ORGANOMETALLICS

pubs.acs.org/Organometallics Article

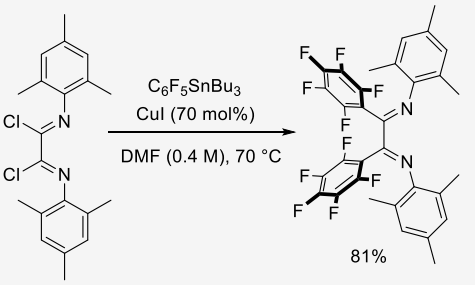
Copper Iodide-Mediated Synthesis of α-Diimine Ligands from Bis(imidoyl chlorides) and Arylstannanes

Thien Lieu and Olafs Daugulis*

Cite This: https://doi.org/10.1021/acs.organomet.2c00264 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Aryl-substituted α-diimines were prepared by means of an operationally simple copper iodide-mediated Stille-type coupling between polyfluoro(chloro)-aryl tributylstannanes and bis(imidoyl chlorides). Reactions proceed in commercial grade *N, N*-dimethylformamide (DMF) solvent at 70 °C and require no additives or bases. Couplings are successful for aryl stannanes possessing two or more fluoro or chloro substituents on the aromatic ring. Products are obtained in moderate to good yields. This methodology allows for a simple synthesis of α-diimine ligands potentially useful in olefin polymerization as well as other catalytic transformations.



1. INTRODUCTION

α-Diimines are good σ-donor and π-acceptor ligands in organometallic chemistry.[1,2] Their complexes with transition metals have been widely utilized in catalytic transformations such as oxidation of alkanes, azide−alkyne cycloaddition, reductions, Heck olefination, hydrogenation of alkynes/alkenes, Suzuki coupling, C−H/Si−H functionalization, and allylic amination.[2] Furthermore, nickel and palladium complexes supported by bulky α-diimine ligands are extremely effective as catalysts in olefin polymerization, affording high-molecular-weight polymers with varying branching numbers (Figure 1). These catalytic systems were discovered by Dr.

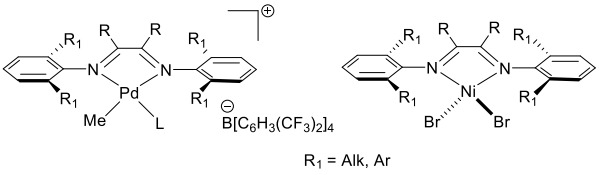
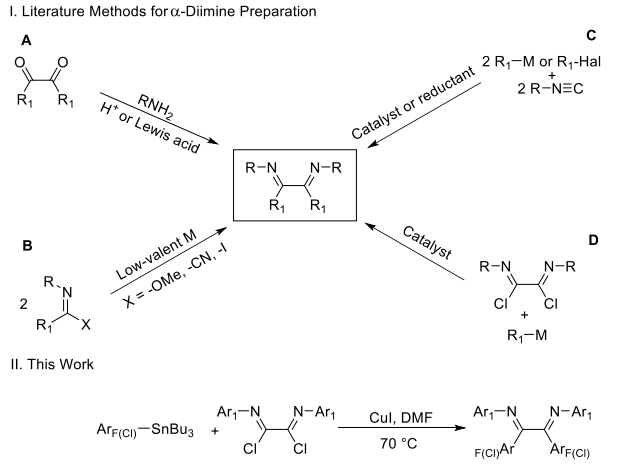


Figure 1. Brookhart-type catalysts for alkene polymerization.

Lynda Johnson in the Brookhart group, which has been instrumental in developing late transition metal catalysts for olefin polymerization.[3] A quarter century after the initial report, modifications of the original diimine systems are still being explored by dozens of research groups. These efforts have resulted in the preparation of a large number of α-diimine ligands and their nickel and palladium complexes. However, some types of α-diimines are nearly unknown because of difficulties in their synthesis. For example, it appears that only a few α-diimines with a highly electrophilic pentafluorphenyl backbone are known, and they have been prepared by employing a reaction of $Pd(C_6F_5)_2(CNR)_2$ with $PdCl_2(NCPh)_2$.[4] In the context of olefin polymerization studies, we required a facile method for the synthesis of diimines with electron-withdrawing backbones. Analysis of the literature revealed that α-diimines can be prepared via four different major pathways (Scheme 1). Imine condensation between α-diketones and primary amines is presumably the most straightforward method (Scheme 1, pathway A).[5] However, condensations often require highly specialized conditions and occasionally are low-yielding.[5e−h] Furthermore, only a limited number of α-diketones are commercially available, and their preparation, which is not always trivial,

Scheme 1. Synthesis of α-Diimines



Special Issue: Organometallic Chemistry Inspired by Maurice Brookhart

Received: May 31, 2022

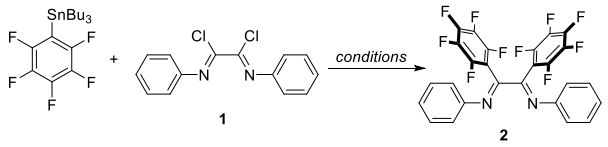
increases the length of synthetic pathways. Alternatively, α-diimines can be synthesized by reductive dimerization of iminoacyl derivatives (Scheme 1, pathway B).[6] The method has increased the availability of α-diimines; however, the reductive conditions employed in this methodology limit its functional group tolerance. The third synthetic route for α-diimine preparation is cross-coupling between isonitriles and aryl halides or arylmetal reagents (Scheme 1, pathway C).[7] The method most relevant to the current study is homologation of bis(imidoyl chlorides) (Scheme 1, pathway D).[8] In 1997, Faust and Göbelt introduced palladium-mediated double Stille coupling of organostannanes with bis(imidoyl chlorides) to afford diimines.[8a,b] This work is based on earlier reports in which (mono)imidoyl chlorides were coupled with organometallic reagents[8c−f] and remains the only example of the use of bis(imidoyl)chlorides in transition-metal-catalyzed coupling reactions to generate 1,2-diimines.[8g] Presumably, coupling reactions producing 1,2-diimines may be problematic because of their high chelating ability toward the transition metal catalyst. A recent paper by Tonks reported diimination of alkynes via a titanium-mediated reaction.[8h]

We report here a copper-promoted Stille coupling between bis(imidoyl chlorides) and perfluoro(chloro)arylstannanes that affords α-diimine ligands containing highly electrophilic backbones.

2. RESULTS AND DISCUSSION

2.1. Optimization of the Reaction Conditions. We examined the cross-coupling reaction of tributyl(2,3,4,5,6-pentafluorophenyl)stannane with *N*,*N*′-diphenyloxalimidoyl dichloride (**1**) using a palladium(0) catalyst, copper(I) iodide cocatalyst, and triphenylphosphine ligand in DMF at 110 °C (Table 1). These conditions mimic known reaction conditions reported earlier with different substrates.[8a] Only a 14% yield of the desired α-diimine **2** was obtained (entry 1). Changing ligands did not result in increased yields (entries 2 and 3). An increase in reaction yield to 40% was observed when the temperature was lowered to 70 °C and the concentration was doubled (entry 4). Somewhat surprisingly, the yield was drastically increased to 66% in a control experiment where the palladium catalyst and ligand were omitted, showing that the reaction is efficiently catalyzed by copper (entry 5). This result is reminiscent of Liebeskind's copper-catalyzed Stille reactions.[9a] Increasing the amount of copper did not lead to higher yields (entry 6), and the use of 30 mol % CuI resulted in a slightly lower yield (entry 7). Liebeskind reported that copper(I) thiophene-2-carboxylate (CuTC) is a superior catalyst for Cu-catalyzed Stille coupling reactions.[9a] However, for bis(imidoyl chloride) coupling a lower yield of the product was obtained (entry 8). Control experiments were conducted in the absence of copper catalyst (entry 9) and with the addition of 1,10-phenanthroline ligand (entry 10). No product was obtained in either case. The reaction promoted by copper(I) iodide at 70 °C afforded the highest yield and was used for further investigations.

Table 1. Reaction Optimization[a]



entry	conditions	yield (%)
1	Pd_2dba_3 10%, PPh_3 70%, CuI 35%, DMF, 110 °C	14
2	Pd_2dba_3 10%, $AsPh_3$ 70%, CuI 35%, DMF, 110 °C	trace
3	Pd_2dba_3 10%, Cy_3P 70%, CuI 35%, DMF, 110 °C	16
4[b]	Pd_2dba_3 10%, PPh_3 70%, CuI 35%, DMF, 70 °C	40
5[b]	CuI (70 mol %), 70 °C	66
6[b]	CuI (1.5 equiv), 70 °C	63
7[b]	CuI (30 mol %), 70 °C	61
8[b]	CuTC (70 mol %), 70 °C	39
9[b]	No catalyst, 70 °C	NR
10[b]	CuI (70 mol %) and phen (70 mol %), 70 °C	NR

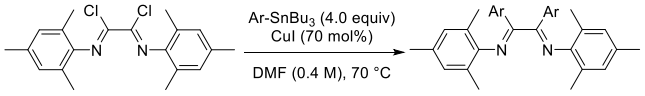
[a]Reaction conditions: 0.2 mmol (1 equiv) of **1** and 0.8 mmol (4 equiv) of stannane in DMF (1.0 mL, 0.2 M) for 15 h. Isolated yields are reported. Abbreviations: $Pd_2(dba)_3$ = tris(dibenzylideneacetone)-dipalladium(0), Cy_3P = tricyclohexylphosphine, phen = 1,10-phenanthroline, CuTC = copper(I) thiophene-2-carboxylate. [b]DMF (0.5 mL, 0.4 M).

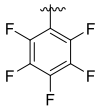
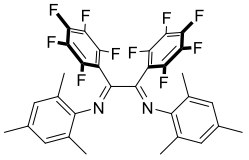
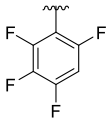
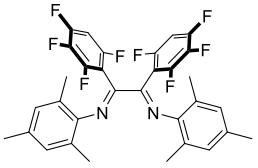
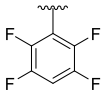
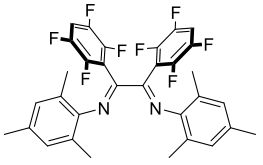
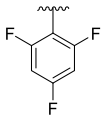
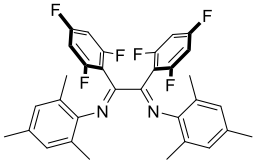
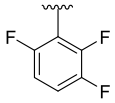
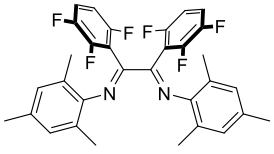
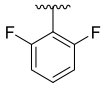
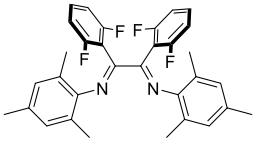
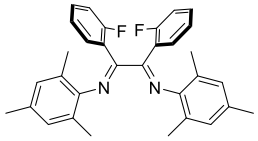
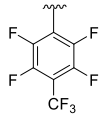
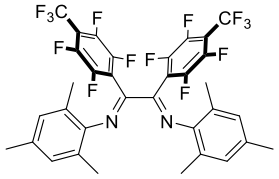
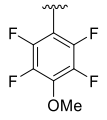
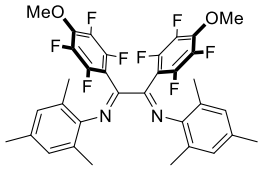
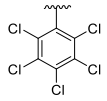
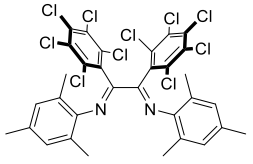
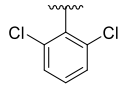
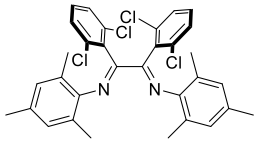
2.2. Reaction Scope with Respect to the Arylstannane Coupling Component. With improved coupling conditions in hand, the reaction scope with respect to arylstannanes was explored. *N*,*N*′-Dimesityloxalimidoyl dichloride was reacted with a number of polyfluoro(chloro)-arylstannanes in the presence of copper(I) iodide (Table 2). Coupling with tributyl(2,3,4,5,6-pentafluorophenyl)stannane afforded the product in 81% yield (entry 1). The yield gradually decreased as the number of fluorines on the aromatic ring of the organotin reagent decreased (entries 2−4). For example, stannanes containing four fluorines on the aromatic ring gave the coupling products in 76 and 77% yield (entries 2 and 3), while those with three fluorines afforded yields of 64 and 77% (entries 4 and 5). An organostannane containing two *o*-fluorines gave only a 13% yield of the coupling product (entry 6). However, the yield increased to 53% when 1.5 equiv of CuI was used at 100 °C. It appears that coupling reaction requires at least two fluorine atoms in the stannane reagent, which may be related to ease of transmetalation from tin to copper.[9] The reaction of tributyl(2-fluorophenyl)stannane with *N*,*N*′-dimesityloxalimidoyl dichloride gave no product (entry 7). Coupling with tributyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)stannane gave the product in 63% yield (entry 8). Tributyl(4-methoxy-2,3,5,6-tetrafluorophenyl)-stannane afforded a 73% yield (entry 9). Interestingly, the reaction was successful with polychlorinated substrates as well. Thus, a 76% yield of coupling product was obtained in the reaction with tributyl(2,3,4,5,6-pentachlorophenyl)stannane (entry 10). The stannane containing two *o*-chlorine atoms on the aromatic ring was reactive, and the product was isolated in 67% yield (entry 11). Monocoupling products were not observed during the reactions. Presumably, the second coupling is faster than the first one.

2.3. Reaction Scope with Respect to the Bis(imidoyl chloride) Coupling Component. Subsequently, we explored reaction scope with respect to substituents on the bis(imidoyl chloride) substrate. Tributyl(2,3,4,5,6-tetrafluorophenyl)-stannane was reacted with bis(imidoyl chlorides) using a copper(I) iodide catalyst (Table 3). A hindered substrate with four *o*-isopropyl substituents gave the coupling product in an excellent 95% yield (entry 1). The *N*-naphthalen-1-yl-

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX

Table 2. Reaction Scope with Respect to Organostannanes[a]



entry	Ar	product	yield (%)
1			81
2			76
3			77
4			64
5			77
6			13 53[b]
7			NR[b]
8			63
9			73
10			76
11			67[b]

[a]Bis(imidoyl chloride) (0.2 mmol, 1.0 equiv), organotin reagent (0.8 mmol, 4.0 equiv), CuI (0.14 mmol, 0.7 equiv), DMF (0.5 mL, 0.4 M), 70 °C, 15 h. Isolated yields are reported. [b]The reaction was performed at 100 °C with 0.3 mmol (1.5 equiv) of CuI.

containing imidoyl chloride reacted to afford the product in 45% yield (entry 2). Coupling with a substrate possessing a 3,5-disubstituted aryl moiety worked well, and the product was isolated in 54% yield (entry 3). The reaction tolerates electron-withdrawing substituents at the 4- and 3,5-positions of the aromatic ring, and coupling with trifluoromethyl- or fluoro-containing substrates gave the products in good yields (entries 4, 5, and 7). Substitution with a strongly electron-donating methoxy group resulted in a somewhat lower product yield of 60% (entry 6).

3. CONCLUSIONS

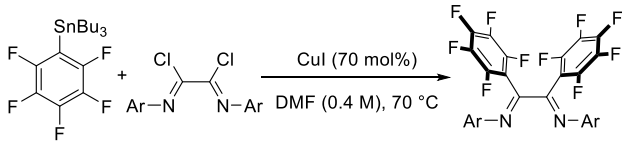
We have reported an alternative methodology for the synthesis of α-diimines bearing electron-deficient backbones that uses a copper-mediated Stille coupling reaction between polyfluoro-(chloro)organostannanes and bis(imidoyl chlorides). The reaction is performed under mild conditions, is operationally simple, requires no additives, ligands, or bases besides copper(I) iodide, and tolerates steric bulk on both coupling partners. The products are obtained in moderate to good yields. This methodology allows for the simple synthesis of α-diimine ligands that are potentially useful in olefin polymerization as well as other catalytic transformations.

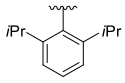
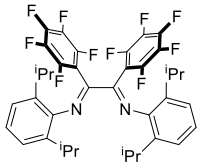
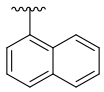
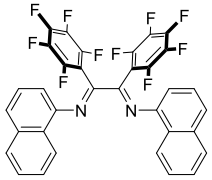
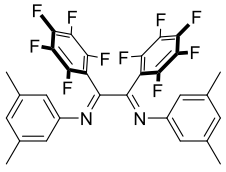
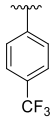
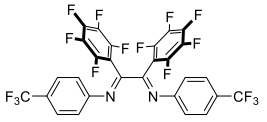
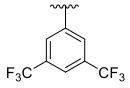
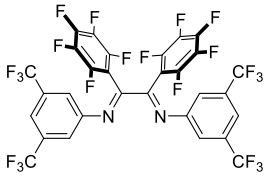
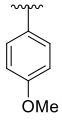
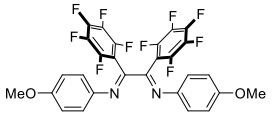
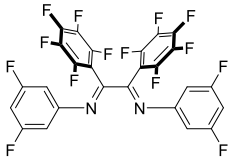
4. EXPERIMENTAL SECTION

4.1. General Materials and Methods. All manipulations of air- and moisture-sensitive compounds were carried out using standard Schlenk, high-vacuum, and glovebox techniques. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on JEOL EC-400 and EC-500 spectrometers using the residual solvent peak as a reference. The following materials and solvents were obtained from commercial sources and used without further purification: DMF, $Pd_2(dba)_3$, CuI, CuTC, $AsPh_3$, Cy_3P, C_6Cl_5H, triphenylphosphine, oxalyl chloride, all of the amines, and all of the fluoroarene starting materials. 1,2,3,4,5-Pentachloro-6-iodobenzene was synthesized according to a known procedure.[10] Toluene, THF, and diethyl ether were purified by a JC

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX

Table 3. Reaction Scope with Respect to Bis(imidoyl Chlorides)[a]



entry	Ar	product	yield (%)
1			95 87[b]
2			45
3			54
4			69
5			76
6			60
7			80

[a]Bis(imidoyl chloride) (0.2 mmol, 1.0 equiv), organotin reagent (0.8 mmol, 4.0 equiv), CuI (0.14 mmol, 0.7 equiv), DMF (0.5 mL, 0.4 M), 15 h, 70 °C. Isolated yields are reported. [b]Reaction scale: 2.0 mmol.

Meyer solvent purification system. Column chromatography was performed on 60 Å silica gel (SiliCycle Inc.). Compounds for HRMS were analyzed by positive-mode electrospray ionization (CI or ESI) using an Agilent QTOF mass spectrometer in the Mass Spectrometry Facility (MSF) of the Department of Chemistry and Biochemistry of the University of Texas at Austin. Infrared spectra were collected on a PerkinElmer Spectrum 100 FT-IR or Nicolet iS10 FT-IR spectrometer.

4.2. General Procedure for α-Diimine Synthesis with Respect to Organostannanes. Outside the glovebox, a 2 dram vial equipped with a magnetic stir bar was charged with CuI (27 mg, 70 mol %) and *N,N′*-dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol, 1.0 equiv). The vial was placed in the glovebox. After that, the organostannane (0.8 mmol, 4.0 equiv) and DMF (0.5 mL) were added. The vial was sealed, taken out of the glovebox, and placed into a heating block preheated to 70 °C for 15 h. Subsequently, the vial was cooled to room temperature. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with brine (3 × 20 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified using column chromatography, followed by washing with cold (0 °C) pentane and drying under vacuum.

N,N′-Diphenyl-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 1). *N,N′*-Diphenyloxalimidoyl dichloride (55 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.80 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−10% CH_2Cl_2 in hexanes); yield 66% (71 mg); R_f = 0.75 (hexanes/EtOAc = 9/1); yellow solid; mp 213−215 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.25 (t, J = 10.0 Hz, 4H), 7.10 (t, J = 10.0 Hz, 2H), 6.72 (d, J = 5.0 Hz, 4H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −136.9 to −137.0 (m, 4F), −150.7 (t, J_{F-F} = 18.8 Hz, 2F), −160.6 to −160.8 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 155.1, 148.8, 144.2−142.2 (m), 143.1−141.0 (m), 138.6−136.5 (m), 129.1, 126.3, 118.2, 109.2 (t, J_{C-F} = 25.6 Hz); HRMS (ESI) calcd for $C_{26}H_{10}F_{10}N_2$ $[M + H]^+$ 541.0757, found 541.0755; FT-IR (neat) $\bar{\nu}$ 2998, 1659, 1616, 1523, 1495, 1310, 1128, 972, 831, 792, 709 cm^{-1}.

N,N′-Dimesityl-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 2, entry 1). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−10% CH_2Cl_2 in hexanes); yield 81% (101 mg); R_f = 0.96 (hexanes/EtOAc = 9/1); deep-yellow solid; mp 229−231 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.75 (s, 4H), 2.19 (s, 6H), 1.96 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −135.9 (dd, J_{F-F} = 18.8, 4.7 Hz, 4F), −150.7 (t, J_{F-F} = 18.8 Hz, 2F), −160.6 to −160.8 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 155.4, 144.6−142.6 (m), 143.7, 142.9−140.9 (m), 138.5−136.5 (m), 134.6, 128.9, 125.4, 110.2 (t, J_{C-F} = 25.6 Hz), 20.7, 17.5; HRMS (ESI) calcd for $C_{32}H_{22}F_{10}N_2$ $[M + H]^+$ 625.1696, found 625.1694; FT-IR (neat) $\bar{\nu}$ 3009, 2920, 1656, 1520, 1494, 1422, 1310, 1201, 1145, 985, 884, 854, 817 cm^{-1}.

N,N′-Dimesityl-1,2-bis(2,3,4,6-tetrafluorophenyl)ethane-1,2-diimine (Table 2, entry 2). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,3,4,6-tetrafluorophenyl)stannane (0.35 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−10% CH_2Cl_2 in hexanes); yield 76% (90 mg); R_f = 0.72 (hexanes/EtOAc = 9/1); deep-yellow solid; mp 198−199 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.73 (s, 4H), 6.71−6.65 (m, 2H), 2.18 (s, 6H), 1.96 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −111.2 to −111.5 (m, 2F), −128.6 to −128.9 (m, 2F), −129.3 to −129.5 (m, 2F), −164.2 to −164.4 (m, 2F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 156.7, 154.8−152.8 (m), 152.3−150.3 (m), 149.6−147.6 (m), 144.0, 138.0−136.0 (m), 134.1, 128.7, 125.6, 110.5 (t, J_{C-F} = 24.3 Hz), 101.2 (t, J_{C-F} = 25.6 Hz), 20.8, 17.5; HRMS (ESI) calcd for $C_{32}H_{24}F_8N_2$ $[M + H]^+$ 589.1885, found 589.1887; FT-IR (neat) $\bar{\nu}$ 2921, 2855, 1648, 1512, 1462, 1377, 1262, 1225, 1162, 1118, 1055, 944, 856, 829, 739 cm^{-1}.

N,N′-Dimesityl-1,2-bis(2,3,5,6-tetrafluorophenyl)ethane-1,2-diimine (Table 2, entry 3). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,3,5,6-trifluorophenyl)stannane (0.35 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−15% CH_2Cl_2 in hexanes); yield 77% (91 mg); R_f = 0.70 (hexanes/EtOAc = 9/1); orange solid; mp 278−281 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.05−6.98 (m, 2H), 6.73 (s, 4H), 2.18 (s, 6H), 1.97 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −136.6 to −136.7 (m, 4F), −138.2 to −138.4 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 156.2, 146.6−144.6 (m), 143.8, 144.3−142.3 (m), 134.3, 128.8, 125.6, 116.1 (t, J_{C-F} = 20.5 Hz), 107.3 (t, J_{C-F} = 21.8 Hz), 20.8, 17.6; HRMS (ESI) calcd for $C_{32}H_{24}F_8N_2$ $[M + H]^+$ 589.1885, found 589.1882; FT-IR (neat) $\bar{\nu}$ 3054, 2918, 1634, 1488, 1383, 1266, 1201, 1179, 1139, 933, 862, 852, 822, 725, 714 cm^{-1}.

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX

N,N′-Dimesityl-1,2-bis(2,4,6-trifluorophenyl)ethane-1,2-diimine (Table 2, entry 4). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,4,6-trifluorophenyl)stannane (0.34 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−15% CH_2Cl_2 in hexanes); yield 64% (71 mg); R_f = 0.72 (hexanes/EtOAc = 9/1); yellow solid; mp 177−178 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.71 (s, 4H), 6.60−6.32 (m, 4H), 2.17 (s, 6H), 1.95 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −104.9 to −105.0 (m, 4F), −105.7 to −105.9 (m, 2F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 164.2−162.2 (m), 161.1−159.1 (m), 157.9, 144.4, 133.6, 128.5, 126.2, 109.8 (t, J_{C-F} = 25.6 Hz), 100.4 (t, J_{C-F} = 25.6 Hz), 20.8, 17.6; HRMS (ESI) calcd for $C_{32}H_{26}F_6N_2$ $[M + H]^+$ 553.2073, found 553.2075; FT-IR (neat) $\bar{\nu}$ 3001, 2922, 2854, 1635, 1597, 1486, 1435, 1211, 1120, 1034, 998, 923, 851, 831, 742 cm^{-1}.

N,N′-Dimesityl-1,2-bis(2,3,6-trifluorophenyl)ethane-1,2-diimine (Table 2, entry 5). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,3,6-trifluorophenyl)stannane (0.34 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−5% EtOAc in hexanes); yield 77% (85 mg); R_f = 0.75 (hexanes/EtOAc = 9/1); yellow solid; mp 258−259 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.09−7.03 (m, 2H), 6.76−6.71 (m, 6H), 2.16 (s, 6H), 1.97 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −113.0 to −113.2 (m, 2F), −130.7 to −130.9 (m, 2F), −142.0 to −142.2 (m, 2F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 157.5, 155.8−153.8 (m), 148.5−146.5 (m), 148.0−146.0 (m), 144.2, 133.8, 128.6, 125.7, 118.1−117.9 (m), 115.3−114.9 (m), 110.4−110.7 (m), 20.8, 17.6; HRMS (ESI) calcd for $C_{32}H_{26}F_6N_2$ $[M + H]^+$ 553.2073, found 553.2074; FT-IR (neat) $\bar{\nu}$ 3049, 2924, 1864, 1631, 1488, 1250, 1198, 1031, 854, 841, 831, 810, 743, 725 cm^{-1}.

N,N′-Dimesityl-1,2-bis(2,6-difluorophenyl)ethane-1,2-diimine (Table 2, entry 6). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,6-difluorophenyl)stannane (0.32 g, 0.8 mmol), CuI (57 mg, 1.5 equiv), and DMF (0.5 mL), 100 °C; purification (0−5% EtOAc in hexanes); yield 53% (55 mg); R_f = 0.70 (hexanes/EtOAc = 9/1); yellow solid; mp 230−233 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.23−7.18 (m, 2H), 6.80−6.76 (m, 4H), 6.68 (s, 4H), 2.15 (s, 6H), 1.97 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −107.9 to −108.0 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 160.8−158.8 (m), 158.9, 144.7, 133.3, 131.1−130.9 (m), 128.4, 125.9, 113.6 (t, J_{C-F} = 25.6 Hz), 111.3 (d, J_{C-F} = 23.0 Hz), 20.8, 17.6; HRMS (ESI) calcd for $C_{32}H_{28}F_4N_2$ $[M + H]^+$ 517.2261, found 517.2261; FT-IR (neat) $\bar{\nu}$ 3003, 2916, 1644, 1623, 1460, 1268, 1212, 998, 939, 813, 787, 771 cm^{-1}.

N,N′-Dimesityl-1,2-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)ethane-1,2-diimine (Table 2, entry 8). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)stannane (0.4 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−10% CH_2Cl_2 in hexanes); yield 63% (91 mg); R_f = 0.83 (hexanes/EtOAc = 9/1); orange solid; mp 248−250 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.77 (s, 4H), 2.20 (s, 6H), 1.96 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −56.3 (t, J_{F-F} = 23.5 Hz, 6F), −134.1 to −134.3 (m, 4F), −139.2 to −139.3 (m, 4F). ^{13}C (128 MHz, $CDCl_3$) δ 154.6, 144.9−142.9 (m), 144.6−142.6 (m), 143.2, 135.1, 129.1, 125.3, 119.4−119.0 (m), 111.1−110.8 (m), 20.8, 17.6 (signal for one carbon could not be located); HRMS (ESI) calcd for $C_{34}H_{22}F_{14}N_2$ $[M + H]^+$ 725.1632, found 725.1620; FT-IR (neat) $\bar{\nu}$ 3009, 2921, 1663, 1629, 1479, 1329, 1191, 1138, 986, 853, 815, 712 cm^{-1}.

N,N′-Dimesityl-1,2-bis(4-methoxy-2,3,5,6-tetrafluorophenyl)-ethane-1,2-diimine (Table 2, entry 9). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(4-methoxy-2,3,5,6-tetrafluorophenyl)stannane (0.38 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−20% CH_2Cl_2 in hexanes); yield 76% (94 mg); R_f = 0.59 (hexanes/EtOAc = 9/1); orange solid; mp 199−201 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.75 (s, 4H), 4.06 (s, 6H), 2.19 (s, 6H), 1.98 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −137.7 (d, J_{F-F} = 14.1 Hz, 4F), −157.6 (d, J_{F-F} = 14.1 Hz, 4F). ^{13}C (128 MHz, $CDCl_3$) δ 156.4, 144.9−142.9 (m), 144.0, 141.4−139.4 (m), 139.4−139.2 (m), 134.1, 128.8, 125.6, 108.3 (t, J_{C-F} = 20.5 Hz), 62.0, 20.8, 17.6; HRMS (ESI) calcd for $C_{34}H_{28}F_8N_2O_2$ $[M + H]^+$ 649.2096, found 649.2093; FT-IR (neat) $\bar{\nu}$ 2961, 2920, 1652, 1506, 1484, 1414, 1199, 1145, 1021, 985, 853, 813, 786 cm^{-1}.

N,N′-Dimesityl-1,2-bis(pentachlorophenyl)ethane-1,2-diimine (Table 2, entry 10). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(pentachlorophenyl)stannane (0.43 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−10% CH_2Cl_2 in hexanes); yield 76% (121 mg); R_f = 0.83 (hexanes/EtOAc = 9/1); yellow solid; mp 293−294 °C (pentane); ^{1}H NMR (500 MHz, CD_2Cl_2, ppm) 6.69 (s, 4H), 2.15 (s, 6H), 1.88 (s, 12H); ^{13}C NMR (128 MHz, CD_2Cl_2, ppm) δ 157.2, 142.1, 136.3, 135.3, 134.2, 132.2, 131.2, 129.0, 127.4, 20.5, 18.8; HRMS (ESI) calcd for $C_{32}H_{22}Cl_{10}N_2$ $[M + H]^+$ 787.8741, found 784.8719; FT-IR (neat) $\bar{\nu}$ 2915, 1636, 1607, 1471, 1449, 1369, 1343, 1265, 1141, 1123, 965, 848, 734, 714, 686 cm^{-1}.

N,N′-Dimesityl-1,2-bis(2,6-dichlorophenyl)ethane-1,2-diimine (Table 2, entry 11). *N,N′*-Dimesityloxalimidoyl dichloride (72 mg, 0.2 mmol), tributyl(2,6-dichlorophenyl)stannane (0.35 g, 0.8 mmol), CuI (57 mg, 1.5 equiv), and DMF (0.5 mL), 100 °C; purification (0−15% CH_2Cl_2 in hexanes); yield 67% (78 mg); R_f = 0.80 (hexanes/EtOAc = 9/1); yellow solid; mp 288−289 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.21 (d, J = 10.0 Hz, 4H), 7.14 (t, J = 10.0 Hz, 2H), 6.67 (s, 4H), 2.16 (s, 6H), 1.94 (s, 12H); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 159.3, 143.1, 135.7, 134.5, 134.2, 129.8, 128.7, 128.3, 127.7, 20.8, 18.9; FT-IR (neat) $\bar{\nu}$ 3003, 2952, 2908, 1642, 1557, 1470, 1427, 1374, 1211, 1187, 1093, 886, 848, 796, 785, 728 cm^{-1}.

4.3. General Procedure for α-Diimine Synthesis with Respect to Bis(imidoyl chlorides). Outside the glovebox, a 2 dram vial equipped with a magnetic stir bar was charged with CuI (27 mg, 70 mol %) and the bis(imidoyl chloride) (0.2 mmol, 1.0 equiv). The vial was placed in the glovebox. After that, tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol, 4.0 equiv) and DMF (0.5 mL) were added. The vial was sealed, taken out of the glovebox, and placed into a heating block preheated to 70 °C for 15 h. Subsequently, the vial was cooled to room temperature. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with brine (3 × 20 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified using column chromatography, followed by washing with cold (0 °C) pentane and drying under vacuum.

N,N′-Bis(2,6-diisopropylphenyl)-1,2-bis(pentafluorophenyl)-ethane-1,2-diimine (Table 3, entry 1). *N,N′*-Bis(2,6-diisopropylphenyl)oxalimidoyl dichloride (89 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−10% CH_2Cl_2 in hexanes); yield 95% (134 mg); R_f = 0.83 (hexanes/EtOAc = 9/1); yellow solid; mp 168−171 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.06−7.01 (m, 6H), 2.74 (td, J = 10.0, 5.0 Hz, 4H), 1.10 (d, J = 10.0 Hz, 12H), 0.92 (d, J = 5.0 Hz, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −137.0 (dd, J_{F-F} = 14.1, 9.4 Hz, 4F), −150.6 (t, J_{F-F} = 18.8 Hz, 2F), −161.1 to −161.2 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 154.6, 144.7−142.7 (m), 143.7, 140.7−138.7 (m), 138.5−136.5 (m), 135.5, 125.9, 122.6, 109.6 (t, J_{C-F} = 25.6 Hz), 28.0, 23.9, 21.4; HRMS (ESI) calcd for $C_{38}H_{34}F_{10}N_2$ $[M + H]^+$ 709.2635, found 709.2623; FT-IR (neat) $\bar{\nu}$ 2969, 2867, 1654, 1626, 1520, 1495, 1424, 1327, 1131, 992, 977, 834, 798, 777, 745 cm^{-1}.

N,N′-Bis(naphthalen-1-yl)-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 3, entry 2). *N,N′*-Bis(naphthalen-1-yl)oxalimidoyl dichloride (75 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)-stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−20% CH_2Cl_2 in hexanes); yield 45% (58 mg); R_f = 0.62 (hexanes/EtOAc = 9/1); red solid; mp 185−186 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.84−7.78 (m, 4H), 7.65 (d, J = 10.0 Hz, 2H), 7.57−7.52 (m, 4H), 7.30 (t, J = 10.0 Hz, 2H), 6.64 (d, J = 10.0 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −137.0 to −137.1 (m, 4F), −150.6 (t, J_{F-F} = 18.8 Hz, 2F), −160.3 to −160.4 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 155.3, 145.1, 144.5−142.5 (m), 143.0−141.0 (m), 138.5−136.5 (m), 133.9, 128.0,

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX

127.1, 127.0, 126.7, 126.0, 125.3, 123.1, 112.4 (one carbon signal could not be located); HRMS (ESI) calcd for $C_{34}H_{14}F_{10}N_2$ $[M + H]^+$ 641.1070, found 641.1057; FT-IR (neat) $\bar{\nu}$ 3057, 1654, 1612, 1518, 1494, 1425, 1312, 1264, 1129, 993, 970, 822, 841, 794, 767, 736 cm^{-1}.

N,N′-Bis(3,5-dimethylphenyl)-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 3, entry 3). N,N′-Bis(3,5-dimethylphenyl)-oxalimidoyl dichloride (67 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−15% CH_2Cl_2 in hexanes); yield 54% (65 mg); R_f = 0.81 (hexanes/EtOAc = 9/1); yellow solid; mp 247−249 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.71 (s, 2H), 6.31 (s, 4H), 2.21 (s, 12H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −137.0 to −137.2 (m, 4F), −151.2 (t, J_{F-F} = 18.8 Hz, 2F), −160.9 to −161.1 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 154.6, 148.9, 144.1−142.1 (m), 142.5−140.5 (m), 138.8, 138.4−136.4 (m), 127.8, 115.6, 109.5 (t, J_{C-F} = 25.6 Hz), 21.3; HRMS (ESI) calcd for $C_{30}H_{18}F_{10}N_2$ $[M + H]^+$ 597.1383, found 597.1384; FT-IR (neat) $\bar{\nu}$ 3100, 2924, 1654, 1519, 1494, 1421, 1314, 1149, 1125, 992, 973, 888, 847, 806, 688 cm^{-1}.

N,N′-Bis(4-trifluoromethylphenyl)-1,2-bis(pentafluorophenyl)-ethane-1,2-diimine (Table 3, entry 4). N,N′-Bis(4-trifluoromethylphenyl)oxalimidoyl dichloride (83 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (5−15% CH_2Cl_2 in hexanes); yield 69% (93 mg); R_f = 0.76 (hexanes/EtOAc = 9/1); light-yellow solid; mp 221−222 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.53 (d, J = 10.0 Hz, 4H), 8.81 (d, J = 10.0 Hz, 4H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −62.2 (s, 6F), −136.9 to −137.0 (m, 4F), −148.8 (t, J_{F-F} = 18.8 Hz, 2F), −159.4 to −159.7 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 156.0, 151.4, 143.7−141.7 (m), 138.4−136.4 (m), 128.5 (q, J_{C-F} = 32.0 Hz), 126.5 (q, J_{C-F} = 3.8 Hz), 123.8 (q, J_{C-F} = 276.5 Hz), 118.1, 107.9 (t, J_{C-F} = 56.3 Hz) (the signal for one carbon could not be located); HRMS (CI) calcd for $C_{28}H_8F_{16}N_2$ $[M]^+$ 676.0432, found 676.0430; FT-IR (neat) $\bar{\nu}$ 2910, 1636, 1522, 1496, 1424, 1323, 1209, 1175, 1123, 1104, 1014, 994, 974, 856, 814, 799, 745 cm^{-1}.

N,N′-Bis(3,5-bis(trifluoromethyl)phenyl)-1,2-bis-(pentafluorophenyl)ethane-1,2-diimine (Table 3, entry 5). N,N′-Bis(3,5-bis(trifluoromethyl)phenyl)oxalimidoyl dichloride (110 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−25% CH_2Cl_2 in hexanes); yield 76% (124 mg); R_f = 0.52 (hexanes/EtOAc = 9/1); light-yellow solid; mp 213−214 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.67 (s, 2H), 7.16 (s, 4H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −63.0 (s, 12F), −136.7 to −136.8 (m, 4F), −147.3 (t, J_{F-F} = 18.8 Hz, 2F), −158.6 to −158.7 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 157.5, 149.3, 144.0−142.0 (m), 138.8−136.8 (m), 133.0 (q, J_{C-F} = 35.8 Hz), 122.5 (q, J_{C-F} = 277.8 Hz), 120.2 (q, J_{C-F} = 3.8 Hz), 118.7−118.5 (m), 107.3−107.1 (m) (the signal for one carbon could not be located); HRMS (CI) calcd for $C_{30}H_6F_{22}N_2$ $[M]^+$ 812.0180, found 812.0161; FT-IR (neat) $\bar{\nu}$ 3300, 2900, 1645, 1520, 1504, 1458, 1367, 1320, 1272, 1170, 1131, 1107, 983, 907, 886, 806, 715, 680 cm^{-1}.

N,N′-Bis(4-methoxyphenyl)-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 3, entry 6). N,N′-Bis(4-methoxyphenyl)-oxalimidoyl dichloride (67 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−25% CH_2Cl_2 in hexanes); yield 60% (72 mg); R_f = 0.55 (hexanes/EtOAc = 9/1); yellow solid; mp 215−216 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.76 (d, J = 10.0 Hz, 4H), 6.68 (d, J = 10.0 Hz, 4H), 3.76 (s, 6H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −137.1 to −137.2 (m, 4F), −151.3 (t, J_{F-F} = 18.8 Hz, 2F), −160.8 to −160.9 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 158.4, 153.7, 144.3−142.3 (m), 142.9−140.9 (m), 141.8, 138.5−136.5 (m), 121.0, 114.2, 109.9 (t, J = 23.0 Hz), 55.5; HRMS (ESI) calcd for $C_{28}H_{14}F_{10}N_2O_2$ $[M + H]^+$ 601.0968, found 601.0963; FT-IR (neat) $\bar{\nu}$ 3031, 2950, 2840, 1654, 1623, 1598, 1492, 1440, 1297, 1167, 1126, 1034, 995, 970, 934, 848, 825, 732, 717, 701 cm^{-1}.

N,N′-Bis(3,5-difluorophenyl)-1,2-bis(pentafluorophenyl)ethane-1,2-diimine (Table 3, entry 7). N,N′-Bis(3,5-difluorophenyl)-oxalimidoyl dichloride (70 mg, 0.2 mmol), tributyl(2,3,4,5,6-pentafluorophenyl)stannane (0.37 g, 0.8 mmol), CuI (27 mg, 70 mol %), and DMF (0.5 mL); purification (0−15% CH_2Cl_2 in hexanes); yield 80% (98 mg); R_f = 0.79 (hexanes/EtOAc = 9/1); light-yellow solid; mp 216−217 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.57 (t, J_{H-F} = 10.0 Hz, 2H), 6.26 (d, J_{H-F} = 5.0 Hz, 4H); ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ −107.4 (t, J = 9.4 Hz, 4F), −138.6 to −138.9 (m, 4F), −148.5 (t, J_{F-F} = 18.8 Hz, 2F), −159.2 to −159.4 (m, 4F); ^{13}C NMR (128 MHz, $CDCl_3$, ppm) δ 163.1 (dd, J_{C-F} = 256.0, 14.1 Hz), 156.4, 150.3 (t, J_{C-F} = 12.8 Hz), 144.0−142.0 (m), 138.7−136.7 (m), 107.8 (t, J = 25.6 Hz), 101.9−101.5 (m), 101.4 (the signal for one carbon could not be located); HRMS (CI) calcd for $C_{26}H_6F_{14}N_2$ $[M]^+$ 612.0307, found 612.0313; FT-IR (neat) $\bar{\nu}$ 3089, 1654, 1635, 1613, 1522, 1450, 1439, 1324, 1316, 1142, 1123, 1009, 985, 957, 867, 852, 807, 779, 679 cm^{-1}.

4.4. Gram-Scale Experiment. Outside the glovebox, a 40 dram vial equipped with a magnetic stir bar was charged with N,N′-bis(2,6-diisopropylphenyl)oxalimidoyl dichloride (0.89 g, 2.0 mmol) and CuI (0.27 g, 70 mol %). The vial was placed in the glovebox. After that, tributyl(2,3,4,5,6-pentafluorophenyl)stannane (3.66 g, 4.0 equiv) and DMF (5.0 mL, 0.4 M) were added. The vial was sealed, taken out of the glovebox, and placed into a heating block preheated to 70 °C for 15 h. Subsequently, the vial was cooled to room temperature. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with brine (3 × 100 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified using column chromatography, followed by washing with cold (0 °C) pentane and drying under vacuum, yielding 1.23 g of the product (87% yield).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00264.

Details of optimization experiments, synthesis of starting materials, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Olafs Daugulis − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States;* orcid.org/0000-0003-2642-2992; Email: olafs@uh.edu

Author

Thien Lieu − *Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.2c00264

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Welch Foundation (Chair E-0044) and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC0021403).

■ REFERENCES

(1) (a) Van Koten, G.; Vrieze, K. 1,4-Diaza-1,3-butadiene (α-diimine) ligands: their coordination modes and the reactivity of their metal complexes. *Adv. Organomet. Chem.* **1982**, *21*, 151−239. (b) Van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. Stable 1,4-diaza-1,3-butadiene(α-diimine)-zinc and -aluminium radicals formed in single electron transfer reactions: their consequences for organic syntheses.

J. Organomet. Chem. **1983**, *250*, 49−61. (c) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. Platinum diimine complexes: towards a molecular photochemical device. *Coord. Chem. Rev.* **2000**, *208*, 115−137. (d) Zhang, R.; Wang, Y.; Zhao, Y.; Redshaw, C.; Fedushkin, I. L.; Wu, B.; Yang, X.-J. Main-group metal complexes of α-diimine ligands: structure, bonding and reactivity. *Dalton Trans.* **2021**, *50*, 13634−13650. (e) Bernauer, J.; Pölker, J.; von Wangelin, A. J. Redox-active BIAN-based Diimine Ligands in Metal-Catalyzed Small Molecule Syntheses. *ChemCatChem* **2022**, *14*, e202101182.

(2) (a) Li, L.; Lopes, P. S.; Rosa, V.; Figueira, C. A.; Lemos, M. N. D. A.; Duarte, M. T.; Avilés, T.; Gomes, P. T. Synthesis and structural characterisation of (aryl-BIAN) copper (I) complexes and their application as catalysts for the cycloaddition of azides and alkynes. *Dalton Transactions* **2012**, *41*, 5144−5154. (b) Gottumukkala, A. L.; Teichert, J. F.; Heijnen, D.; Eisink, N.; van Dijk, S.; Ferrer, C.; van den Hoogenband, A.; Minnaard, A. J. Pd-Diimine: A highly selective catalyst system for the base-free oxidative Heck reaction. *J. Org. Chem.* **2011**, *76*, 3498−3501. (c) Villa, M.; Miesel, D.; Hildebrandt, A.; Ragaini, F.; Schaarschmidt, D.; von Wangelin, A. J. Synthesis and Catalysis of Redox-Active Bis(imino)acenaphthene (BIAN) Iron Complexes. *ChemCatChem* **2017**, *9*, 3203−3209. (d) van Laren, M. W.; Elsevier, C. J. Selective Homogeneous Palladium(0)-Catalyzed Hydrogenation of Alkynes to (Z)-Alkenes. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715−3717. (e) Bermejo, A.; Ros, A.; Fernández, R.; Lassaletta, J. M. C2-Symmetric Bis-Hydrazones as Ligands in the Asymmetric Suzuki−Miyaura Cross-Coupling. *J. Am. Chem. Soc.* **2008**, *130*, 15798−15799. (f) Kim, J.; Hong, S. H. Ligand-Promoted Direct C−H Arylation of Simple Arenes: Evidence for a Cooperative Bimetallic Mechanism. *ACS Catal.* **2017**, *7*, 3336−3343. (g) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. Convenient and Efficient Suzuki−Miyaura Cross-Coupling Catalyzed by a Palladium/Diazabutadiene System. *Org. Lett.* **2001**, *3*, 1077−1080. (h) Fang, X.; Scott, B. L.; Watkin, J. G.; Kubas, G. J. C−H and Si−H Activation on Palladium(II) and Platinum(II) Complexes with a New Methoxyalkyl-Substituted Diimine Ligand. *Organometallics* **2000**, *19*, 4193−4195. (i) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. Unexpected Selectivities in C−H Activations of Toluene and p-Xylene at Cationic Platinum(II) Diimine Complexes. New Mechanistic Insight into Product-Determining Factors. *J. Am. Chem. Soc.* **2001**, *123*, 6579−6590. (j) Cenini, S.; Ragaini, F.; Tollari, S.; Paone, D. Allylic Amination of Cyclohexene Catalyzed by Ruthenium Complexes. A New Reaction Involving an Intermolecular C−H Functionalization. *J. Am. Chem. Soc.* **1996**, *118*, 11964−11965.

(3) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and alpha-Olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-metal catalysts for ethylene homo- and copolymerization. *Chem. Rev.* **2000**, *100*, 1169−1203. (c) Chen, Z.; Brookhart, M. Exploring Ethylene/Polar Vinyl Monomer Copolymerizations Using Ni and Pd α-Diimine Catalysts. *Acc. Chem. Res.* **2018**, *51*, 1831−1839. (d) Wang, F.; Chen, C. A continuing legend: the Brookhart-type α-diimine nickel and palladium catalysts. *Polym. Chem.* **2019**, *10*, 2354−2369.

(4) Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E. Reactions of $[Pd(C_6F_5)_2(CNR)_2]$ with $[PdCl_2(NCPh)_2]$. Insertion of p-MeC_6H_4NC into Pd-C_6F_5 Bonds. *J. Organomet. Chem.* **1983**, *254*, 371−379.

(5) (a) Dieck, H. t.; Svoboda, M.; Greiser, T. Bis(diazadien)metall-(O)-Komplexe, IV. Nickel(O)-bis(chelate) mit aromatischen N-Substituenten. *Z. Naturforsch. B* **1981**, *36*, 823−832. (b) Dieck, H. t.; Dietrich, J. Diazadienes as Controlling Ligands in Catalysis, 5[1]. Synthesis of Chiral Diazadienes R*−N═CR′−CR′═N−R*. *Chem. Ber.* **1984**, *117*, 694−701. (c) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. Synthesis and characterization of rigid bidentate nitrogen ligands and some examples of coordination to divalent palladium. X-ray crystal structures of bis (p-tolylimino) acenaphthene and methylchloro [bis (o, o′-diisopropylphenyl-imino) acenaphthene] palladium (II). *Recueil des Travaux Chimiques des Pays-Bas* **1994**, *113*, 88−98. (d) Gasperini, M.; Ragaini, F.; Cenini, S. Synthesis of Ar-BIAN ligands (Ar-BIAN = bis(aryl)-acenaphthenequinonediimine) having strong electron-withdrawing substituents on the aryl rings and their relative coordination strength toward palladium(0) and -(II) complexes. *Organometallics* **2002**, *21*, 2950−2957. (e) Rosa, V.; Avilés, T.; Aullon, G.; Covelo, B.; Lodeiro, C. A new bis(1-naphthylimino)acenaphthene compound and its Pd(II) and Zn(II) complexes: Synthesis, characterization, solid-state structures and density functional theory studies on the *syn* and *anti* isomers. *Inorg. Chem.* **2008**, *47*, 7734−7744. (f) Zhang, D.; Nadres, E. T.; Brookhart, M.; Daugulis, O. Synthesis of Highly Branched Polyethylene Using "Sandwich" (8-p-Tolyl naphthyl alpha-diimine)-nickel(II) Catalysts. *Organometallics* **2013**, *32*, 5136−5143. (g) Gordon, J. C.; Shukla, P.; Cowley, A. H.; Jones, J. N.; Keogh, D. W.; Scott, B. L. Dialkyl aluminium amides: new reagents for the conversion of C═O into C═NR functionalities. *Chem. Commun.* **2002**, 2710−2711. (h) Rhinehart, J. L.; Mitchell, N. E.; Long, B. K. Enhancing α-Diimine Catalysts for High-Temperature Ethylene Polymerization. *ACS Catal.* **2014**, *4*, 2501−2504.

(6) (a) Walia, J. S.; Singh, J.; Chattha, M. S.; Satyanarayana, M. A general and convenient route to α-diketanils and α-diketones. *Tetrahedron Lett.* **1969**, *10*, 195−198. (b) Jin, W.-S.; Taniguchi, Y. Preparation of vicinal diimines: a new dehydrogenative coupling reaction of aldimines mediated by ytterbium metal. *Chem. Commun.* **1998**, 1101−1102. (c) Amii, H.; Kohda, M.; Seo, M.; Uneyama, K. A novel route to the fluorinated diimines: carbon monoxide-promoted reductive homocoupling of fluorinated imidoyl iodides in the presence of a palladium catalyst. *Chem. Commun.* **2003**, 1752−1753. (d) Sadighi, J. P.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. Synthesis of a perfluoroalkyl-substituted α-diimine by Sm-mediated reductive coupling. *Tetrahedron Lett.* **2003**, *44*, 8073−8076. (e) Diel, B. N.; Deardorff, P. J.; Zelenski, C. M.; Incarvito, C.; Liable-Sands, L.; Rheingold, A. M. Carbon−carbon bond formation in the reductive coupling of trifluoroacetonitrile and pentafluorobenzonitrile − synthetic routes to new perfluoroalkyl- and perfluoroaryl-substituted α-diimines: versatile synthons for heterocycle synthesis. *Inorg. Chim. Acta* **2004**, *357*, 3902−3910.

(7) (a) Murakami, M.; Masuda, H.; Kawano, T.; Nakamura, H.; Ito, Y. Facile synthesis of vicinal di- and tricarbonyl compounds by samarium diiodide-mediated double insertion of isocyanides into organic halides. *J. Org. Chem.* **1991**, *56*, 1−2. (b) Dechert-Schmitt, A.-M.; Garnsey, M. R.; Wisniewska, H. M.; Murray, J. I.; Lee, T.; Kung, D. W.; Sach, N.; Blackmond, D. G. Highly modular synthesis of 1, 2-diketones via multicomponent coupling reactions of isocyanides as CO equivalents. *ACS Catal.* **2019**, *9*, 4508−4515. (c) Kobiki, Y.; Kawaguchi, S.-i.; Ogawa, A. Palladium-catalyzed synthesis of α-diimines from triarylbismuthines and isocyanides. *Org. Lett.* **2015**, *17*, 3490−3493.

(8) (a) Faust, R.; Göbelt, B. First 2, 3-dialkynyl-1, 4-diazabutadienes by Pd-catalyzed cross-coupling of bis (imidoyl chlorides) and alkynylstannanes. *Tetrahedron Lett.* **1997**, *38*, 8017−8020. (b) Faust, R.; Göbelt, B.; Weber, C.; Krieger, C.; Gross, M.; Gisselbrecht, J.-P.; Boudon, C. 2,3-Dialkynyl-1,4-diazabuta-1,3-dienes as Novel π-Systems: Synthesis, Structure, and Electronic Properties. *Eur. J. Org. Chem.* **1999**, *1999*, 205−214. (c) Uneyama, K.; Watanabe, H. Palladium-catalyzed coupling reactions of trifluoroacetimidoyl iodides with olefins and 1-alkynes. *Tetrahedron Lett.* **1991**, *32*, 1459−1462. (d) Kobayashi, T.-a.; Sakakura, T.; Tanaka, M. Synthesis of ketimines via palladium complex-catalyzed cross-coupling of imidoyl chlorides with organotin compounds. *Tetrahedron Lett.* **1985**, *26*, 3463−3466. (e) Würthwein, E.-U.; Weigmann, R. First Synthesis of N-Methylene-Ynamines (2-Azabut-l-en-3-ynes). *Angew. Chem., Int. Ed.* **1987**, *26*, 923−924. (f) Kosugi, M.; Koshiba, M.; Atoh, A.; Sano, H.; Migita, T. Palladium-Catalyzed Coupling between Organic Halides and Organotin Compounds Involving C-N Unsaturated Bonds at the Reaction Centers. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 677−679. Also see: (g) Chen, C.-T.; Fischer, M. E.; Windsor, C.; Vei, I. C.; Calatayud, D. G.; Green, M. L. H.; Pascu, S. I. Investigations into the reactivity of lithium indenyl with alpha diimines with chlorinated

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX

backbones and formation of related functional ligands and metal complexes. *Polyhedron* **2016**, *119*, 532−547. (h) Frye, C. W.; Egger, D. T.; Kounalis, E.; Pearce, A. J.; Cheng, Y.; Tonks, I. A. α-Diimine synthesis via titanium-mediated multicomponent diimination of alkynes with C-nitrosos. *Chem. Sci.* **2022**, *13*, 1469−1477.

(9) (a) Allred, G. D.; Liebeskind, L. S. Copper-mediated cross-coupling of organostannanes with organic iodides at or below room temperature. *J. Am. Chem. Soc.* **1996**, *118*, 2748−2749. (b) Cox, P. A.; Reid, M.; Leach, A. G.; Campbell, A. D.; King, E. J.; Lloyd-Jones, G. C. Base-Catalyzed Aryl-B$(OH)_2$ Protodeboronation Revisited: From Concerted Proton Transfer to Liberation of a Transient Aryl Anion. *J. Am. Chem. Soc.* **2017**, *139*, 13156−13165.

(10) Do, H.-Q.; Daugulis, O. A Simple Base-Mediated Halogenation of Acidic sp^2 C-H Bonds under Noncryogenic Conditions. *Org. Lett.* **2009**, *11*, 421−423.

https://doi.org/10.1021/acs.organomet.2c00264
Organometallics XXXX, XXX, XXX−XXX