

Selective Alkylation of 2,6-Diiminopyridine Ligands by Dialkylmanganese Reagents: A “One-Pot” Synthetic Methodology

Juan Cámpora,* Carmen M. Pérez, Antonio Rodríguez-Delgado, A. Marcos Naz, Pilar Palma, and Eleuterio Alvarez

Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, c/ Américo Vespucio, 49, Sevilla, Spain

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Summary: A “one pot” synthesis of new 2,6-diimine-4-alkylpyridines is reported. The addition of 2,6-[2,6-ⁱPr₂C₆H₃N=C(Me)]₂C₅H₃N to the preformed MnR₂(THF)_n (R = CH₂CMe₂Ph, CH₂Ph, CH₂CH=CH₂), followed by hydrolysis affords a mixture of 4-alkyl 2,6-bis(imino) derivatives of pyridine and 1,4-dihydropyridine in a variable ratio. Treatment of the mixture with a substoichiometric amount of CrO₃/K₂CO₃ in THF provides the 4-alkyl-2,6-diiminopyridines in good isolated yields and in a highly selective manner.

Introduction

2,6-Diiminopyridines (PDI) are versatile ligands that have found wide applications in coordination chemistry^{1,2} and catalysis.^{3–6} Despite being known for more than 30 years, these 6-electron donors have received considerable attention over the past decade, mainly due to the discovery of the high catalytic activity of their Fe and Co complexes in olefin polymerization catalysis.³ Moreover, these ligands have found use in many other catalytic processes, such as olefin epoxidation,⁴ hydrogenation and hydrosilation,⁵ and aerobic oxidation reactions.⁶ In part, the success of diiminopyridine ligands stems from the ready availability of their derivatives with different kinds of substituents at the terminal imine nitrogen atoms and their straightforward synthesis from condensation reactions. Nevertheless, structural modification of the central pyridine ring is a more challenging task, despite the extensive nucleophilic substitution chemistry of electron-deficient pyridines.⁷ In fact, it is now known that the reaction of PDI ligands with main-group organometallics often cause deprotonation,^{8a,b} reduction,^{8c} or complex addition patterns.^{8b,d–f} Introducing different substituents in the pyridine ring may lead to significant changes in the catalyst performance, since these depend on the extensive

interaction of the π -electron system with the partially filled metal d orbitals.⁹ There are few examples of such substituted ligands in the literature, these being hitherto limited to a 4-*tert*-butyl-2,6-diiminopyridine derivative, prepared by Grassi through a radical substitution reaction.¹⁰ Herein we report the use of dialkylmanganese(II) reagents for the direct alkylation of the pyridine ring in a highly selective manner. Monoalkylmanganese species, usually formulated as Mn(X)R, have been used as mild nucleophiles for selective C–C bond forming reactions.¹¹ Although the nature of these paramagnetic species is not precisely known, a number of Mn(II) dialkyl complexes have been structurally characterized.¹² However, the latter compounds have not found practical applications.

Results and Discussion

The reaction of the homoleptic manganese alkyl [Mn(CH₂-CMe₂Ph)₂]₂ with 2,6-[(2,6-ⁱPr₂C₆H₃)N=C(Me)]₂C₅H₃N (abbreviated as ⁱPrPDI) in toluene leads to a dark red solution, from which a microcrystalline burgundy compound, **1**, can be isolated. Although its elemental analysis agrees with the composition MnR₂(ⁱPrPDI), its color and magnetic susceptibility (4.7 μ_B) are reminiscent of those of the Mn(I) methyl derivative MeMn(ⁱPrPDI), reported by Gambarotta et al.¹³ On controlled methanolysis under an inert atmosphere, **1** quantitatively yields the

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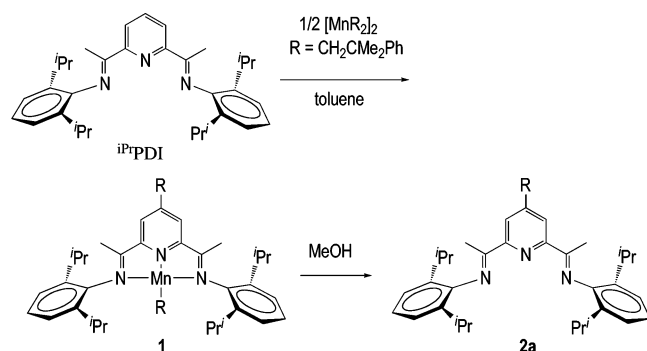
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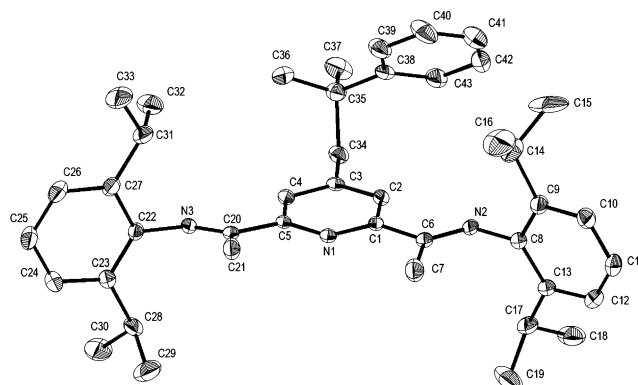
Scheme 1



4-alkylated 2,6-diiminopyridine derivative **2a**. Therefore, we tentatively assign **1** the structure shown in Scheme 1. The migration of the alkyl group to position 4 of the pyridine ring finds precedents in related transformations involving Cr¹⁴ and Al^{1b} alkyl complexes. However, these reactions lead either to dimeric compounds or to mixtures of products, whose transformations into free organic compounds have not been explored.

The clean production of compound **2a** suggested to us that the reaction in Scheme 1 could provide the basis for a convenient synthetic methodology for the selective alkylation of 2,6-diiminopyridine derivatives, if the experimental difficulties associated with the isolation and manipulation of the highly air-sensitive manganese dialkyl species could be avoided.

For synthetic purposes, Mn(X)R reagents are usually generated *in situ* by reacting the corresponding organolithium or -magnesium reagents with anhydrous manganese chloride in ethereal solvents.^{10a} Mn(II) dialkyls can be formed in a similar fashion. Thus, the reaction of MnCl₂ with 2 equiv of Mg(Cl)CH₂CMe₂Ph proceeds readily, producing a pale brown solution. On addition of *i*PrPDI at -78 °C, a rapid sequence of color changes ensues, ending up in a deep red color, similar to that of complex **1**. Quenching this reaction with a small amount of water or methanol under inert atmosphere, followed by a standard workup for the separation of paramagnetic Mn species, provides an extract which contains the organic product of the reaction. Unexpectedly, the ¹H NMR spectrum of the crude mixture is complex and indicates that compound **2a** is formed together with a second organic product, **3a**. The **2a/3a** ratio varies appreciably from one experiment to another, but **3a** is invariably the major product. In spite of the apparent complexity of the NMR spectra of this mixture, it can be readily deduced that, like **2a**, **3a** displays a symmetric substitution pattern. A combination of ¹³C, ¹H, and two-dimensional NMR spectroscopy allowed the identification of the major product as a 1,4-dihydropyridine derivative (Scheme 2). Accordingly, the EI-MS spectrum of the crude reaction mixture consists of two signal clusters corresponding to the molecular ions [**2a** + H]⁺ and [**3a** + H]⁺, confirming that only these two organic products are formed in significant amounts (Scheme 2).

Figure 1. ORTEP drawing of compound **2a**.

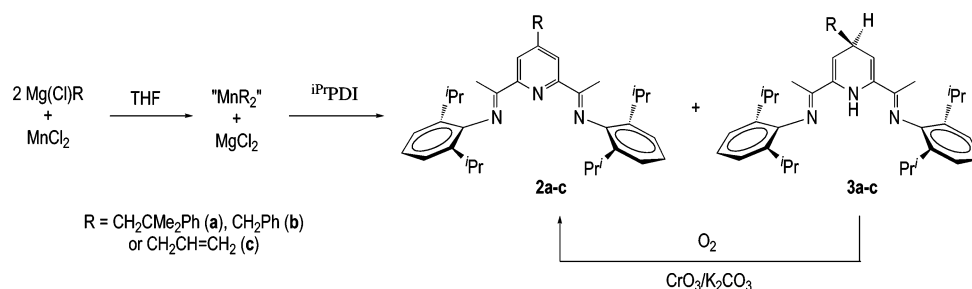
Not surprisingly, attempts to separate the products by fractional crystallization in air caused the slow aerobic oxidation of **3a** to **2a**, and pure samples of the latter were isolated. 1,4-Dihydropyridine aromatization is generally a facile process, and a number of oxidizing reagents can be used for this transformation.¹⁵ We found that **3a** is efficiently converted into **2a** when the organic extract is treated with a catalytic amount of CrO₃/K₂CO₃ in air. It is worth mentioning the convenience of removing the inorganic manganese compounds prior to this oxidative treatment, as they may interfere with the aromatization reaction.

This methodology has been successfully applied to the synthesis of other 4-alkylated *i*PrPDI derivatives, even when the corresponding MnR₂ precursors have never been isolated. Thus, with the benzyl or allyl Grignard reagents as starting materials, the corresponding **2** + **3** mixtures were produced, from which the derivatives **2b** and **2c** were obtained in excellent yields by aerobic oxidation in the presence of CrO₃/K₂CO₃. It is worth noting that the intermediate bis(allyl)manganese complex appears to be thermally sensitive, as standing at room temperature for more than 40 min results in substantially decreased yields of **2c**.

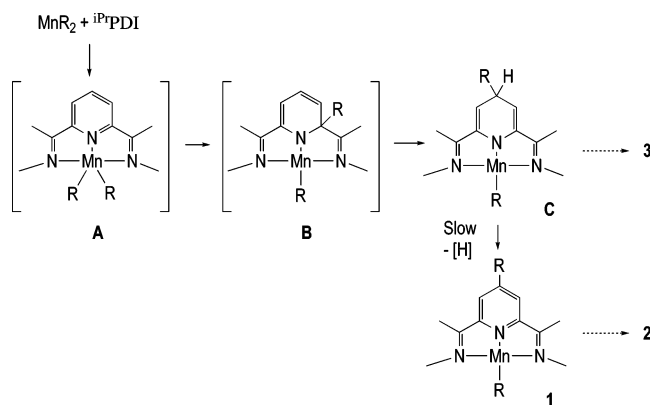
An X-ray diffraction study of **2a** (Figure 1) confirmed the structure proposed for the alkylated diiminopyridine compounds. Apart from the expected CH₂CMe₂Ph group in the position 4 of the pyridine ring, its structural features are unexceptional and show no significant differences from those of the unsubstituted *i*PrPDI ligand.¹⁶

From a mechanistic point of view, the identification of the dihydropyridine derivatives **3** as the major products is consistent with an intramolecular alkyl migration process that involves the initial formation of a unstable MnR₂(*i*PrPDI) species (**A**), which undergoes two consecutive 1,3-alkyl shifts, leading to a Mn(II) alkyl dihydropyridine amide (**C**) (Scheme 3). Copéret has observed that similar 1,3-alkyl migrations take place in related MnR₂(α-diimine) complexes.¹⁷ Interestingly, the species **C** tends to spontaneously dehydrogenate in solution, leading to **1**, which is the only organometallic species isolated (in 67% yield), from the reaction of [Mn(CH₂CMe₂Ph)₂]₂ with *i*PrPDI.

Scheme 2



Scheme 3



In summary, the reaction of manganese dialkyls with *iPr*PDI leads initially to unstable organomanganese(II) compounds, which evolves via consecutive 1,3-alkyl shifts to 4-substituted 2,6-diiminopyridine alkylmanganese complexes. On the basis of this reaction, we have designed a one-pot synthetic methodology that allows the selective alkylation of the diiminopyridines at the position 4 in the pyridine ring. We are currently testing the performance of the new alkylated ligands in olefin polymerization, using the corresponding complexes of Fe, Co, and Cr. The introduction of suitably functionalized alkyl groups in the 2,6-diiminopyridine system may find interesting applications. For example, these may be used as attaching points to anchor the complexes at surfaces (immobilization) while the active site is kept isolated from the influence of the solid support. In addition, the alkyl group can be used as a tether to connect the pyridine diimine moiety to other potentially interesting molecules.

Experimental Section

All preparations were carried out under oxygen-free nitrogen by conventional Schlenk techniques unless otherwise stated. Solvents were rigorously dried and degassed before use. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer and NMR spectra on Bruker DRX 300, 400, and 500 MHz spectrometers. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. MnCl_2 was obtained from Sigma Aldrich and Co. and purified by methods described in the literature.¹⁸ $[\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2]_n$ ^{11a} was prepared according to literature methods. The *iPr*PDI ligand and Grignard reagents RMgCl ($\text{R} = \text{PhCMe}_2\text{CH}_2$, PhCH_2 , $\text{CH}_2\text{CH}=\text{CH}_2$) were prepared following conventional synthetic methods.

Synthesis of Complex 1. A 20 mL toluene solution of $[\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2]_n$ (1.41 g, 4.39 mmol) was added dropwise to a 20 mL toluene suspension of *iPr*PDI (2.06 g, 4.29 mmol) at -40°C . The resultant mixture turned instantaneously from yellow to dark red. The mixture was stirred vigorously for 5 min at -40°C and for 1 h at room temperature. Then, solvents and volatiles were removed under reduced pressure to obtain an oily solid residue, which was extracted with 3×20 mL of pentane. The filtrate was cooled at -80°C for several days, and complex **1** was isolated as

a crystalline red-purple solid. Yield: 2.32 g, 67%. IR (Nujol mull): $\nu(\text{C}=\text{N})$ 1640, 1589 cm^{-1} . Anal. Calcd for $\text{C}_{47}\text{H}_{56}\text{MnN}_3$: C, 75.45; H, 7.18; N, 5.87. Found: C, 75.42; H, 6.91; N, 6.00. μ_{eff} (20°C , magnetic susceptibility balance): 4.70 μ_{B} .

Methanolysis of Compound 1. Anhydrous methanol (5 mL) was added to a 20 mL hexane solution of **1** (0.15 g, 0.19 mmol) at room temperature. The resultant mixture turned instantaneously from a purple solution to a green suspension with a brown precipitate. The solution was filtered through a pad of silica previously treated with Et_3N , and after solvent evaporation a yellow solid was obtained, which was identified as **2a**. Yield: 0.10 g, 86%.

"One Pot" Synthesis of *iPr*PDI-4- $\text{CH}_2\text{CMe}_2\text{Ph}$ (2a**).** A pink suspension of MnCl_2 (187 mg, 1.48 mmol) in 20 mL of THF was mixed with 2.1 equiv of a colorless 1.3 M Et_2O solution of $(\text{PhCMe}_2\text{CH}_2)\text{MgCl}$ (2.43 mL) at -78°C . The reaction mixture was stirred for 10 min and then warmed gradually, while it turned from pale green to brown. After 10–15 min at room temperature, the mixture became pale brown. The solution was transferred over a cold (-78°C) suspension of *iPr*PDI (580 mg, 1.19 mmol) in hexane. A thick, dark brown solution formed instantaneously, which was vigorously stirred for 10 min at -78°C and then warmed to room temperature. The stirring was continued for 90 min, during which time the color changed again to deep purple. Then, an excess of anhydrous methanol (8–10 mL) was added to quench the reaction. After solvent and volatiles were removed from the resultant clear red solution, an orange oil was isolated, which was extracted with 3×25 mL of hexane and 2×20 mL of toluene, leaving behind a pale brown precipitate. The orange oil isolated after solvent removal (0.65 g, 89%) was identified as a 1:2 mixture of **2a** and **3a**. Then, the oily mixture was redissolved in THF and, in air, treated with a catalytic amount of CrO_3 (ca. 10 mg, 10 mol %) and 1.5 g of K_2CO_3 for 1 h at room temperature. The solvent and volatiles were removed under reduced pressure, and **2a** was extracted in hexane (2×15 mL). A yellow solid was isolated, after filtration and solvent evaporation. Yield: 0.52 g, 71%.

2a: ^1H NMR (C_6D_6 , 298 K, 500 MHz) δ 1.15 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.17 (s, 6H, $\text{CH}_2\text{CMe}_2\text{Ph}$), 1.22 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 2.27 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 2.65 (s, 2H, $\text{CH}_2\text{CMe}_2\text{Ph}$), 2.89 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 7.13–7.02 (m, 6H, CH_{ar}), 7.22–7.16 (m, 5H, $\text{CH}_{\text{ar}}(\text{Ph})$), 8.22 (s, 2H, $\text{CH}(\text{py})$); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 16.9 ($\text{CH}_3\text{C}=\text{N}$), 23.0, 23.2 (CHMe_2), 26.9 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 28.4 (CHMe_2), 38.3 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 49.9 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 123.2 (3,5- C_{ar}), 123.9 (4- C_{ar}), 124.3 (s, 3,5- $\text{C}_{\text{ar}}(\text{py})$), 125.8 (4- $\text{C}_{\text{ar}}(\text{Ph})$), 125.9 (2,6- $\text{C}_{\text{ar}}(\text{Ph})$), 128.0 (3,5- $\text{C}_{\text{ar}}(\text{Ph})$), 135.6 (C_{ar}), 146.8 (C_{ar}), 147.2 ($\text{C}_{\text{ar}}(\text{py})$), 148.9 (C_{ar}), 154.6 ($\text{C}_{\text{ar}}(\text{py})$), 166.8 ($\text{CH}_3\text{C}=\text{N}$); IR (Nujol mull) $\nu(\text{C}=\text{N})$ 1641, 1590, 1553 cm^{-1} ; ESI-MS (m/z) 614.4 ($\text{M} + 1$).

3a: ^1H NMR (CDCl_3 , 298 K, 300 MHz) δ 0.970 (d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.05 (d, 12 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.23 (d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.42 (s, 6H, $\text{CH}_2\text{CMe}_2\text{Ph}$), 1.60 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 2.04 (d, 2H, $^3J_{\text{HH}} = 6$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$), 2.60 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 3.33 (q, 1H, $^3J_{\text{HH}} = 4.5$ Hz, 4- $\text{CH}(\text{py})$), 4.71 (bs, 2H, 3,5- $\text{CH}(\text{py})$), 7.14–6.95 (m, 6H, CH_{ar}), 7.47–7.13 (m, 5H, $\text{CH}_{\text{ar}}(\text{Ph})$), 8.17 (bs, H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 15.0 ($\text{CH}_3\text{C}=\text{N}$), 22.5, 22.6 (CHMe_2), 23.1 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 28.34 (CHMe_2), 28.8 (4- $\text{CH}(\text{py})$), 29.4 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 32.5 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 37.2 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 55.2 ($\text{CH}_2\text{CMe}_2\text{Ph}$), 106.4 (3,5- $\text{C}(\text{py})$), 123.7 (3,5- C_{ar}), 123.8 (4- C_{ar}), 124.9 (3,5- $\text{C}_{\text{ar}}(\text{py})$), 125.1 (4- $\text{C}_{\text{ar}}(\text{Ph})$), 125.5 (2,6- $\text{C}_{\text{ar}}(\text{Ph})$), 128.0 (3,5- $\text{C}_{\text{ar}}(\text{Ph})$), 134.59 (C_{ar}), 135.5 (C_{ar}), 136.46 (C_{ar}), 146.3 (C_{ar}), 149.4 (C_{ar}), 159.5 ($\text{CH}_3\text{C}=\text{N}$); IR (Nujol mull) $\nu(\text{H}-\text{N})$ 3376 cm^{-1} , $\nu(\text{C}=\text{N})$ 1637, 1589, 1555 cm^{-1} ; ESI-MS (m/z) 616.4 ($\text{M} + 1$).

Synthesis of *iPr*PDI-4- CH_2Ph (2b**).** To a fine pink suspension of MnCl_2 in THF (150 mg, 1.19 mmol) stirred at -78°C was added 2.1 equiv (2.49 mmol, 2.5 mL) of a 0.97 M solution of $\text{Mg}(\text{CH}_2\text{Ph})\text{Cl}$ in Et_2O . After 10 min the cooling bath was removed and the mixture was stirred for 60 min more. The resultant solution was added to

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a suspension of $^{10}\text{PrPDI}$ (0.46 g, 0.952 mmol) in toluene (30 mL) at -78°C . Color changes were similar to those observed in the previous case. After quenching with anhydrous methanol and evaporation, a yellow solid was obtained (0.41 g 92%), composed mainly of the dihydropyridine derivative **3b**. A 0.10 g portion of this solid was dissolved in THF and the solution stirred in an air atmosphere together with CrO_3 (ca. 10 mol %) and K_2CO_3 (1 g) for 1 h at room temperature. The volatiles were removed under reduced pressure, and the residue was extracted with 20 mL of hexane. After concentration and cooling, **2b** was isolated as a yellow crystalline solid. Yield: 0.09 g, 81%.

2b: ^1H NMR (C_6D_6 , 298 K, 500 MHz) δ 1.15 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.17 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 2.29 (s, 6H, $\text{CH}_3\text{C}=\text{N}_{\text{ar}}$), 2.91 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 3.59 (s, 2H, $\text{CH}_2(\text{benc})$), 6.90–7.12 (m, 6H, CH_{ar}), 7.21–7.19 (m, 5H, $\text{CH}_{\text{ar}}(\text{Ph})$), 8.53 (s, 2H, 3- $\text{CH}_{\text{ar}}(\text{py})$); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 17.0 ($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$), 22.9, 22.6 (CHMe_2), 28.5 (CHMe_2), 41.2 ($\text{CH}_2(\text{benc})$), 122.7 (C_{ar}), 123.2 (C_{ar}), 124.0 (C_{ar}), 126.4 (C_{ar}), 128.5 (C_{ar}), 129.0 (C_{ar}), 135.6 (C_{ar}), 146.7 (C_{ar}), 147.7 (C_{ar}), 151.7 (C_{ar}), 155.6 (C_{ar}), 166.8 ($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$); IR (Nujol mull) $\nu(\text{C}=\text{N})$ 1644, 1592, 1554 cm^{-1} ; ESI-MS (m/z) 572.5 ($M + 1$).

3b: ^1H NMR (CDCl_3 , 298 K, 300 MHz) δ 0.970 (d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.05 (d, 12 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.23 (d, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 1.42 (s, 6H, $\text{CH}_2\text{CMe}_2\text{Ph}$), 1.60 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 2.04 (d, 2H, $^3J_{\text{HH}} = 6$ Hz, $\text{CH}_2\text{CMe}_2\text{Ph}$), 2.60 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, CHMe_2), 3.33 (q, 1H, $^3J_{\text{HH}} = 4.5$ Hz, 4- $\text{CH}(\text{py})$), 4.71 (bs, 2H, 3,5- $\text{CH}(\text{py})$), 7.14–6.95 (m, 6H, CH_{ar}), 7.47–7.13 (m, 5H, $\text{CH}_{\text{ar}}(\text{Ph})$), 8.17 (bs, H, NH); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 15.0 ($\text{CH}_3\text{C}=\text{N}$), 22.5, 22.2 (CHMe_2), 27.7 (4- $\text{CH}(\text{py})$), 37.2 (CH_2Ph), 106.4 (3,5- $\text{C}(\text{py})$), 123.7 (3,5- C_{ar}), 123.8 (4- C_{ar}), 124.9 (3,5- $\text{C}_{\text{ar}}(\text{py})$), 125.1 (4- $\text{C}_{\text{ar}}(\text{Ph})$), 125.5 (2,6- $\text{C}_{\text{ar}}(\text{Ph})$), 128.0 (3,5- $\text{C}_{\text{ar}}(\text{Ph})$), 134.59 (C_{ar}), 135.5 (C_{ar}), 136.46 (C_{ar}), 138.5 ($\text{C}_{\text{ar}}(\text{Ph})$), 146.3 (C_{ar}), 149.4 ($\text{C}_{\text{ar}}(\text{py})$), 159.5 ($\text{CH}_3\text{C}=\text{N}$); IR (Nujol mull) $\nu(\text{H}-\text{N})$ 3377 cm^{-1} , $\nu(\text{C}=\text{N})$ 1630, 1587, 1554 cm^{-1} ; ESI-MS (m/z): 574.4 ($M + 1$).

Synthesis of $^{10}\text{PrPDI-4-CH}_2\text{CH}=\text{CH}_2$ (2c). A fine pink suspension of MnCl_2 (200 mg, 1.58 mmol) in THF (20 mL) was cooled to -78°C , and 2.1 equiv of a cold (0°C) 2 M THF solution (1.66 mL) of allylmagnesium chloride was slowly added to the vigorously stirred suspension via syringe. The resultant mixture was dark brown when the addition was complete. The cold bath was removed, and the mixture was warmed for 15 min. After 10 min at room temperature, it was transferred to a flask containing a cold (-78°C) suspension of $^{10}\text{PrPDI}$. The color of the resultant mixture was dark brown. The cold bath was then removed after 10 min. The reaction mixture stirred at room temperature for 50 min, and the resulting dark purple solution was quenched with 5 mL of MeOH. The solvent and volatiles were removed, leaving a brown oil, which was extracted with hexane (3×30 mL). Vacuum evaporation left 470 mg (88%) of a yellow foam, composed almost exclusively of the dihydropyridine **3c**. A 0.10 g portion of this product was dissolved in THF, and this solution was exposed to the atmosphere and stirred for 1 h with a catalytic amount of CrO_3 (ca. 10 mol %) and 1 g of K_2CO_3 at room temperature. After the solvent and volatiles were removed under reduced pressure, **2c** was extracted with hexane (20 mL). A yellow powdery solid was isolated, after filtration and solvent evaporation. Yield: 0.082 g. Total yield: 72%.

2c: ^1H NMR (CDCl_3 , 298 K, 300 MHz) δ 1.14 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, CHMe_2), 1.16 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, CHMe_2), 2.25 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 2.76 (sept, 4H, $^3J_{\text{HH}} = 6.6$ Hz, CHMe_2), 3.56 (d, 2H, $^3J_{\text{HH}} = 6.6$ Hz CH_2), 5.18 (m, 2H, $\text{CH}=\text{CH}_2$), 6.05–5.99 (m, 1H, $\text{CH}=\text{CH}_2$), 7.17–7.04 (m, 6H, CH), 8.30 (s, 2H, 3,5- $\text{CH}_{\text{ar}}(\text{py})$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 75 MHz) δ 17.6 ($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$), 23.3 (CHMe_2), 22.5 (CHMe_2), 28.5 (CHMe_2), 40.1 ($\text{CH}_2\text{CH}=\text{CH}_2$), 117.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 122.56 (C_{ar}), 123.3 (C_{ar}), 135.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 136.1 (C_{ar}), 146.7 (C_{ar}), 150.5 (C_{ar}), 155.6 (C_{ar}), 167.4

($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$); IR (Nujol mull): $\nu(\text{H}-\text{N})$ 3377 cm^{-1} , $\nu(\text{C}=\text{N})$ 1643, 1589, 1556 cm^{-1} ; ESI-MS (m/z) 524.4 ($M + 1$).

3c: ^1H NMR (CDCl_3 , 298 K, 500 MHz) δ 1.01 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 1.03 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 1.08 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 1.10 (d, 6H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 1.84 (s, 6H, $\text{CH}_3\text{C}=\text{N}$), 2.39 (t, 2H, $^3J_{\text{HH}} = 7.0$ Hz, CH_2), 2.59 (sept, 2H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 2.62 (sept, 2H, $^3J_{\text{HH}} = 7.0$ Hz, CHMe_2), 3.6 (q, $^3J_{\text{HH}} = 7.0$ Hz, 1H 4- $\text{CH}(\text{py})$), 5.10–5.11 (m, 2H, $\text{CH}=\text{CH}_2$), 5.12–5.14 (m, 2H, 3,5- $\text{CH}(\text{py})$), 5.87–5.92 (m, 1H, $\text{CH}=\text{CH}_2$), 6.92–7.01 (m, 6H, CH), 8.33 (bs, 1H, N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 75 MHz) δ 15.5 ($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$), 22.6 (CHMe_2), 23.1 (CHMe_2), 28.2 (CHMe_2), 35.6, (4- $\text{C}(\text{py})$), 43.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 104.3 (3,5- $\text{C}(\text{py})$), 116.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 122.7 (C_{ar}), 123.0 (2,4- $\text{C}(\text{py})$), 123.3 (C_{ar}), 135.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 135.9, 137.3 (C_{ar}), 145.9 (C_{ar}), 159.14 ($\text{CH}_3\text{C}=\text{N}_{\text{ar}}$); IR (Nujol mull) $\nu(\text{H}-\text{N})$ 3377 cm^{-1} ; $\nu(\text{C}=\text{N})$ 1644, 1592, 1559 cm^{-1} ; ESI-MS (m/z): 524.4 ($M + 1$).

X-ray Structural Determination. One crystal coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream ($T = 100(2)$ K). Intensity data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer equipped with a Mo $\text{K}\alpha_1$ radiation ($\lambda = 0.71073$ Å) source and graphite monochromator. The data were reduced (SAINT)²⁰ and corrected for Lorentz–polarization and absorption effects by multiscan methods (SADABS).²¹ The structure was solved by direct methods (SIR-2002)²² and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12),²³ minimizing $w[F_o^2 - F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined riding on the carbon atoms which they are bonded, with the isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding carbon atoms. Crystal data for **2a**: $\text{C}_{46}\text{H}_{55}\text{D}_3\text{N}_3$ ($\text{C}_{43}\text{H}_{55}\text{N}_3 \cdot 0.5\text{C}_6\text{D}_6$), $M_r = 655.97$, yellow plate ($0.44 \times 0.16 \times 0.08$ mm³) from deuterated benzene, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.6811(6)$ Å, $b = 15.1172(14)$ Å, $c = 16.2449(16)$ Å, $\alpha = 73.095(3)^\circ$, $\beta = 85.004(3)^\circ$, $\gamma = 77.590(4)^\circ$, $V = 1991.4(3)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.094$ g cm⁻³, $F(000) = 710$, $\mu = 0.063$ mm⁻¹, 16 455 reflections were collected in the range $5.54 < 2\theta < 52.76^\circ$, index ranges $-10 \leq h \leq 10$, $-17 \leq k \leq 18$, $-20 \leq l \leq 20$, 8002 independent reflections ($R_{\text{int}} = 0.0706$), 4336 reflections observed with $I > 2\sigma(I)$, final $R1$ ($I > 2\sigma(I)$) = 0.0691, $wR2$ (all data) = 0.2133, $w = [\sigma^2(F_o^2) + (0.0775P)^2 + 0.1648P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$; 8002/0/442 data/restraints/parameters, goodness of fit on F^2 1.030. In the final difference map, the highest residual peaks, those above $0.2 \text{ e } \text{\AA}^{-3}$, were located close to the isopropyl groups and have no chemical meaning.

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Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and a CIF file giving crystallographic data for **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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