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Ligand Design | *Very Important Paper* |

Bulky 1,1′-Ferrocenyl Ligands Featuring Diazaphospholene or Dioxaphosphepine Donor Fragments: Catalytic Screening in Nickel-Catalyzed C-N Cross-Coupling

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Abstract: 1,1′-Ferrocenyl ligands featuring either bulky dioxaphosphepine (**L1**) or diazaphospholene (**L2**) donor moieties have been prepared, crystallographically characterized, and tested in representative nickel-catalyzed C–N cross-coupling reactions. Ligand **L1** proved competent in cross-couplings involving primary/secondary alkylamine or indole nucleophiles with (hetero)aryl chlorides, with the catalytic performance of *rac* and *meso*-**L1** differing in the case of some substrate pairings. Conversely, **L2** proved ineffective under analogous conditions.

Introduction

The palladium-catalyzed C–N cross-coupling of NH substrates and (hetero)aryl (pseudo)halides (i.e., Buchwald-Hartwig amination, BHA) is used widely in the synthesis of sought-after (hetero)anilines, including those found in pharmaceuticals and conjugated materials (Figure 1).[1] The successful evolution of BHA from an academic curiosity to a robust synthetic protocol can be attributed in large part to advances in ancillary ligand design,[2] with sterically demanding and electron-rich ligands such as monophosphines[3] and N-heterocyclic carbenes[4] proving particularly effective, especially in transformations of inexpensive and abundant (hetero)aryl chlorides where oxidative addition can be challenging.[5] Notwithstanding the success of BHA, the costly and relatively rare nature of palladium has created motivation for the development of competitive "drop-in" catalyst replacements that make use of base metals.[6]

The generally poor performance of copper-catalyzed C–N cross-coupling methods[7] and nickel-catalyzed photoredox[8] or electrochemical[9] protocols with (hetero)aryl chloride electrophiles has prompted the exploration of alternative approaches. One strategy involves the repurposing of useful ancillary ligands from the BHA domain, including bisphosphines[10] (e.g., DPPF,[11] Figure 1) and N-heterocyclic carbenes (e.g., IPr[12]), as a means of enabling photoredox/electrochemical-free nickel-catalyzed C–N cross-coupling. However, the collective scope attained by such means falls short of that achieved by use of BHA methods; furthermore, state-of-the-art ligands from BHA (e.g., Buchwald's biaryl monophosphines) have generally proven ineffective in C–N cross-couplings employing nickel. In this context, the success of ancillary ligand design in enabling the advancement of BHA methods suggests that efforts tailored specifically to the properties of nickel may similarly prove advantageous. Despite such opportunities, little attention has been focussed on the design of ancillary ligands for use in nickel-catalyzed C–N cross-coupling.

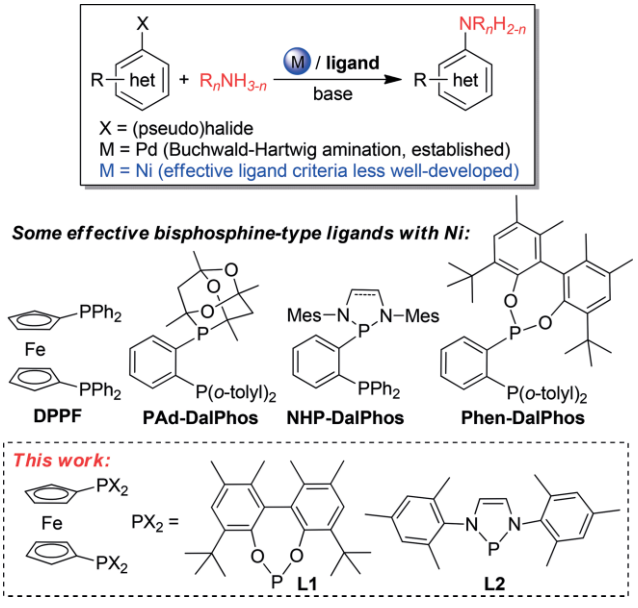

Figure 1. C–N cross-coupling employing group 10 metals, highlighting some effective bisphosphine-type ligands used with nickel, and the bulky ferrocenyl ligands **L1** and **L2** examined in this work.

Our research efforts over the past few years have been focussed in part on advancing nickel-catalyzed C–N cross-coupling, including through the synthesis and screening of new

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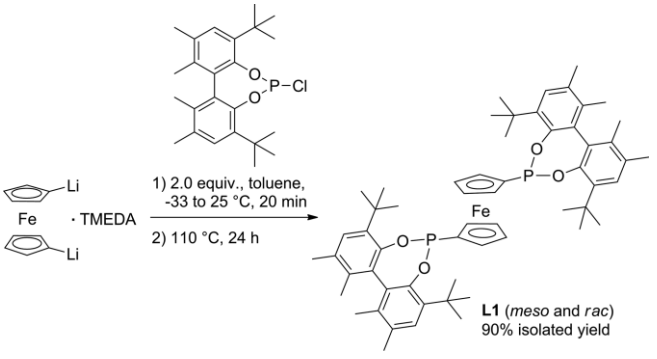
and known ancillary ligands. One particularly successful aspect of this work involved the development of the PAd-DalPhos[13] bisphosphine ligand class, featuring a phosphaadamantane (CgP) donor fragment (Figure 1). Given the established propensity of L_nNi^0 species to engage in (hetero)aryl chloride oxidative addition,[5] we envisioned that bulky and only modestly electron-donating ligands featuring the CgP group would work particularly well in promoting rate-limiting C–N reductive elimination within a presumptive Ni(0/II) ("palladium-like") catalytic cycle, while also discouraging unwanted comproportionation to form potentially less active Ni^I species.[14] Indeed, PAd-DalPhos and related variants[13,15] are amongst the most effective ligands known for nickel-catalyzed C–N cross-coupling, enabling a range of challenging NH substrate/(hetero)aryl (pseudo)halide pairings, in a manner that is commonly competitive with, or superior to, the best palladium catalysts known.

Encouraged by this success, we continue to explore new ancillary ligand designs that adhere to these design principles, with the goal of gaining an increased understanding of the ligand structure/properties that give rise to effective nickel C–N cross-coupling catalysis. In this vein, we recently showed that replacing the CgP group with a bulky N-heterocyclic phosphine[16] moiety, or phosphonite donor group derived from commercially available 5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol, affords ancillary ligands (i.e., NHP-DalPhos[17] and Phen-DalPhos,[18] Figure 1) that are highly effective in enabling otherwise challenging classes of nickel-catalyzed C–N cross-couplings involving (hetero)aryl chlorides, including at room temperature. Building on this work, we sought to merge the beneficial structural features of DPPF, NHP-DalPhos, and Phen-DalPhos through the preparation and application of 1,1′-ferrocenyl ligands[19] featuring sterically demanding and modestly electron-donating NHP or phosphonite donor fragments. Herein we report on the synthesis and characterization of **L1** and **L2** (Figure 1), and our efforts to apply such ligands in nickel-catalyzed C–N cross-coupling chemistry.

Results and Discussion

Preparation of the BIPHEN-derived ferrocene **L1** (98 % purity) was carried out in high yield on gram-scale as outlined in Scheme 1, via treatment of (BIPHEN)PCl[20] with 1,1′-dilithioferrocene-tetramethylethylenediamine adduct[21] in toluene. The stereogenic nature of the BIPHEN unit arising from atropisomerism about the aryl–aryl linkage results in both *meso* (*RS*,*SR*) and *rac* (*RR*,*SS*) isomers of **L1**, which are formed in ≈ 1:1 ratio as is apparent in the $^{31}P\{^1H\}$ NMR (180.7 and 180.3 ppm, corresponding to the *rac* and *meso* isomers of **L1**, respectively) and ^1H NMR spectroscopic data. Crystallization of **L1** afforded a minute quantity of *meso*-**L1**, which was characterized by use of NMR spectroscopic and X-ray crystallographic methods. Moreover, use of enantiopure (*S*)-(BIPHEN)PCl allowed for the selective synthesis of $\mathbf{L1}^{SS}$ (i.e., representative of *rac*-**L1**), thereby allowing for the independent spectroscopic characterization of *meso* and *rac* **L1**. For each diastereomer of **L1**, the chiral dibenzo[*d*,*f*][1,3,2]-dioxaphosphepinyl units themselves possesses no internal symmetry; however, the two dibenzo[*d*,*f*][1,3,2]-dioxaphosphepinyl groups within each diastereomer are related either by a C_2 (*rac*-**L1**) or a C_S (*meso*-**L1**) symmetry element. In this regard, crystallographically imposed symmetry relating the phosphorus donor fragments is observed in the solid-state structure of *meso*-**L1** (Figure 2). The solid-state structure of *meso*-**L1** can be compared to a related bis(phosphonite)ferrocene ligand reported by Pastor and co-workers;[22] however, unlike **L1**, the lack of substitution at the 6,6′ positions in their system results in rapid ring inversion within their chosen dibenzo[*d*,*f*][1,3,2]-dioxaphosphepinyl groups, and atropisomerism is not observed.



Scheme 1. Synthesis of **L1** (TMEDA = tetramethylethylenediamine).

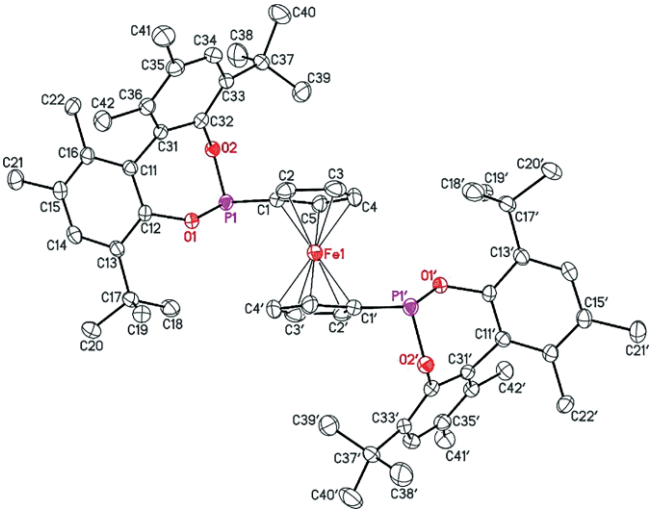


Figure 2. Single-crystal X-ray structure of *meso*-**L1** shown with 30 % displacement ellipsoids and with hydrogen atoms and solvate omitted for clarity. Primed atoms are generated via crystallographic symmetry (inversion center at 0.5, 0.5, 0.5).

In surveying the literature we identified a publication by Gudat and co-workers[23] in which the preparation of *P*-cyclopentadienyl-substituted 1,3,2-diazaphospholenes is reported, including lithiation of an *N*-mesityl variant and quenching with $FeCl_2$ to afford **L2**, which in turn was spectroscopically characterized. Herein we report an alternative complementary route to **L2** by using a method similar to that employed in the synthesis of **L1** (Scheme 1) starting from 1,1′-dilithioferrocene-tetramethylethylenediamine. The crystal structure of **L2** is presented in Figure 3, and exhibits geometrical parameters associated with the NHP unit that are analogous to those found in some

other *N*-mesityl-substituted 1,3,2-diazaphospholene compounds.[17]

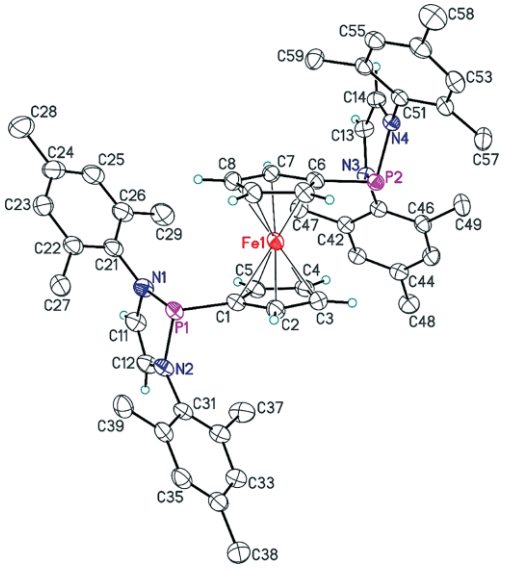


Figure 3. Single-crystal X-ray structure of **L2** shown with 30 % displacement ellipsoids and with the solvate and selected hydrogen atoms omitted for clarity.

With **L1** (*meso* + *rac*), **L1**^{SS}, and **L2** in hand, we conducted a reactivity survey employing these ligands in a selection of representative nickel-catalyzed C–N cross-couplings involving (hetero)aryl chlorides (5 mol % Ni, 80 °C, 16 h; Figure 4). Cross-couplings involving furfurylamine, 2-thiophenemethylamine, or *N*-octylamine, with 4-chlorobenzonitrile or 4-chloroquinaldine, afforded synthetically useful conversions to the target C–N cross-coupling products **1a**–**1c** when using **L1**; in the case of **1b** the product was isolated in 89 % yield following chromatographic purification. In contrast, <10 % conversion of the starting materials was achieved when using **L2** under analogous conditions, with these or the other substrate pairings examined herein. Given that **L1** is composed of a mixture of *meso* and *rac* isomers (vide supra), we became interested in exploring further the performance of **L1** vs. **L1**^{SS} (representative of *rac*-**L1**) in cross-couplings leading to the formation of **1d**–**1g**. While modest differences in conversion were noted in reactions involving furfurylamine (giving **1d** and **1e**), more pronounced and divergent variation in conversion was noted in transformations of indole or morpholine with 4-chlorobenzonitrile (giving **1f** and **1g**), with *rac*-**L1** apparently proving more effective in the former and *meso*-**L1** in the latter. These observations are in keeping with our prior findings that the *meso* and *rac* isomers of PAd2-DalPhos, featuring two chiral (racemic) phosphaadamantane (CgP) donor fragments, exhibit different catalytic competencies in nickel-catalyzed C–N cross-coupling.[15c] While the results featured in Figure 4 establish the basic competence of **L1** in such transformations, the poor (< 10 %) conversion achieved by use of Ni(COD)$_2$/**L1** in reactions of more challenging electron-rich electrophiles such as 4-chloroanisole or 2-chloro-1,4-dimethylbenzene with furfurylamine or indole highlights the inferiority of **L1** vs. DPPF itself and variants featuring substitution on the P-aryl rings.[24]

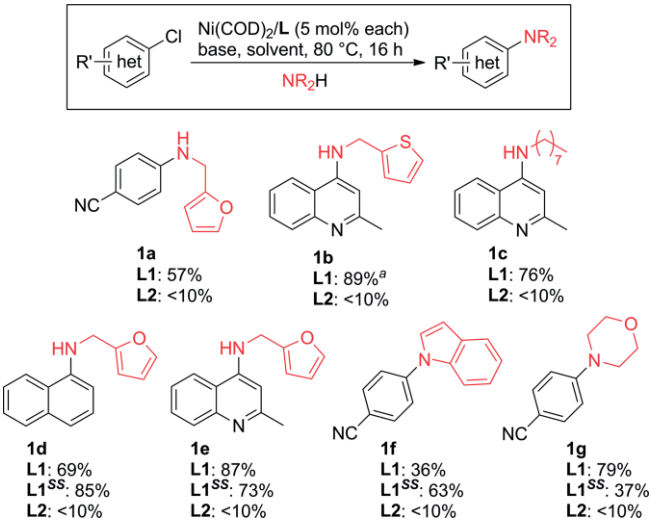


Figure 4. Reaction screening involving **L1** (*meso* + *rac* mixture), **L1**^{SS}, and **L2** in selected nickel-catalyzed C–N cross-couplings of (hetero)aryl chlorides, with conversion to the product given on the basis of calibrated GC data employing authentic materials and using dodecane or 1-phenyldodecane as internal standards. In all cases the mass balance corresponds primarily to unreacted starting materials. [a]Isolated yield following column chromatography on silica. See the Experimental Section for complete details.

Conclusion

In conclusion, we have developed synthetic routes to bulky, crystallographically characterized 1,1′-ferrocenyl ligands featuring either dioxaphosphepine (**L1**) or diazaphospholene (**L2**) donor moieties, and have tested their ability to promote some representative nickel-catalyzed C–N cross-coupling reactions. While **L2** proved ineffective in the test reactions examined under the conditions employed, **L1** proved competent in cross-couplings involving primary/secondary alkylamine or indole nucleophiles with (hetero)aryl chlorides, with the catalytic performance of *rac* and *meso*-**L1** differing in the case of some substrate pairings. While the catalytic performance of **L1** did not exceed that of DPPF or related P-aryl variants disclosed previously, the competence of **L1** in the nickel-catalyzed C–N cross-couplings disclosed herein serves to expand the "tool box" of ligands that are available to synthetic chemists in the quest to solve currently unmet challenges in cross-coupling chemistry and beyond.

Experimental Section

General Considerations: Unless otherwise indicated, all experimental procedures were conducted in a nitrogen-filled, inert atmosphere glove-box using oven-dried glassware and purified solvents, with the exception of the workup of catalytic reaction mixtures, which was conducted on the benchtop in air using unpurified solvents. For solvents used within the glove-box, the following purification methods were used: tetrahydrofuran was dried with Na/benzophenone followed by distillation under an atmosphere of nitrogen gas; toluene and hexanes were each deoxygenated by sparging with nitrogen gas followed by passage through a double column solvent purification system packed with alumina and cop-

per-Q5 reactant and storage over activated 4 Å molecular sieves; CH_2Cl_2 was deoxygenated by sparging with nitrogen gas followed by passage through a double column solvent purification system packed with alumina and storage over activated 4 Å molecular sieves; cyclopentyl methyl ether (CPME) and CH_3CN were each degassed by use of three freeze-pump-thaw cycles and was stored over activated 4 Å molecular sieves. (BIPHEN)PCl,[20] 1,1′-dilithioferrocene-tetramethylethylenediamine adduct,[21] and 2-bromo-1,3-dimesityl-1,3,2-diaza-phospholene[25] were prepared according to literature protocols. All other commercial solvents, reagents, and materials were used as received. GC data were obtained on an instrument equipped with an SGE BP-5 column (30 m, 0.25 mm i.d.). Flash column chromatography was carried out in air using Silicycle Siliaflash 60 silica (particle size 40–63 μm; 230–400 mesh). All ^1H NMR (500 and 300 MHz), $^{13}C\{^1H\}$ NMR (125.8 and 75.4 MHz), and $^{31}P\{^1H\}$ NMR (202.5 and 121.5 MHz) spectra were recorded at 300 K and were referenced to residual protio solvent peaks (^1H), deuterated solvent peaks ($^{13}C\{^1H\}$), or external 85 % H_3PO_4 ($^{31}P\{^1H\}$). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode. Crystallographic data were obtained at or below –80 °C, on a Bruker D8/APEX II CCD diffractometer equipped with a CCD area detector using Cu-K_α (α = 1.54178 Å) (microfocus source) radiation for *meso*-**L1** or graphite-monochromated Mo-K_α (α = 0.71073) radiation for **L2** employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Data reduction, correction for Lorentz polarization, and absorption correction (Gaussian integration; face-indexed) were each performed. Structure solution by using intrinsic phasing was carried out, followed by least-squares refinement on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters, while all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom.

CCDC 1885150 (for *meso*-**L1**), and 1885151 (for **L2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of L1: In a dinitrogen filled glove-box, a Schlenk flask containing a magnetic stir bar was charged with 1,1′-dilithioferrocene-tetramethylethylenediamine adduct (933 mg, 2.97 mmol) and toluene (10 mL), and was cooled to –33 °C. A separate vial containing a magnetic stir bar was charged with racemic (BIPHEN)PCl (2.49 g, 5.94 mmol) and toluene (18 mL), and magnetic stirring was initiated to dissolve (BIPHEN)PCl, followed by cooling to –33 °C. To the stirring solution of 1,1′-dilithioferrocene-tetramethylethylenediamine adduct was added the solution of (BIPHEN)PCl dropwise, and the resulting mixture was allowed to reach room temperature before the flask was sealed, taken out of the glove-box, and heated at 110 °C for 24 h under the influence of magnetic stirring. The flask was then brought back into the glove-box and was cooled to –33 °C for 30 minutes. The resulting mixture was filtered through Celite and the collected eluent was concentrated in vacuo to afford **L1** in a ≈ 1:1 ratio of *meso* (*RS*,*SR*) and *rac* (*RR*,*SS*) isomers as estimated on the basis of both $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopic data (2.55 g, 90 %). In synthesizing **L1**^{SS}, an analogous procedure was followed implementing enantiopure (*S*)-(BIPHEN)PCl, giving rise to a similarly high yield of **L1**^{SS} (88 %). Data for **L1**^{SS} (i.e., representative of *rac*-**L1**) ^1H NMR (500 MHz, $CDCl_3$): δ = 7.15 (s, 2H, ArH), 6.86 (s, 2H, ArH), 4.60 (br s, 2H, CpH), 4.50, (br s, 2H, CpH), 4.40 (br s, 2H, CpH), 3.61 (br s, 2H, CpH), 2.25 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 1.81 (s, 6H, CH_3), 1.70 (s, 6H, CH_3), 1.51 (s, 18H, $C(CH_3)_3$), 1.00 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ UDEFT NMR (125.8 MHz, $CDCl_3$): δ = 148.0 (ArC), 145.9 (d, $J_{C\text{-}P}$ = 5.8 Hz, ArC), 138.1 (ArC), 137.2 (ArC), 135.0 (ArC), 133.7 (ArC), 133.3 (d, $J_{C\text{-}P}$ = 5.3 Hz, ArC), 132.4 (ArC), 131.4 (d, $J_{C\text{-}P}$ = 2.3 Hz, ArC), 131.2 (ArC), 128.4 (ArC), 127.9 (ArC), 78.8 (d, $J_{C\text{-}P}$ = 37.7 Hz, CpC), 74.4 (d, $J_{C\text{-}P}$ = 40.8 Hz, CpC), 71.7 (CpC), 71.3 (d, $J_{C\text{-}P}$ = 7.5 Hz, CpC), 70.7 (CpC), 35.0 [*C*(CH_3)$_3$], 34.9 [*C*(CH_3)$_3$], 32.3 [C(*C*H$_3$)$_3$], 31.4 (d, $J_{C\text{-}P}$ = 4.8 Hz, (C(*C*H$_3$)$_3$)), 20.8 (CH_3), 20.5 (CH_3), 16.7 (CH_3), 16.5 (CH_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 180.7 (s). Diastereomerically pure crystals of *meso*-**L1** (*confirmed through X-ray crystallographic analysis*) were obtained through vapor diffusion of acetonitrile into a solution of **L1** in tetrahydrofuran, allowing for full independent NMR characterization of the as-prepared *meso*/*rac* mixture. Data for *meso*-**L1**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.16 (s, 2H, ArH), 6.89 (s, 2H, ArH), 4.57 (br s, 2H, CpH), 4.52 (br s, 2H, CpH), 4.40 (br s, 2H, CpH), 3.87 (br s, 2H, CpH), 2.26 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.73 (s, 6H, CH_3), 1.54 (s, 18H, $C(CH_3)_3$), 1.00 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ UDEFT NMR (125.8 MHz, $CDCl_3$): δ = 148.0 (ArC), 145.7 (d, $J_{C\text{-}P}$ = 5.6 Hz, ArC), 138.1 (d, $J_{C\text{-}P}$ = 2.4 Hz, ArC), 137.2 (ArC), 135.1 (ArC), 133.8 (ArC), 133.3 (d, $J_{C\text{-}P}$ = 5.0 Hz, ArC), 132.4 (ArC), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz, ArC), 131.3 (ArC), 128.5 (ArC), 127.9 (ArC), 79.0 (d, $J_{C\text{-}P}$ = 38.8 Hz, CpC), 74.6 (d, $J_{C\text{-}P}$ = 40.3 Hz, CpC), 71.7 (CpC), 71.4 (d, $J_{C\text{-}P}$ = 7.3 Hz, CpC), 70.4 (CpC), 35.0 (*C*(CH_3)$_3$, two overlapping resonances) 32.3 [C(*C*H$_3$)$_3$], 31.5 (d, $J_{C\text{-}P}$ = 4.9 Hz, $C(CH_3)_3$), 20.8 (CH_3), 20.6 (CH_3), 16.9 (CH_3), 16.5 (CH_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 180.3 (s). HRMS *m*/*z* ESI$^+$ found 973.4114 $[M + Na]^+$ calculated for $C_{58}H_{72}FeNaO_4P_2$ 973.4147.

Synthesis of L2: Although this compound has been reported previously,[23] an alternative synthetic method is described herein. The reaction was setup using an inert-atmosphere protocol similar to that described for the synthesis of **L1**, employing 1,1′-dilithioferrocene-tetramethylethylenediamine adduct (1.08 mmol), and 2-bromo-1,3-dimesityl-1,3,2-diazaphospholene (2.26 mmol) in place of (BIPHEN)PCl, in toluene (6 mL) at –33 °C. Upon combination of the reagents, the reaction mixture was stirred magnetically with warming to room temperature over the course of 4 h. The reaction mixture was dried in vacuo, subsequently dissolved in dichloromethane (10 mL) and filtered through a sintered glass frit containing Celite and silica. The solvent from the collected eluent was removed in vacuo, the resultant residue was washed with hexanes (3 × 4 mL), and the resultant solid was dried in vacuo to afford the product in 32 % yield (290 mg, 0.35 mmol) as a yellow solid. NMR spectroscopic data for **L2** were in agreement with the literature.[23]

General Procedure for the Monoarylation of Primary Amines and Indoles with Aryl Chlorides (GP1): *For primary amines:* Within a dinitrogen filled glove-box, **L1** (0.05 equiv.), NaO*t*Bu (2.0 equiv.), and aryl chloride (1.0 equiv.) were added to a screw capped vial containing a magnetic stir bar, followed by the addition of bis(cyclooctadiene)-nickel(0) (0.05 equiv.) dissolved in toluene (0.12 M aryl halide). To this solution was added furfurylamine (1.1 equiv.), and the vial was sealed with a cap containing a PTFE septum, removed from the glove-box and placed in a temperature-controlled aluminum heating block set to 80 °C for 16 h under the influence of magnetic stirring. *For indoles:* Analogous conditions were followed except LiO*t*Bu (1.5 equiv.) was utilized as base, and indole was added just prior to the addition of bis(cyclooctadiene)-nickel(0) solution. After cooling to room-temperature, either dodecane or 1-phenyldodecane (0.12 mmol) was added to the reaction mixture as an internal standard, so that the resulting mixtures could be quantitatively analyzed by using GC methods following the workup method stated below.

General Procedure for the N-Arylation of Morpholine with Aryl Chlorides (GP2): Within a dinitrogen filled glove-box, **L1**

(0.05 equiv.), LiO*t*Bu (1.5 equiv.), and aryl chloride (1.0 equiv.) were added to a screw capped vial containing a magnetic stir bar, followed by the addition of bis(cyclooctadiene)-nickel(0) (0.05 equiv.) dissolved in CPME (0.5 M aryl halide). To this solution was added morpholine (1.5 equiv.), and the vial was sealed with a cap containing a PTFE septum, removed from the glove-box and placed in a temperature-controlled aluminum heating block set to 80 °C for 16 h under the influence of magnetic stirring. After cooling to room-temperature, dodecane (0.12 mmol) was added to the reaction mixture as an internal standard, so that the resulting mixture could be quantitatively analyzed by using GC methods following the workup method stated below.

Workup Method for Preparation of GC Samples: Following GP1 or GP2, (employing 0.12 mmol aryl halide) in air the reaction mixture was diluted using ethyl acetate and was passed through a Kimwipe filter containing Celite and silica gel, with the eluent collected in a GC vial. Response-factor calibrated GC estimates are given on the basis of data obtained from authentic materials using dodecane or 1-phenyldodecane as internal standards.

Isolation of 2-Methyl-*N*-(2-thienylmethyl)–4-quinolinamine (1b): The title compound was synthesized from the corresponding aryl chloride (1.0 mmol) according to GP1. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with brine (3 × 20 mL), and the organic layer was dried with sodium sulfate. The solvent was removed in vacuo and the compound was purified by flash column chromatography on silica gel using a trimethylamine/ethyl acetate eluent (4 % triethylamine) which afforded the title product in 89 % isolated yield (226 mg, 0.89 mmol) as an off-white solid. ^{1}H NMR (300 MHz; $CDCl_3$): δ = 7.93 (m, 1H), 7.69 (m, 1H), 7.61 (m, 1H), 7.38 (m, 1H), 7.29 (dd, 1H, J_1 = 5.1 Hz, J_2 = 1.2), 7.10 (m, 1H), 7.02 (dd, 1H, J_1 = 5.1 Hz, J_2 = 3.5), 6.46 (s, 1H), 5.22 (br. s, 1H), 4.70 (d, 2H, J = 5.2 Hz), 2.63 (s, 3H). ^{13}C{^{1}H} UDEFT NMR (125.8 MHz, $CDCl_3$): δ = 160.0, 149.3, 148.7, 141.0, 129.7, 129.5, 127.5, 126.4, 125.7, 124.5, 119.4, 117.7, 100.1, 43.0, 26.2. HRMS *m/z* ESI$^+$ found 255.0957 [M + H]$^+$ calculated for $C_{15}H_{15}N_2S$ 255.0950.

Acknowledgments

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Keywords: Amination · C–N cross-coupling · Ferrocenyl ligands · Ligand design · Nickel

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