphyrinyl Grignard reagents reacted with various carbonyl compounds as powerfully as typical aryl Grignard reagents. Furthermore, transmetalation of the porphyrinyl Grignard reagents with copper and zinc salts proceeded efficiently. The resulting porphyrinyl copper and zinc species were employed for their specific reactions, such as 1,4-addition to enones and Negishi cross-coupling, respectively. Further applications of the Grignard reagents to synthesize new porphyrinoids are underway in our laboratory.

Experimental Section

Preparation of *i*PrMgCl·LiCl (1.0 M in THF):[11a] A flask containing magnesium turnings (0.67 g, 27.5 mmol) and anhydrous LiCl (1.06 g, 25 mmol) was dried in vacuo (1–3 Torr) for 3 h at 150 °C and then purged with argon. After the flask had cooled to room temperature, dry THF (12 mL) and 1,2-dibromoethane (0.05 mL) were added. A solution of *i*PrCl (2.28 mL, 25 mmol) in dry THF (12 mL) was then slowly added at room temperature. The reaction started within a few minutes. After the completion of the addition, the reaction mixture was stirred further for 12 h at room temperature. The resulting gray solution of *i*PrMgCl·LiCl was cannulated into another argon-filled Schlenk tube, to ensure that it was free of remaining magnesium metal. The solution was stored at –20 °C and could be kept for at least 1 month without significant decomposition.

Synthesis of 3Ni–6Ni: A Schlenk tube containing Ni^{II} β-iodoporphyrin **1Ni** (106 mg, 100 μmol) was purged with argon and then charged with dry THF (2.0 mL). After the solution had been cooled to –40 °C, *i*PrMgCl·LiCl (1.0 M solution in THF, 0.15 mL, 150 μmol) was slowly added, and then the reaction mixture was stirred for 2 h at –40 °C. An electrophile (200 μmol) was added to the resulting red solution. After having been stirred for 2 h at room temperature, the reaction mixture was quenched with a sufficient amount of NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography with elution with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **4Ni**–**6Ni**. For the synthesis of **3Ni**, D_2O (ca. 0.05 mL) was added as an electrophile and the resulting mixture was stirred for 5 min.

Compound 3Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1 H, *meso*), 9.13 (d, J = 4.6 Hz, 1 H, β), 8.93 (m, 2 H, β), 8.83 (m, 4 H, β), 7.90 (d, J = 1.8 Hz, 4 H, Ar-*o*), 7.87 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.74 (t, J = 1.8 Hz, 2 H, Ar-*p*), 7.71 (t, J = 1.8 Hz, 1 H, Ar-*p*), 1.49 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. HRMS (APCI-TOF): calcd for $C_{62}H_{71}DN_4{}^{58}Ni$ 931.5168 $[M]^-$; found 931.5174.

Compound 4Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 9.91 (s, 1 H, *meso*), 9.04 (d, J = 5.0 Hz, 1 H, β), 8.86 (d, J = 5.0 Hz, 1 H, β), 8.78 (s, 4 H, β), 8.75 (s, 1 H, β), 7.88 (d, J = 1.9 Hz, 2 H, Ar-*o*), 7.87 (br. s, 2 H, Ar-*o*), 7.85 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.78 (d, J = 7.8 Hz, 2 H, Ph), 7.75 (t, J = 1.9 Hz, 1 H, Ar-*p*), 7.73 (t, J = 1.8 Hz, 1 H, Ar-*p*), 7.71 (t, J = 1.8 Hz, 1 H, Ar-*p*), 7.40 (m, 3 H, Ph and benzyl), 7.32 (t, J = 7.8 Hz, 1 H, Ph), 2.80 (d, J = 4.1 Hz, 1 H, OH), 1.49 (s, 18 H, *tert*-butyl), 1.47 (s, 36 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.11, 149.03, 146.49, 143.80, 143.23, 143.19, 143.05, 142.69, 141.16, 140.39, 140.20, 140.06, 139.96, 132.88, 132.51, 132.45, 132.33, 132.29, 131.07, 129.22, 128.92, 128.83, 128.05, 127.32, 121.24, 121.23, 120.89,

120.12, 120.09, 102.36, 72.04, 35.16, 35.14, 31.85, 31.83 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (2.6×10^5), 525 nm (1.9×10^4). HRMS (APCI-TOF): calcd for $C_{69}H_{78}ON_4{}^{58}Ni$ 1036.5524 $[M]^-$; found 1036.5531.

Compound 5Ni: ^1H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 10.58 (s, 1 H, *meso*), 9.14 (d, J = 4.6 Hz, 1 H, β), 8.88 (d, J = 4.6 Hz, 1 H, β), 8.77 (m, 5 H, β), 7.90 (m, 4 H, Ar-*o*), 7.87 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.75 (m, 2 H, Ar-*p*), 7.72 (t, J = 1.8 Hz, 1 H, Ar-*p*), 2.72 (d, J = 13.3 Hz, 2 H, cyclohexyl), 2.55–2.49 (m, 2 H, cyclohexyl), 2.49 (s, 1 H, OH), 2.19–2.13 (m, 2 H, cyclohexyl), 1.93–1.85 (m, 3 H, cyclohexyl), 1.59–1.52 (m, 1 H, cyclohexyl), 1.51 (s, 18 H, *tert*-butyl), 1.50 (s, 18 H, *tert*-butyl), 1.47 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 151.76, 149.13, 149.10, 149.02, 143.03, 142.93, 142.88, 142.54, 142.49, 142.43, 140.64, 140.52, 140.28, 140.23, 140.12, 132.74, 132.55, 132.43, 132.26, 132.21, 129.28, 128.92, 128.83, 121.24, 121.18, 121.11, 120.49, 119.92, 119.40, 104.83, 73.12, 40.80, 35.19, 35.16, 35.13, 31.87, 31.84, 26.11, 22.76 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (2.6×10^5), 524 nm (1.9×10^4). HRMS (APCI-TOF): calcd for $C_{68}H_{82}ON_4{}^{58}Ni$ 1028.5837 $[M]^-$; found 1028.5846.

Compound 6Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.01 (s, 1 H, formyl), 10.69 (s, 1 H, *meso*), 9.37 (s, 1 H, β), 9.17 (d, J = 4.6 Hz, 1 H, β), 8.86 (d, J = 4.6 Hz, 1 H, β), 8.78 (m, 3 H, β), 8.74 (d, J = 4.9 Hz, 1 H, β), 7.88 (s, 2 H, Ar-*o*), 7.86 (s, 2 H, Ar-*o*), 7.83 (s, 2 H, Ar-*o*), 7.78 (s, 1 H, Ar-*p*), 7.74 (s, 1 H, Ar-*p*), 7.72 (s, 1 H, Ar-*p*), 1.50 (s, 18 H, *tert*-butyl), 1.49 (s, 18 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 188.04, 149.31, 149.21, 144.72, 144.64, 144.41, 143.75, 143.50, 142.76, 140.20, 139.77, 139.63, 139.52, 139.47, 139.34, 137.32, 134.00, 133.50, 133.46, 133.21, 133.06, 132.54, 128.87, 128.72, 122.99, 121.79, 121.43, 121.22, 119.84, 104.71, 35.18, 35.17, 35.14, 31.83, 31.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 426 (2.1×10^5), 535 (1.3×10^4), 577 (1.2×10^4). HRMS (APCI-TOF): calcd for $C_{63}H_{72}ON_4{}^{58}Ni$ 958.5054 $[M]^-$; found 958.5080.

Synthesis of 3Zn and 5Zn: This procedure is similar to that used for the synthesis of **3Ni**–**6Ni** except that iodine–magnesium exchange of **1Zn** was performed at –80 °C. Recrystallization from CH_2Cl_2/methanol gave **3Zn** (85 mg, 90 μmol, 90%) and **5Zn** (70 mg, 68 μmol, 68%).

Compound 3Zn: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.27 (s, 1 H, *meso*), 9.42 (d, J = 4.7 Hz, 1 H, β), 8.93 (m, 2 H, β), 9.06 (d, J = 4.6 Hz, 2 H, β), 9.03 (d, J = 4.6 Hz, 2 H, β), 8.12 (d, J = 1.9 Hz, 4 H, Ar-*o*), 8.09 (d, J = 2.0 Hz, 2 H, Ar-*o*), 7.82 (t, J = 1.9 Hz, 2 H, Ar-*p*), 7.79 (t, J = 2.0 Hz, 1 H, Ar-*p*), 1.55 (s, 36 H, *tert*-butyl), 1.52 (s, 18 H, *tert*-butyl) ppm. HRMS (APCI-TOF): calcd for $C_{62}H_{71}DN_4{}^{64}Zn$ 937.5106 $[M]^-$; found 937.5120.

Compound 5Zn: ^1H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 10.84 (s, 1 H, *meso*), 9.41 (d, J = 4.6 Hz, 1 H, β), 9.11 (d, J = 4.6 Hz, 1 H, β), 9.03 (m, 3 H, β), 8.99 (d, J = 4.6 Hz, 1 H, β), 8.85 (s, 1 H, β), 8.12 (m, 4 H, Ar-*o*), 8.09 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.83 (m, 2 H, Ar-*p*), 7.81 (br. s, 1 H, Ar-*p*), 2.72 (d, J = 13.3 Hz, 2 H, cyclohexyl), 2.55–2.49 (m, 2 H, cyclohexyl), 2.43 (s, 1 H, OH), 2.14–2.09 (m, 2 H, cyclohexyl), 1.94–1.86 (m, 3 H, cyclohexyl), 1.58 (s, 18 H, *tert*-butyl), 1.56 (s, 18 H, *tert*-butyl), 1.54 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 60 °C): δ = 150.76, 150.68, 150.30, 150.14, 149.71, 148.91, 148.88, 148.78, 148.31, 147.78, 142.39, 142.22, 142.13, 132.60, 132.40, 132.27, 132.20, 132.08, 131.93, 130.37, 129.85, 129.74, 129.27, 122.84, 122.17, 121.67, 121.02, 120.99, 120.81, 106.14, 73.24, 41.07, 35.31, 35.28, 35.21, 32.00, 21.97, 26.13, 22.79 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 418 (6.1×10^5), 545 nm (2.4×10^4). HRMS (APCI-TOF): calcd for $C_{68}H_{82}ON_4{}^{64}Zn$ 1034.5775 $[M]^-$; found 1034.5788.

Synthesis of 9Ni and 10Ni: A Schlenk tube containing Ni^{II} β,β′-diiodoporphyrin **7Ni** (118 mg, 100 μmol) was purged with argon and then charged with dry THF (2.0 mL). After the solution had been cooled to –40 °C, *i*PrMgCl·LiCl (1.0 M solution in THF, 0.30 mL, 300 μmol) was slowly added, and then the reaction mixture was stirred for 2 h at –40 °C. DMF (32 μL, 400 μmol) was added to the resulting red solution. After having been stirred for 2 h at room temperature, the reaction mixture was quenched with a sufficient amount of NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography with elution with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **10Ni** (76 mg, 77 μmol, 77%). For the synthesis of **9Ni** (88 mg, 94 μmol, 94%), D_2O (ca. 0.1 mL) was added instead of DMF and the resulting mixture was stirred for 5 min.

Compound 9Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1 H, *meso*), 8.93 (s, 2 H, β), 8.83 (m, 4 H, β), 7.90 (d, J = 1.8 Hz, 4 H, Ar-*o*), 7.87 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.74 (t, J = 1.8 Hz, 2 H, Ar-*p*), 7.71 (t, J = 1.8 Hz, 1 H, Ar-*p*), 1.49 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. HRMS (APCI-TOF): calcd for $C_{62}H_{70}D_2N_4{}^{58}Ni$ 932.5231 $[M]^-$; found 932.5235.

Compound 10Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.38 (s, 1 H, *meso*), 11.16 (s, 1 H, formyl), 9.38 (s, 2 H, β), 8.77 (d, J = 4.6 Hz, 2 H, β), 8.75 (d, J = 4.6 Hz, 2 H, β), 7.84 (d, J = 1.8 Hz, 4 H, Ar-*o*), 7.81 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.73 (t, J = 1.8 Hz, 2 H, Ar-*p*), 7.73 (t, J = 1.8 Hz, 1 H, Ar-*p*), 1.50 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 187.45, 149.54, 149.41, 144.83, 144.15, 140.90, 140.10, 139.59, 139.32, 139.00, 138.76, 133.81, 133.59, 128.84, 128.64, 122.85, 122.02, 121.69, 103.76, 35.19, 35.16, 31.82, 31.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 441 (2.0×10^5), 551 (1.4×10^4), 592 (1.1×10^4). HRMS (APCI-TOF): calcd for $C_{64}H_{72}O_2N_4{}^{58}Ni$ 986.5003 $[M]^-$; found 986.5032.

Synthesis of 13Ni–16Ni: This procedure is similar to that used for the synthesis of **3Ni**–**6Ni** except for the starting material.

Compound 13Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.14 (d, J = 4.6 Hz, 2 H, β), 8.93 (d, J = 4.6 Hz, 2 H, β), 8.84 (m, 4 H, β), 7.90 (d, J = 1.8 Hz, 4 H, Ar-*o*), 7.88 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.74 (t, J = 1.8 Hz, 2 H, Ar-*p*), 7.71 (t, J = 1.8 Hz, 1 H, Ar-*p*), 1.49 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. HRMS (APCI-TOF): calcd for $C_{62}H_{71}DN_4{}^{58}Ni$ 931.5168 $[M]^-$; found 931.5196.

Compound 14Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.28 (d, J = 5.0 Hz, 2 H, β), 8.76 (m, 4 H, β), 8.74 (d, J = 4.6 Hz, 2 H, β), 8.01 (d, J = 3.7 Hz, 1 H, benzyl), 7.83 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.81 (d, J = 1.3 Hz, 4 H, Ar-*o*), 7.69 (s, 3 H, Ar-*p*), 7.57 (d, J = 7.8 Hz, 2 H, Ph), 7.28 (d, J = 7.8 Hz, 2 H, Ph), 7.23 (d, J = 7.8 Hz, 1 H, Ph), 3.36 (d, J = 3.7 Hz, 1 H, OH), 1.45 (s, 54 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.12, 147.02, 142.81, 142.40, 142.02, 141.82, 139.3, 133.63, 132.83, 132.44, 130.62, 128.70, 128.26, 126.82, 126.51, 121.31, 120.85, 120.04, 116.58, 75.13, 35.12, 31.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 418 (2.5×10^5), 533 nm (1.7×10^4). HRMS (APCI-TOF): calcd for $C_{64}H_{72}O_2N_4{}^{58}Ni$ 1036.5524 $[M]^-$; found 1036.5546.

Compound 15Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.67 (d, J = 5.0 Hz, 2 H, β), 8.67 (m, 4 H, β), 8.60 (d, J = 5.0 Hz, 2 H, β), 7.79 (br. s, 2 H, Ar-*o*), 7.76 (br. s, 4 H, Ar-*o*), 7.67 (m, 3 H, Ar-*p*), 3.37 (m, 2 H, cyclohexyl), 2.46 (d, J = 14.2 Hz, 2 H, cyclohexyl), 2.14–2.06 (m, 2 H, cyclohexyl), 2.01 (br. d, 1 H, cyclohexyl), 1.91 (m, 2 H, cyclohexyl), 1.76 (m, 1 H, cyclohexyl), 1.58 (s, 1 H, OH), 1.45 (s, 36 H, *tert*-butyl), 1.43 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.10, 141.99, 141.45, 139.90,

139.61, 139.47, 139.42, 133.66, 132.68, 132.63, 132.04, 128.62, 122.53, 121.18, 120.34, 119.20, 44.86, 35.10, 31.79, 25.77, 23.18 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 419 (2.4×10^5), 533 (1.6×10^4). HRMS (APCI-TOF): calcd for $C_{68}H_{82}ON_4{}^{58}Ni$ 1028.5837 $[M]^-$; found 1028.5865.

Compound 16Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 12.05 (s, 1 H, formyl), 9.79 (d, J = 5.3 Hz, 2 H, β), 8.88 (d, J = 5.3 Hz, 2 H, β), 8.69 (d, J = 4.7 Hz, 2 H, β), 8.62 (d, J = 4.6 Hz, 2 H, β), 7.80 (m, 6 H, Ar-*o*), 7.73 (t, J = 1.8 Hz, 2 H, Ar-*p*), 7.73 (t, J = 1.9 Hz, 1 H, Ar-*p*), 1.47 (s, 36 H, *tert*-butyl), 1.45 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 192.89, 149.39, 149.31, 144.75, 144.54, 142.08, 141.16, 139.16, 135.83, 133.69, 132.25, 130.63, 128.61, 128.49, 124.94, 122.39, 121.66, 105.87, 35.15, 31.80, 31.78 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 427 (2.1×10^5), 554 (1.0×10^4), 596 nm (1.5×10^4). HRMS (APCI-TOF): calcd for $C_{63}H_{72}ON_4{}^{58}Ni$ 958.5054 $[M]^-$; found 958.5072.

Synthesis of 13Zn, 15Zn and 16Zn: This procedure is similar to that used for the synthesis of **3Zn** and **5Zn** except for the starting material.

Compound 13Zn: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.42 (d, J = 4.7 Hz, 1 H, β), 9.15 (d, J = 4.7 Hz, 2 H, β), 9.06 (d, J = 4.6 Hz, 2 H, β), 9.03 (d, J = 4.6 Hz, 2 H, β), 8.12 (d, J = 1.9 Hz, 4 H, Ar-*o*), 8.09 (d, J = 2.0 Hz, 2 H, Ar-*o*), 7.82 (t, J = 1.9 Hz, 2 H, Ar-*p*), 7.79 (t, J = 2.0 Hz, 1 H, Ar-*p*), 1.55 (s, 36 H, *tert*-butyl), 1.52 (s, 18 H, *tert*-butyl) ppm. HRMS (APCI-TOF): calcd for $C_{62}H_{71}DN_4{}^{64}Zn$ 937.5106 $[M]^-$; found 937.5133.

Compound 15Zn: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.08 (d, J = 4.6 Hz, 2 H, β), 8.90 (d, J = 4.6 Hz, 2 H, β), 8.84 (m, 4 H, β), 8.04 (d, J = 1.9 Hz, 2 H, Ar-*o*), 8.03 (d, J = 1.9 Hz, 4 H, Ar-*o*), 7.78 (br. s, 2 H, Ar-*p*), 7.75 (br. s, 1 H, Ar-*p*), 3.83 (m, 2 H, cyclohexyl), 2.76 (d, J = 14.7 Hz, 2 H, cyclohexyl), 2.34 (s, 1 H, OH), 2.30 (m, 2 H, cyclohexyl), 2.12 (m, 1 H, cyclohexyl), 2.05 (m, 2 H, cyclohexyl), 1.96 (m, 1 H, cyclohexyl), 1.53 (s, 36 H, *tert*-butyl), 1.51 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 150.33, 150.00, 149.07, 148.90, 148.86, 148.65, 142.23, 141.89, 132.17, 131.76, 130.93, 129.70, 129.63, 122.98, 122.22, 121.00, 79.35, 46.27, 35.25, 31.97, 31.94, 25.88, 23.80 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 424 (4.0×10^5), 557 nm (1.8×10^4). HRMS (APCI-TOF): calcd for $C_{68}H_{82}ON_4{}^{64}Zn$ 1034.5775 $[M]^-$; found 1034.5760.

Compound 16Zn: ^1H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 12.28–12.20 (br. s, 1 H, formyl), 9.93 (br. s, 2 H, β), 9.07 (d, J = 5.0 Hz, 2 H, β), 8.90 (d, J = 4.6 Hz, 2 H, β), 8.84 (d, J = 4.6 Hz, 2 H, β), 8.03 (d, J = 1.9 Hz, 4 H, Ar-*o*), 8.01 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.81 (br. s, 2 H, Ar-*p*), 7.78 (br. s, 1 H, Ar-*p*), 1.53 (s, 36 H, *tert*-butyl), 1.50 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 60 °C): δ = 195.23, 153.35, 152.29, 149.66, 149.26, 148.88, 148.74, 141.45, 141.32, 135.08, 133.40, 131.77, 129.51, 129.44, 128.76, 128.53, 125.42, 121.29, 35.20, 35.14, 31.93, 31.83 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 429 (4.3×10^5), 560 (1.5×10^4), 604 nm (2.1×10^4). HRMS (APCI-TOF): calcd for $C_{63}H_{72}ON_4{}^{64}Zn$ 964.4992 $[M]^-$; found 964.5010.

Preparation of CuCN·2LiCl (0.2 M in THF):[16] A Schlenk tube containing CuCN (36 mg, 0.40 mmol) and anhydrous LiCl (34 mg, 0.80 mmol) was dried in vacuo (1–3 Torr) for 3 h at 150 °C and then purged with argon. After the flask had cooled to room temperature, THF (2.0 mL) was added. After the reaction mixture had been stirred for 30 min at room temperature, a yellow solution of CuCN·2 LiCl was obtained.

Synthesis of 17Ni and 18Ni: After **2Ni** had been generated as described in the synthesis of **3Ni**–**6Ni**, CuCN·2 LiCl (0.2 M solution in THF, 0.10 mL, 20 μmol) and an electrophile (200 μmol) were sequentially added. After having been stirred for 2 h at room temperature, the reaction mixture was quenched with an NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. After concentration, the residue was purified on silica gel with elution with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **17Ni** (78 mg, 72 μmol, 72%) and **18Ni** (78 mg, 80 μmol, 80%).

Compound 17Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.56 (s, 1 H, *meso*), 9.16 (m, 2 H, β), 8.88 (d, J = 4.6 Hz, 1 H, β), 8.81 (m, 3 H, β), 8.78 (d, J = 4.8 Hz, 1 H, β), 8.71 (s, 1 H, naphthyl), 8.38 (d, J = 8.2 Hz, 1 H, naphthyl), 8.06 (d, J = 8.2 Hz, 1 H, naphthyl), 7.98 (d, J = 8.2 Hz, 1 H, naphthyl), 7.92 (d, J = 8.2 Hz, 1 H, naphthyl), 7.90 (d, J = 1.9 Hz, 2 H, Ar-*o*), 7.90 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.90 (d, J = 1.8 Hz, 2 H, Ar-*o*), 7.74 (t, J = 1.9 Hz, 1 H, Ar-*p*), 7.72 (t, J = 1.8 Hz, 1 H, Ar-*p*), 7.65 (t, J = 8.7 Hz, 1 H, naphthyl), 7.63 (t, J = 1.8 Hz, 1 H, Ar-*p*), 7.56 (t, J = 8.7 Hz, 1 H, naphthyl), 1.49 (s, 18 H, *tert*-butyl), 1.47 (s, 18 H, *tert*-butyl), 1.41 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 193.40, 149.27, 149.16, 144.27, 143.97, 143.33, 142.73, 142.82, 141.05, 139.94, 139.76, 139.63, 139.18, 138.06, 137.61, 137.50, 135.60, 133.96, 133.25, 132.94, 132.65, 132.50, 132.41, 129.90, 128.93, 128.84, 128.76, 128.59, 128.52, 127.99, 126.86, 126.15, 122.25, 121.53, 121.41, 120.97, 119.82, 105.19, 35.17, 35.15, 35.08, 31.84, 31.82, 31.79 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 427 (2.0×10^5), 534 (1.5×10^4), 574 nm (1.1×10^4). HRMS (APCI-TOF): calcd for $C_{73}H_{78}ON_4{}^{58}Ni$ 1084.5524 $[M]^-$; found 1084.5533.

Compound 18Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1 H, *meso*), 9.12 (d, J = 5.0 Hz, 1 H, β), 8.92 (d, J = 5.0 Hz, 1 H, β), 8.83–8.79 (m, 4 H, β), 8.68 (s, 1 H, β), 7.89 (m, 4 H, Ar-*o*), 7.88 (d, J = 1.9 Hz, 2 H, Ar-*o*), 7.73 (m, 2 H, Ar-*p*), 7.71 (t, J = 1.9 Hz, 1 H, Ar-*p*), 6.59–6.52 (m, 1 H, allyl), 5.45 (d, J = 16.9 Hz, 1 H, allyl), 5.31 (d, J = 8.7 Hz, 1 H, allyl), 4.70 (d, J = 6.0 Hz, 2 H, allyl), 1.50 (s, 18 H, *tert*-butyl), 1.49 (s, 18 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.08, 148.97, 143.45, 143.18, 142.88, 142.69, 142.56, 142.38, 142.15, 142.10, 140.37, 140.29, 140.23, 137.36, 132.77, 132.44, 132.17, 132.09, 131.78, 131.14, 129.19, 128.94, 128.84, 121.22, 121.16, 121.08, 120.82, 120.19, 119.15, 116.70, 101.48, 35.17, 35.14, 32.94, 31.86 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 411 (2.4×10^5), 523 nm (1.7×10^4). HRMS (APCI-TOF): calcd for $C_{65}H_{76}N_4{}^{58}Ni$ 970.5418 $[M]^-$; found 970.5442.

Synthesis of 19Ni: After **2Ni** had been generated as described in the synthesis of **3Ni**–**6Ni**, CuCN·2LiCl (0.2 M solution in THF, 0.10 mL, 20 μmol), cyclohex-2-en-1-one (19 μL, 200 μmol), and chlorotrimethylsilane (25 μL, 200 μmol) were successively added. After the mixture had been stirred for 2 h at room temperature, HCl (3 M) was added to deprotect the resulting silyl ether. The organic layer was extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. Concentration followed by chromatographic purification with elution with CH_2Cl_2/hexane afforded a solid. Recrystallization from CH_2Cl_2/methanol gave **19Ni** (70 mg, 68 μmol, 68%).

Compound 19Ni: ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.76 (s, 1 H, *meso*), 9.12 (d, J = 4.6 Hz, 1 H, β), 8.92 (d, J = 4.6 Hz, 1 H, β), 8.81–8.78 (m, 4 H, β), 8.69 (s, 1 H, β), 7.90–7.84 (br. s, 6 H, Ar-*o*), 7.74 (t, J = 1.9 Hz, 2 H, Ar-*p*), 7.73 (t, J = 1.9 Hz, 2 H, Ar-*p*), 7.70 (t, J = 1.9 Hz, 1 H, Ar-*p*), 4.72 (m, 1 H, cyclohexyl), 3.29 (m, 1 H, cyclohexyl), 3.06 (t, J = 12.84 Hz, 1 H, cyclohexyl), 2.78 (m, 1 H, cyclohexyl), 2.69 (m, 1 H, cyclohexyl), 2.64 (m, 1 H, cyclohexyl), 2.40 (m, 2 H, cyclohexyl), 2.22 (m, 1 H, cyclohexyl), 1.50 (s, 18 H, *tert*-butyl), 1.49 (s, 18 H, *tert*-butyl), 1.46 (s, 18 H,

tert-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 211.17, 149.12, 149.01, 148.07, 143.25, 143.02, 142.80, 142.64, 142.52, 140.68, 140.22, 140.15, 140.06, 132.60, 132.28, 132.26, 132.00, 129.24, 128.91, 128.83, 128.49, 121.29, 121.22, 121.17, 120.89, 120.28, 119.31, 100.76, 49.86, 41.70, 38.11, 35.18, 35.16, 35.13, 34.02, 31.85, 31.82, 25.87 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (2.6×10^5), 524 nm (1.9×10^4). HRMS (APCI-TOF): calcd for $C_{68}H_{80}ON_4{}^{58}Ni$ 1026.5680 $[M]^-$; found 1026.5703.

Synthesis of 20Ni: After **2Ni** had been generated as described in the synthesis of **9Ni** and **10Ni**, CuCN·2 LiCl (0.2 M solution in THF, 0.20 mL, 40 μmol) and 2-naphthoyl chloride (76 mg, 400 μmol) were added. The resulting mixture was stirred for 2 h at room temperature and then quenched with an NH_4Cl solution. The organic compounds were extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography with elution with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **20Ni** (77 mg, 62 μmol, 62%).

Compound 20Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.11 (s, 1 H, *meso*), 9.13 (s, 2 H, β), 8.81 (d, *J* = 5.0 Hz, 2 H, β), 8.79 (d, *J* = 5.0 Hz, 2 H, β), 8.68 (s, 2 H, naphthyl), 8.35 (d, *J* = 8.7 Hz, 2 H, naphthyl), 8.00 (d, *J* = 8.7 Hz, 2 H, naphthyl), 7.94 (d, *J* = 8.3 Hz, 2 H, naphthyl), 7.89 (d, *J* = 8.7 Hz, 2 H, naphthyl), 7.88 (d, *J* = 1.9 Hz, 4 H, Ar-*o*), 7.85 (d, *J* = 1.9 Hz, 2 H, Ar-*o*), 7.73 (t, *J* = 1.8 Hz, 2 H, Ar-*p*), 7.64 (t, *J* = 1.8 Hz, 1 H, Ar-*p*), 7.62 (t, *J* = 8.3 Hz, 2 H, naphthyl), 7.53 (t, *J* = 8.3 Hz, 2 H, naphthyl), 1.47 (s, 18 H, *tert*-butyl), 1.42 (s, 36 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 192.65, 149.33, 144.22, 143.82, 141.64, 140.34, 140.20, 139.64, 139.29, 137.35, 137.14, 135.63, 133.34, 133.23, 132.61, 132.50, 129.90, 128.83, 128.70, 128.49, 128.46, 127.98, 126.75, 126.17, 121.92, 121.67, 121.54, 121.33, 105.87, 35.16, 35.10, 31.82, 31.79 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 439 (2.1×10^5), 544 (1.8×10^4), 580 nm (9.5×10^3). HRMS (APCI-TOF): calcd for $C_{84}H_{84}O_2N_4{}^{58}Ni$ 1238.5942 $[M]^-$; found 1238.5948.

Synthesis of 22Ni–24Ni: Porphyrinyl Grignard reagent **2Ni** was generated as described in the synthesis of **3Ni**–**6Ni**. $ZnCl_2$(tmeda) (38 mg, 150 μmol) was added to the resulting red solution. After the system had been stirred for 30 min at room temperature, $Pd_2(dba)_3$ (1.5 mg, 1.7 μmol), Ruphos (3.1 mg, 6.7 μmol), and the appropriate aryl bromide (83 μmol) were added, and the reaction mixture was stirred for 6 h at 60 °C. The reaction mixture was quenched with water, extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography with elution with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **22Ni**–**24Ni**.

Compound 22Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1 H, *meso*), 9.05 (d, *J* = 4.6 Hz, 1 H, β), 8.90 (d, *J* = 4.6 Hz, 1 H, β), 8.86 (s, 1 H, β), 8.82 (m, 4 H, β), 8.01 (d, *J* = 8.7 Hz, 2 H, 4-OMe-Ph), 7.91 (d, *J* = 2.0 Hz, 2 H, Ar-*o*), 7.89 (d, *J* = 1.9 Hz, 2 H, Ar-*o*), 7.88 (d, *J* = 1.9 Hz, 2 H, Ar-*o*), 7.73 (m, 2 H, Ar-*p*), 7.71 (t, *J* = 1.9 Hz, 1 H, Ar-*p*), 7.28 (d, *J* = 8.7 Hz, 2 H, 4-OMe-Ph), 4.01 (s, 3 H, OMe), 1.48 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 159.63, 149.10, 149.01, 145.54, 143.26, 143.15, 143.05, 142.77, 142.71, 142.66, 141.76, 140.91, 140.28, 140.23, 140.12, 132.76, 132.55, 132.33, 132.31, 132.24, 132.03, 130.09, 129.20, 128.98, 128.94, 128.85, 121.22, 121.21, 120.59, 120.15, 119.40, 114.65, 104.35, 55.67, 35.15, 35.14, 31.86 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (2.5×10^5), 526 nm (2.0×10^4). HRMS (APCI-TOF): calcd for $C_{69}H_{78}ON_4{}^{58}Ni$ 1036.5524 $[M]^-$; found 1036.5531.

Compound 23Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.85 (s, 1 H, *meso*), 9.03 (d, *J* = 4.6 Hz, 1 H, β), 8.96 (s, 1 H, β), 8.89 (d, *J* = 4.6 Hz, 1 H, β), 8.82 (m, 4 H, β), 8.18 (d, *J* = 8.3 Hz, 2 H, 4-Bpin-Ph), 8.11 (d, *J* = 8.3 Hz, 2 H, 4-Bpin-Ph), 7.92 (d, *J* = 1.8 Hz, 2 H, Ar-*o*), 7.89 (d, *J* = 1.9 Hz, 2 H, Ar-*o*), 7.88 (d, *J* = 1.8 Hz, 2 H, Ar-*o*), 7.73 (m, 2 H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1 H, Ar-*p*), 1.48 (s, 36 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl), 1.45 (s, 12 H, Bpin) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.16, 149.12, 149.02, 145.48, 143.28, 143.15, 142.97, 142.79, 141.51, 140.67, 140.24, 140.14, 140.08, 139.46, 135.47, 132.83, 132.55, 132.45, 132.34, 132.23, 130.77, 130.64, 129.07, 128.95, 128.85, 121.26, 121.21, 120.65, 120.12, 119.72, 104.30, 84.14, 35.18, 35.16, 35.14, 31.85, 25.13 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (2.1×10^5), 526 nm (1.9×10^4). HRMS (APCI-TOF): calcd for $C_{74}H_{87}O_2N_4{}^{11}B^{58}Ni$ 1132.6282 $[M]^-$; found 1132.6261.

Compound 24Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.81 (s, 1 H, *meso*), 9.03 (d, *J* = 4.6 Hz, 1 H, β), 8.96 (s, 1 H, β), 8.90 (d, *J* = 4.6 Hz, 1 H, β), 8.82 (m, 4 H, β), 8.80 (s, 1 H, 3-CO_2TIPS-Ph), 8.31 (d, *J* = 7.8 Hz, 1 H, 3-CO_2TIPS-Ph), 8.27 (d, *J* = 7.8 Hz, 1 H, 3-CO_2TIPS-Ph), 7.90 (d, *J* = 1.9 Hz, 2 H, Ar-*o*), 7.89 (d, *J* = 1.8 Hz, 2 H, Ar-*o*), 7.87 (d, *J* = 1.8 Hz, 2 H, Ar-*o*), 7.82 (t, *J* = 7.8 Hz, 1 H, 3-CO_2TIPS-Ph), 7.74 (m, 2 H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1 H, Ar-*p*), 1.49 (s, 18 H, *tert*-butyl), 1.48 (s, 18 H, *tert*-butyl), 1.46 (s, 18 H, *tert*-butyl), 1.45 (m, *J* = 7.3 Hz, 3 H, TIPS), 1.16 (d, *J* = 7.3 Hz, 18 H, TIPS) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 166.47, 149.14, 149.05, 144.44, 143.27, 143.20, 143.10, 142.99, 142.82, 142.78, 141.36, 140.41, 140.17, 140.04, 140.03, 136.98, 135.58, 132.69, 132.64, 132.60, 132.97, 132.51, 132.48, 132.44, 132.33, 130.95, 129.42, 129.22, 128.95, 128.84, 128.80, 121.41, 121.30, 121.25, 120.73, 120.12, 119.75, 103.95, 35.17, 31.86, 31.83, 18.09, 12.28 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (2.4×10^5), 527 nm (1.8×10^4). HRMS (APCI-TOF): calcd for $C_{78}H_{96}O_2N_4{}^{58}NiSi$ 1206.6651 $[M]^-$; found 1206.6636.

Crystal Data

Compound 6Ni: $C_{64}H_{74}ON_4Cl_2Ni$; M_r = 1044.88; monoclinic; space group *C2/c* (No. 15); *a* = 36.906(12), *b* = 15.540(4), *c* = 25.945(8) Å; β = 131.579(5)°; *V* = 11131(6) Å^3; *Z* = 8; $\rho_{calcd.}$ = 1.247 g cm^{-3}; *T* = 93 K; R_1 = 0.0564 [$I>2\sigma(I)$]; R_w = 0.1554 (all data); GOF = 1.043. Crystals were grown from CH_2Cl_2/MeOH.

Compound 15Ni: $C_{74.51}H_{89.22}O_{1.19}N_4Ni$; M_r = 1118.71; monoclinic; space group *C2/c* (No. 15); *a* = 39.08(3), *b* = 9.117(5), *c* = 38.96(3) Å; β = 116.07(2)°; *V* = 12471(15) Å^3; *Z* = 8; $\rho_{calcd.}$ = 1.192 g cm^{-3}; *T* = 93 K; R_1 = 0.1049 [$I>2\sigma(I)$]; R_w = 0.2909 (all data); GOF = 1.092. Crystals were grown from toluene/MeOH.

Compound 20Ni: $C_{87}H_{84}O_2N_{4.84}Cl_{3.49}Ni$; M_r = 1411.70; triclinic, space group $P\bar{1}$ (No. 2); *a* = 13.491(5), *b* = 17.043(4), *c* = 17.188(4) Å; α = 102.5100(14), β = 92.344(9), γ = 106.854(8)°; *V* = 3669.7(17) Å^3; *Z* = 2; $\rho_{calcd.}$ = 1.278 g cm^{-3}; *T* = 93 K; R_1 = 0.0697 [$I>2\sigma(I)$]; R_w = 0.2269 (all data); GOF = 1.057. Crystals were grown from $CHCl_3$/MeCN.

CCDC-991731 (for **6Ni**), -991732 (for **15Ni**), and -991733 (for **20Ni**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details, copies of the ^{1}H NMR, ^{13}C NMR, and HRMS spectra of all compounds, as well as X-ray crystal structures of **6Ni**, **15Ni**, and **20Ni**.

Acknowledgments

The work was supported by Grants-in-Aid from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) (grant numbers 24106721, *Reaction Integration* and 25107002, *Science of Atomic Layers*) and from the Japan Society for the Promotion of Science (JSPS) {grant numbers 25220802 [Scientific Research (S)], 24685007 [Young Scientists (A)], 23655037 and 26620081 (Exploratory Research)}.

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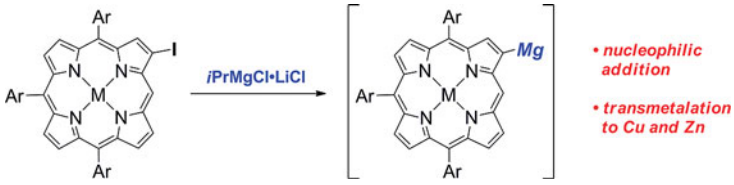
Received: April 11, 2014
Published Online: ■

EurJOC European Journal of Organic Chemistry



Iodine–magnesium exchange between iodoporphyrins and *i*PrMgCl·LiCl has allowed the formation of porphyrinyl Grignard reagents for the first time. Thanks to their high reactivity, these Grignard reagents not only react with various carbonyl compounds but also undergo transmetalation to afford porphyrinyl copper and zinc species, which participate in 1,4-addition and Negishi coupling, respectively.

Keywords: Porphyrinoids / Iodine–magnesium exchange / Grignard reaction / Metalation

