ORGANOMETALLICS

Synthesis and Ethylene Reactivity of Dinuclear Iron and Cobalt Complexes Supported by Macrocyclic Bis(pyridine-diimine) Ligands Containing *o*-Terphenyl Linkers

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ABSTRACT: The	synthesis and ethylene	reactivity of a new	family of	i ^{Bu}

dinuclear Co₂Br₄ and Fe₂Br₄ complexes supported by binucleating macrocyclic bis(pyridine-diimine) (PDI) ligands that contain 4,4"-R₂-3,3"-o-terphenyl linkers (1, R = H; 2, R = Me; 3, R = ⁱPr) are described. In the solid state, (1-3)M₂Br₄ (M = Zn, Fe, Co) adopt C_s -skew-syn structures in which the (PDI)M planes are skewed 49–82° relative to each other and both middle rings of the o-terphenyl bridges are on the same side of the molecule. The metal-metal distances range between 5.7600(8) and 6.232(1) Å. In solution, (1)M₂Br₄ (M = Zn, Co, Fe) undergo a fluxional process that permutes the two inequivalent (PDI)M units, while (2)M₂Br₄ and (3)M₂Br₄ are static and adopt C_s -symmetric structures similar to those observed in the solid state. Activation of (2)Fe₂Br₄ and (3)Fe₂Br₄ with MMAO-12 or triisobutylaluminum (TIBA) in the presence of ethylene generates catalysts that produce solid polyethylene ($M_w = 4500-280000$ Da), which contrasts with the reported production of α -



olefins by analogous mononuclear (PDI)FeCl₂ catalysts. (3)Fe₂Br₄/TIBA and (3)Fe₂Br₄/MMAO-12 produce polyethylenes with broad molecular weight distributions (MWDs) due to chain transfer to Al. (3)Co₂Br₄/1000 TIBA and (3)Co₂Br₄/1000 MMAO-12 also produce polyethylenes with broad MWDs. However, in these cases chain transfer to Al is not operative and the broad MWDs result from multisite behavior.

■ INTRODUCTION

The ethylene polymerization behavior of pyridine-diimine (PDI) Fe and Co complexes activated by Al reagents (MAO or MMAO) was first reported by Brookhart and Gibson in the late 1990s.^{1,2} These compounds exhibit very high activity in ethylene homopolymerization to produce linear polyethylene.³⁻⁶ More recently, PDI metal complexes have been used in catalytic hydrosilylation,⁷⁻¹⁰ hydroboration,¹¹⁻¹⁴ [2 + 2]cycloaddition,¹⁵⁻¹⁸ CO₂/ethylene coupling,¹⁹ and ring-opening polymerization of epoxides, lactide, and caprolactone.² However, despite their high activities in ethylene polymerization, (PDI)Fe and (PDI)Co catalysts suffer from poor thermal stability at elevated temperatures and short catalyst lifetimes (often <15 min). One strategy that has been explored to improve the performance of (PDI)M catalysts is to incorporate the (PDI)M unit into a multinuclear structure using linear or macrocyclic bi- or polynucleating ligands.^{27–34}

Chart 1 shows the structures of several multinuclear Fe and Co complexes supported by macrocyclic multinucleating PDI ligands that have been examined for ethylene polymerization. In the *anti*-double-decker complexes (A)M₂Cl₄ (M = Fe, Co) reported by Takeuchi, the two PDI planes are arranged in a parallel orientation and the MCl₂ units are positioned on opposite sides of the molecule.²⁷ The two PDI units are

connected by a 1,2-bis(2-phenylene)ethylene bridge. When they are activated by MMAO-12, the (A)Fe₂Cl₄ and $(A)Co_2Cl_4$ complexes are more active and the $(A)Co_2Cl_4$ complexes produce polyethylene with higher molecular weight (MW) in comparison to mononuclear analogues. Furthermore, these complexes are thermally stable up to 80 °C and display longer catalyst lifetimes than their mononuclear analogues. Takeuchi has also reported the analogous syn-double-decker complexes (\mathbf{B}) Fe₂Cl₄, in which the PDI units are linked by 4,5xanthene bridges and the FeCl₂ units are positioned on the same side of the molecule.²⁸ Interestingly, (**B**) Fe_2Cl_4 (**R**¹ = **R**² = H) generates slightly branched polyethylene, with selective formation of Et and Pr branches, while the mononuclear analogue generates polyethylene with Me, Et, and Pr branches. Li has reported the trinuclear complex $(C)Fe_3Cl_6$, in which the (PDI)Fe units are linked by bis(4-phenylene)methylene bridges. (C)Fe₃Cl₆ is more active, exhibits longer catalyst

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Chart 1. Multinuclear Fe and Co Ethylene Polymerization Catalysts Supported by Macrocyclic Multinucleating PDI Ligands



lifetime, and produces polyethylene with higher MW in comparison to the mononuclear analogue when it is activated by MMAO-12 or triisobutylaluminum (TIBA).³⁴ On the basis of these results, it is of interest to investigate other macrocyclic bis-PDI metal complexes in order to probe how variation of the bis-PDI ligand structure influences catalyst performance. Here we report the synthesis of a new family of macrocyclic bis-PDI ligands 1-3 and the corresponding dinuclear metal complexes $(1-3)M_2Br_4$ (M = Zn, Fe, Co), in which the PDI units are connected by a 3,3''-o-terphenyl linker (Chart 1). The ethylene homopolymerization behavior of $(1-3)Fe_2Br_4$ and $(1-3)Co_2Br_4$ is also reported.

RESULTS AND DISCUSSION

Synthesis of Bis-PDI Ligands. The reaction of 4-tertbutyl-2,6-diacetylpyridine with the appropriate dianiline under Dean–Stark imine-condensation conditions results in the formation of the 30-membered macrocyclic bis-PDI ligands 1-3 in 50–65% isolated yield (Scheme 1). The NMR features of 1-3 are consistent with the bis-PDI form of the ligand and indicative of highly symmetric structures, as only one set of *m*pyridine, imine-Me, and terphenyl-Me resonances are present.

Synthesis and Structures of Metal Complexes. The reaction of 1-3 with 2 equiv of MBr₂ affords the dinuclear complexes $(1-3)M_2Br_4$ in >70% isolated yield (Scheme 1). Xray-quality crystals of (1) $Zn_2Br_4 \cdot 4C_2H_4Cl_2$, {(1) Co_2Br_4)}{(1)- $Co_2Br_4 \cdot 0.23H_2O$ $\cdot 2C_2H_4Cl_2$, (2) $Zn_2Br_4 \cdot 5C_2H_4Cl_2$, (2) $Co_2Br_4 \cdot Co_2H_4Cl_2$, (2) $Co_2H_4Cl_2$, (2 $6C_2H_4Cl_2$, and (3)Fe₂Br₄·4C₂H₄Cl₂ were grown by slow diffusion of hexanes into a 1,2-dichloroethane solution of the corresponding complex (Figures 1-5, respectively). In the solid state, all of the complexes adopt approximately C_s symmetric angular structures in which the (PDI)M planes are skewed 49-82° relative to each other and both middle rings of the o-terphenyl bridges are on the same side of the molecule: i.e., Cs-skew-syn structures. The metal-metal distances for $(1-3)M_2Br_4$ are given in Table 1 and range from 5.7600(8) to 6.232(1) Å. Similar distances were observed for macrocyclic bis-PDI complexes in which the PDI units are Scheme 1. Synthesis of Macrocyclic Bis-PDI Ligands 1-3and Their Metal Complexes $(1-3)M_2Br_4$ (M = Zn, Co, Fe)



bridged by *m*-xylylene linkers, including ([D]Cu₂Im]- $[CF_3SO_3]_3$ (Cu-Cu = 5.9181(9) Å), $[E]Zn_2Ox][CF_3SO_3]_2$ $(Zn-Zn = 5.3849(6) \text{ Å}), (F)Zn_2Cl_4 (Zn-Zn = 5.515(1) \text{ Å}),$ and (F)Co₂Cl₄ (Co-Co = 5.501(1) Å), which are shown in Chart 2.³⁵⁻³⁹ In contrast, the Co-Co distance in (A)Co₂Cl₄ $(R^1 = R^2 = H; 7.731(2) \text{ Å})$ is much longer. While the syndouble-decker complexes (B)Fe2Cl4 have not been crystallographically characterized, Groysman has reported a similar $[(B)Co_2(CH_3CN)_4][Co(CO)_4]_2$ complex with a Co-Co distance of 4.628(1) Å.⁴⁰ The other metrical parameters for the $(1-3)M_2Br_4$ complexes are consistent with those for mononuclear (PDI)MX₂ (X = Cl, Br) complexes.^{2,41} (1)-Zn₂Br₄·4C₂H₄Cl₂ contains one distorted-square-pyramidal Zn center and one trigonal-bipyramidal Zn center (Br1-Zn1-Br2 = $111.27(3)^{\circ}$, Br3–Zn2–Br4 = $125.03(3)^{\circ}$). In the other four structures, the metal centers adopt distorted-square-pyramidal geometries with Br-M-Br angles in the range of 108-118°. There are two independent molecules of $(1)Co_2Br_4$ in the asymmetric unit of $\{(1)Co_2Br_4\}\{(1)Co_2Br_4\cdot(H_2O)_{0.23}\}$. $2C_2H_4Cl_2$, which have similar C_s -skew-syn structures. One $(1)Co_2Br_4$ molecule is shown in Figure 2. The second Co site contains 23% of (1)Co₂Br₄·H₂O, in which one of the Co centers has a distorted-octahedral geometry with an adventitious H₂O ligand (see the Supporting Information).



Figure 1. Solid-state structure of $(1)Zn_2Br_4\cdot4C_2H_4Cl_2$. H atoms, $C_2H_4Cl_2$ molecules, and the disorder of the 'Bu groups are omitted. Key bond distances (Å): C2–N1 1.287(5), C12–N3 1.280(5), N1–Zn1 2.251(3), N3–Zn1 2.254(3), N2–Zn1 2.076(3), Zn1–Br1 2.4261(7), Zn1–Br2 2.365(1), C41–N6 1.274(4), C35–N4 1.276(4), N6–Zn2 2.273(3), N4–Zn2 2.259(3), N5–Zn2 2.092(2), Zn2–Br3 2.364(1), Zn2–Br4 2.3676(8). Key bond angles (deg): N1–Zn1–N3 146.6(1), N1–Zn1–N2 73.5(1), N3–Zn1–N2 73.9(1), N2–Zn1–Br1 108.94(8), N2–Zn1–Br2 139.76(8), Br1–Zn1–Br2 111.27(3), N4–Zn2–N6 146.6(1), N4–Zn2–N5 73.4(1), N6–Zn2–N5 73.4(1), N5–Zn2–Br3 124.74(9), N5–Zn2–Br4 110.18(8), Br3–Zn2–Br4 125.03(3). Color key: C, gray; N, light blue; Zn, light gray; Br, brown.

NMR Characterization of (1–3)M₂Br₄ Complexes. The ¹H NMR spectra of $(1)Zn_2Br_4$ indicate that this complex undergoes a fluxional process that permutes the two PDI units. The ^IH NMR and ¹H-¹H COSY spectra of $(1)Zn_2Br_4$ collected at -78 °C show the presence of two C_s-symmetric species in an ca. 2/1 ratio. Two *m*-pyridine resonances and two sets of resonances for the aromatic hydrogens of the central and lateral rings of the *o*-terphenyl linker in a 1/1 ratio are observed for both species (the imine-Me, terphenyl-Me, and ^tBu resonances for both species overlap). These isomers likely differ in the conformation of the macrocyclic bis-PDI ligand. The ¹H NMR spectrum at room temperature is broad. However, the ¹H NMR spectrum at 100 °C contains sharp singlets for the *m*-pyridine, imine-Me, and terphenyl-Me hydrogens, indicative of fast exchange of the (PDI)M units and concomitant fast interconversion of the two lowtemperature isomers. The paramagnetic ¹H NMR spectra of $(1)Co_2Br_4$ and $(2)Fe_2Br_4$ are broad and uninformative. The room-temperature ¹H NMR spectra for the $(2)M_2Br_4$ and $(3)M_2Br_4$ complexes indicate that these complexes have C_ssymmetric structures and that permutation of the two PDI units is slow on the NMR time scale. Two m-pyridine, imine-Me, terphenyl-Me, and ^tBu resonances in an 1/1 intensity ratio are observed for (2)Zn₂Br₄ and (3)Zn₂Br₄.⁴² Likewise, the paramagnetic ¹H NMR spectra of $(2)M_2Br_4$ and $(3)M_2Br_4$ (M



Figure 2. Structure of one $(1)Co_2Br_4$ molecule in $\{(1)Co_2Br_4\}\{(1)-Co_2Br_4\cdot 0.23H_2O\}\cdot 2C_2H_4Cl_2$. H atoms and $C_2H_4Cl_2$ molecules are omitted. Key bond distances (Å): C8–N3 1.284(8), C2–N1 1.281(8), N3–Co1 2.156(5), N1–Co1 2.196(5), N2–Co1 2.046(5), Co1–Br1 2.497(1), Co1–Br2 2.385(1), C37–N6 1.267(9), C34–N4 1.275(9), N6–Co2 2.181(6), N4–Co2 2.198(5), N5–Co2 2.047(5), Co2–Br3 2.401(1), Co2–Br4 2.438(1). Key bond angles (deg): N3–Co1–N1 144.3(2), N3–Co1–N2 74.1(2), N1–Co1–N2 74.3(2), N2–Co1–Br1 90.8(1), N2–Co1–Br2 160.7(1), Br1–Co1–Br2 108.45(4), N6–Co2–N4 145.9(2), N6–Co2–N5 74.5(2), N5–Co2–N4 73.9(2), N5–Co2–Br3 147.3(2), N5–Co2–Br4 94.5(2), Br3–Co2–Br4 118.11(4). Color key: C, gray; N, light blue; Co, blue; Br, brown.

= Fe, Co) are sharp and are consistent with C_s -symmetric structures.⁴³ These data indicate that the Me and ⁱPr substituents in (2)M₂Br₄ and (3)M₂Br₄ slow the fluxional process that is observed for (1)M₂Br₄.

Magnetic Data. Magnetic data for mononuclear (PDI)-CoCl₂ and (PDI)FeCl₂ are consistent with high-spin complexes with S = 3/2 Co²⁺ and S = 2 Fe²⁺ centers, respectively.² Due to an unquenched angular moment, the experimentally determined μ_{eff} values for these complexes (4.6–4.9 μ_{B} for (PDI)CoCl₂ and 4.7–5.5 μ_{B} for (PDI)FeX₂ (X = Cl, Br)) are typically larger than the spin-only values (μ_{SO}) of 3.9 μ_{B} for Co²⁺ and 4.9 for Fe^{2+,2,44} The μ_{SO} value of a dinuclear metal complex with noninteracting metal centers is given by eq 1

$$\mu_{\rm SO} = 2\sqrt{S_1(S_1+1) + S_2(S_2+1)} \tag{1}$$

in which S_1 and S_2 are the spin states of the two metal centers.^{45,46} The μ_{eff} values for (1)Co₂Br₄ and (3)Co₂Br₄ determined by the Evans method are 7.9(7) and 7.8(8) μ_{B} , respectively, consistent with two independent high-spin ($S_1 = S_2 = 3/2$) Co²⁺ centers ($\mu_{\text{SO}} = 5.5 \ \mu_{\text{B}}$, eq 1). The μ_{eff} values for (1)Fe₂Br₄ and (3)Fe₂Br₄ determined by the Evans method are 8.4(7) and 8.9(5) μ_{B} , respectively, consistent with two independent high-spin ($S_1 = S_2 = 2$) Fe²⁺ centers ($\mu_{\text{SO}} = 6.9$



Figure 3. Structure of $(2)Zn_2Br_4 \cdot SC_2H_4Cl_2$. H atoms and $C_2H_4Cl_2$ molecules are omitted. Key bond distances (Å): C37–N6 1.276(6), C43–N4 1.286(6), N6–Zn2 2.248(4), N4–Zn2 2.238(3), N5–Zn2 2.081(4), Zn2–Br3 2.3694(7), Zn2–Br4 2.4216(5), C8–N3 1.262(6), C2–N1 1.277(5), N3–Zn1 2.278(4), N1–Zn1 2.289(3), N2–Zn1 2.097(3), Zn1–Br1 2.3424(8), Zn1–Br2 2.3903(7). Key bond angles (deg): N6–Zn2–N4 145.0(1), N6–Zn2–N5 73.4(1), N5–Zn2–N4 73.5(1), N5–Zn2–Br3 141.9(1), N5–Zn2–Br4 107.0(1), Br3–Zn2–Br4 111.09(3), N3–Zn1–N1 142.9(1), N3–Zn1–N2 72.7(1), N2–Zn1–N1 72.6(1), N2–Zn1–Br1 141.9(1), N2–Zn1–Br2 101.4(1), Br1–Zn1–Br2 116.68(3). Color key: C, gray; N, light blue; Zn, light gray; Br, brown.

 $\mu_{\rm B}$, eq 1). Complexes of 2 are poorly soluble in CD₂Cl₂, which precludes accurate determination of $\mu_{\rm eff}$ by the Evans method.

Ethylene Reactivity. The ethylene reactivity of (1-3)Fe₂Br₄ is summarized in Table 2. (1)Fe₂Br₄/1000 TIBA reacts with ethylene to produce 1-butene with low activity (entry 1). The attempted activation of (1)Fe₂Br₄ with MAO or MMAO-12 in the presence of ethylene resulted in fast decomposition to Fe^{0} , indicating that these Al-Me reagents are able to reduce the Fe^{2+} centers.⁴⁷⁻⁴⁹ However, (2)Fe₂Br₄/ 1000 MMAO-12 (entry 2) and (3)Fe₂Br₄/1000 MMAO-12 or TIBA (entries 3 and 4) produce linear polyethylenes with broad and typically bimodal molecular weight distributions (MWDs) and $T_{\rm m}$ values between 125 and 130 °C. (3)Fe₂Br₄/ 1000 MMAO-12 is about twice as active and produces polyethylene with a much higher M_w value in comparison to (2)Fe₂Br₄/1000 MMAO-12 (entries 2 and 3). (3)Fe₂Br₄/1000 TIBA is more active than $(3)Fe_2Br_4/1000$ MMAO-12 but produces polyethylene with a much lower M_w value. One possible reason for the lower activity of (3)Fe₂Br₄/MMAO-12 vs (3)Fe₂Br₄/TIBA is that access of the large linear/cyclic chains of MMAO-12 to the intermetallic cavity is hindered by steric factors.^{50–53}



Figure 4. Structure of $(2)Co_2Br_4 \cdot 6C_2H_4Cl_2$. H atoms and $C_2H_4Cl_2$ molecules are omitted. Key bond and atom distances (Å): C43–N6 1.280(6), C37–N4 1.285(7), N6–Co2 2.178(6), N4–Co2 2.166(6), N5–Co2 2.062(4), Co2–Br3 2.467(1), Co2–Br4 2.4044(9), C8–N3 1.290(8), C2–N1 1.277(9), N3–Co1 2.197(5), N1–Zn1 2.181(6), N2–Zn1 2.061(5), Co1–Br1 2.441(1), Co1–Br2 2.388(1). Key bond angles (deg): N6–Co2–N4 146.2(2), N6–Co2–N5 74.3(2), N5–Co2–N4 74.5(2), N5–Co2–Br3 100.2(1), N5–Co2–Br4 152.4(1), Br3–Co2–Br4 107.34(4), Br1–Co1–Br2 110.30(4), N3–Co1–N1 142.3(2), N3–Co1–N2 73.7(2), N2–Co1–N1 73.6(2), N2–Co1–Br1 93.6(1), N2–Co1–Br2 156.1(1), Br1–Co1–Br2 110.30(4). Color key: C, gray; N, light blue; Co, blue; Br, brown.

The broad MWDs observed for the polymers produced by (2)Fe₂Br₄/MMAO-12 and (3)Fe₂Br₄/MMAO-12 are not surprising, as similar results have been observed for mononuclear (PDI)FeX₂ complexes activated by MAO or MMAO-12. $^{1,2,34,47,54-58}$ This phenomenon is due to fast chain transfer to Al. In the initial stage of the polymerization when the Al-Me concentration is high, chain transfer to Al is fast and low-MW polymer is formed. In the later stages of the polymerization when the Al-Me concentration is low, chain transfer via β -H elimination predominates and results in the high-MW fraction. However, activation of mononuclear or multinuclear (PDI)FeCl₂ precatalysts with TIBA normally results in narrow MWDs, as chain transfer to Al is slow with this activator.^{59,60} For example, (C)Fe₃Cl₆/1000 MMAO-12 produces polyethylene with a polydispersity (D) of ca. 50, while (C)Fe₃Cl₆/1200 TIBA generates polyethylene with a Dvalue of ca. 4.³⁴ Surprisingly, however, (3) $Fe_2Br_4/TIBA$ produces polyethylene with a broad MWD, and the overall $M_{\rm w}$ value decreases as the Al/Fe ratio is increased from 500 to 10000 (Table 2, entries 7 and 8). These observations indicate that chain transfer to Al occurs in these systems.



Figure 5. Structure of (3)Fe₂Br₄·4C₂H₄Cl₂. H atoms, C₂H₄Cl₂ molecules, and disorder of the trigonal-bipyramidal geometry of Fe2 due to H bonding to a C₂H₄Cl₂ solvent molecule are omitted. Key bond and atom distances (Å): C78–N3 1.272(5), C7–N1 1.280(6), N3–Fe1 2.177(4), N1–Fe1 2.190(4), N2–Fe1 2.106(3), Fe1–Br1 2.5159(8), Fe1–Br2 4168(6), C46–N6 1.276(6), C40–N4 1.274(6), N6–Fe2 2.258(4), N4–Fe2 2.289(3), N5–Fe2 2.141(4), Fe2–Br3 2.419(1), Fe2–Br4 2.4384(8). Key bond angles (deg): N3–Fe1–N1 143.4(1), N3–Fe1–N2 72.9(1), N2–Fe1–N1 72.7(1), N2–Fe1– Br1 95.5(1), N2–Fe1–Br2 155.9(1), Br1–Fe1–Br2 108.53(3), Br3– Fe2–Br4 109.64(4), N6–Fe2–N4 142.8(1), N6–Fe2–N5 71.8(1), N5–Fe2–N4 72.0(1), N5–Fe2–Br3 145.1(1), N5–Fe2–Br4 105.2(1). Color key: C, gray; N, light blue; Fe, orange; Br, brown.

Table 1. Metal-Metal Distances and Angles between the PDI Planes (\angle PDI-PDI) for (1-3)M₂Br₄ Complexes

	M–M distance (Å)	∠PDI-PDI (deg)
$(1)Zn_2Br_4$	5.7600(8)	81.92
$(1)Co_2Br_4$	6.232(1)	54.09
$(1)Co_2Br_4 \cdot 0.23H_2O$	5.821(1)	49.08
$(2)Zn_2Br_4$	5.8668(7)	55.69
$(2)Co_2Br_4$	5.832(1)	56.12
(3)Fe ₂ Br ₄	6.051(1)	57.31

¹H and ¹³CNMR analysis of the polyethylenes produced by (3)Fe₂Br₄/1000 MMAO-12 (Table 2, entry 3), and (3)-Fe₂Br₄/10000 TIBA (entry 8) confirm the operation of a chain transfer to Al pathway in these systems. In both cases the polymer is linear, >98% of the olefin units are vinyl groups, and significantly, the vinyl/saturated end group ratio is ca. 1/1.5. The excess saturated chain ends arise by chain transfer to Al. Interestingly, ¹³C NMR analysis of the polymer produced by (3)Fe₂Br₄/10000 TIBA shows that only a small fraction of

Chart 2. Macrocyclic Bis-PDI Metal Complexes in Which the PDI Units Are Bridged by *m*-Xylylene Linkers



saturated chain ends are ⁱBu ends.⁵⁸ The ⁱBu/ⁿBu chain end ratio is 1/9, whereas a value of 1/2 is expected if the excess of saturated chain ends (not attributable to chain transfer via β -H elimination) arises by exchange of Fe-polymeryl and Al-ⁱBu groups. Two plausible explanations for this difference are (i) Fe-polymeryl/Al-H exchange involving ⁱBu₂AlH generated by thermal decomposition of TIBA is faster than direct Fepolymeryl/Al-ⁱBu exchange involving TIBA⁶¹⁻⁶⁵ and (ii) Fe-ⁱBu species generated by direct Fe-polymeryl/Al-ⁱBu exchange undergo β -H elimination to form Fe-H and isobutene prior to chain growth.

Attempted activation of $(1)Co_2Br_4$ and $(2)Co_2Br_4$ with MMAO-12 results in decomposition to Co^0 , similar to the results for $(1)Fe_2Br_4$ noted above. Activation of $(1)Co_2Br_4$ and $(2)Co_2Br_4$ with 1000 equiv of TIBA generates catalysts that produce 1-butene with low activity (Table 3, entries 1 and 2). However, activation of $(3)Co_2Br_4$ with TIBA or MMAO-12 (Al/Co = 1000) generates catalysts that produces polyethylenes with a moderate M_w value. $(3)Co_2Br_4/1000$ TIBA is much less active than $(3)Co_2Br_4/1000$ MMAO-12 or $(3)Co_2Br_4/1000$ MAO but produces polyethylene with a higher M_w value (Table 3, entry 3).

Interestingly, in all cases, $(3)Co_2Br_4/activator catalysts$ produce polyethylene with broad MWDs. ¹H NMR analysis of the polymer produced by $(3)Co_2Br_4/1000$ MMAO-12 (Table 3, entry 4) shows that the vinyl/saturated end group ratio is 1/1, as expected when chain transfer is occurring exclusively via β -H elimination. Collectively these observations imply that $(3)Co_2Br_4/activator$ systems are multisite catalysts. The multisite behavior may arise in several ways. As noted above, X-ray crystallographic and NMR data show that $(3)Co_2Br_4$ adopts a C_s -symmetric structure with inequivalent metal centers, and it is possible that this feature is retained in the activated form of the catalyst. Alternatively, activation of just one of the two inequivalent metal centers may generate two distinct monoactivated species. Multisite behavior may pubs.acs.org/Organometallics

Tab	le	2.	Ethy	ylene	Reactivit	y of	Dinuc	lear	Fe	Comp	lexes	1
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entry	catalyst	activator	T (°C)	P (bar)	activity ^b $(g_{PE} mmol_{Fe}^{-1} h^{-1})$	TOF (h^{-1})	$M_{\rm w}~({ m Da})$	D^d	$T_{\rm m}$
1	(1)Fe ₂ Br ₄	TIBA	25	2	15(5)	500	56 ^c (1-butene)		
2 ^e	(2)Fe ₂ Br ₄	MMAO-12	25	20	2000(70)	71000	4500 ^d	11 B	126.9
3	(3)Fe ₂ Br ₄	MMAO-12	25	20	4300(200)	150000	280000^{d}	410 B	131.0
4 ^{<i>f</i>}	(3)Fe ₂ Br ₄	TIBA	25	20	9100(30)	325000	19000 ^d	31 B	125.1
5	(3)Fe ₂ Br ₄	TIBA	60	20	5800(400)	210000	22000^{d}	32 B	127.1
6	(3)Fe ₂ Br ₄	TIBA	80	20	6000(600)	210000	16000^{d}	30 B	126.2
7^g	(3)Fe ₂ Br ₄	TIBA	25	20	5900(600)	210000	37000 ^d	54 B	127.9
8 ^h	(3)Fe ₂ Br ₄	TIBA	25	20	7800(400)	280000	17000 ^d	95 M	124.7

^{*a*}Conditions unless specified otherwise: 2.5 μ mol of Fe, 50 mL of PhMe, 1000 equiv of Al/Fe, 0.5 h. ^{*b*}Average of two runs. The value in parentheses is the standard deviation for those runs. ^{*c*}Determined by GC-MS. ^{*d*}Determined by GPC: M = monomodal molecular weight distribution, B = bimodal molecular weight distribution. ^{*c*}C₆-C₂₈ α -olefins also observed; $\alpha = 0.86$. ^{*f*}Exotherm to 80 °C observed upon activation in this case. ^{*g*}S00 equiv of Al/Fe. ^{*h*}0.25 μ mol of Fe, 10000 equiv of Al/Fe.

Table 5. Durylene Reactivity of Dinuclear Co Complexes	Table	3.	Ethylen	e Reactivity	7 of	Dinuclear	Co	Complexe	sa
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entry	catalyst	activator	T (°C)	P (bar)	activity ^b ($g_{PE} \text{ mmol}_{Co}^{-1} \text{ h}^{-1}$)	TOF (h^{-1})	$M_{\rm w}$ (Da)	D^d	$T_{\rm m}$
1	$(1)Co_2Br_4$	TIBA	25	2	15(5)	500	56 ^c (1-butene)		
2	$(2)Co_2Br_4$	TIBA	25	2	30(5)	1000	56^c (1-butene)		
3	$(3)Co_2Br_4$	TIBA	25	20	19(4)	680	180000 ^d	140 B	130.6
4	$(3)Co_2Br_4$	MMAO-12	25	20	260(20)	9300	82000 ^d	220 M	126.5
5	$(3)Co_2Br_4$	MAO	25	20	250(10)	8900	76000 ^d	83 M	126.8

^{*a*}Conditions: 2.5 μ mol of Co, 50 mL of PhMe, 1000 equiv of Al/Co, 0.5 h. ^{*b*}Average of two runs. The number in parentheses is the standard deviation of those runs. ^{*c*}Determined by GC-MS. ^{*d*}Determined by GPC: M = monomodal molecular weight distribution, B = bimodal molecular weight distribution.

also contribute to the broad MWDs observed when $(2)Fe_2Br_4$ and $(3)Fe_2Br_4$ are used.

Comparison to Literature Compounds. Chart 3 shows previously reported (PDI)MCl₂ complexes that are analogues

Chart 3. Mononuclear Analogues for $(1-3)M_2Br_4$ (M = Co, Fe)



of $(1-3)M_2Br_4$. As mononuclear (PDI)FeBr₂ and (PDI)CoBr₂ catalysts exhibit similar activity and produce polyethylene with MWDs similar to those of the corresponding (PDI)MCl₂ catalysts, it is informative to compare the behavior of $(1-3)M_2Br_4$ to that of the benchmark catalysts in Chart 3.^{2,66}

Hanton reported that (G)FeCl₂/500 MMAO-3A (30% ⁱBu groups) oligomerizes ethylene to linear α -olefins with a Schulz–Flory propagation probability of $\alpha = 0.3$ with an activity of 1625 g_{PE} mmol_{Co}⁻¹ h⁻¹, and (G)CoCl₂/500 MMAO-3A dimerizes ethylene to >99% 1-butene with an activity of 3000 g_{PE} mmol_{Co}⁻¹ h^{-1.67} In contrast, both (1)Fe₂Br₄/1000 TIBA and (1)Co₂Br₄/1000 TIBA produce 1-butene selectivity but with much lower activity. However, the activity of (PDI)MCl₂ catalysts generally varies with the activator in the order MAO > MMAOs > TIBA, and thus the

lower activity of the $(1)M_2Br_4$ catalysts may in part reflect the difference in activator.^{59,60}

Article

Gibson and Brookhart reported that (H)FeCl₂/500 MMAO-3A and (H)FeCl₂/1000 MAO generate linear α olefins ($\alpha = 0.8$) with a turnover frequency (TOF) of 1×10^5 h^{-1.68} The dinuclear analogue (2)Fe₂Br₄/MMAO-12 exhibits a similar TOF of 0.7 × 10⁵ h⁻¹ but produces an insoluble polyethylene fraction. (H)CoCl₂/1000 MAO also generates linear α -olefins ($\alpha = 0.65$) but with low activity (25 g mmol_{Co}⁻¹ h⁻¹).⁴⁴ Similar activity is observed with (2)Co₂Br₄/ 1000 TIBA, but 1-butene is selectively generated.

(I)FeCl₂/500 MMAO-3A generates linear α -olefins ($\alpha = 0.8-0.9$) with a TOF of ca. 8 × 10⁴ h^{-1.68} In contrast, (3)Fe₂Br₄/1000 MMAO-12 and (3)Fe₂Br₄/1000 TIBA are 3– 4 times more active and produce solid polyethylene products. The geometric constraints and additional steric crowding imparted by the dinuclear structure of (3)Fe₂Br₄ may contribute to this difference. The ethylene homopolymerization behavior of (I)CoCl₂ has not been reported.

(2)Fe₂Br₄/1000 MMAO-12 is ca. 5 times more active than (B)Fe₂Cl₄/1000 MMAO-12 (R¹ = R² = Me, activity 356 g_{PE} mmol_{Fe1}⁻¹ h⁻¹ at 25 °C) but produces polyethylene with a lower M_w value (4500 Da vs 75 500 Da). (3)Fe₂Br₄/1000 MMAO-12 is ca. 6 times more active than (A)Fe₂Cl₄/1000 MMAO-12 (R¹ = ⁱPr, R² = H, activity = 684 g_{PE} mmol_{Fe}⁻¹ h⁻¹ at 25 °C) and produces polymer with a higher M_w value (280000 Da vs 100 000 Da).

EXPERIMENTAL SECTION

General Procedures. All experiments were performed using drybox or Schlenk techniques under a nitrogen atmosphere unless noted otherwise. Nitrogen was purified by passage through Q-5 oxygen scavenger and activated molecular sieves. CH_2Cl_2 , Et_2O , and THF were dried by passage through activated alumina. Hexanes and toluene were purified by passage through BASF R3-11 oxygen scavenger and activated alumina. CH_2CICH_2CI was dried over

MgSO₄ and then distilled from calcium hydride and stored under nitrogen. CDCl₃, CD₂Cl₂, and CDCl₂CDCl₂ were distilled from and stored over activated 3 Å molecular sieves. The anhydrous metal salts (PPh₃)₄Pd and PdCl₂(dppf) were purchased from Strem Chemical, Inc., and used without further purification. 5-Bromo-2-methylaniline, 3-aminophenylboronic acid pinacol ester, 2,5-dibromo-*o*-xylene, and B₂pin₂ were purchased from AK Scientific and used without further purification. Anhydrous dioxane, TIBA, MAO, and MMAO-12 (5% ⁿBu groups) were purchased from MilliporeSigma. 2-Nitrocumene was purchased from TCI America. 4-*tert*-Butyl-2,6-diacetylpyridine was synthesized according to literature procedures.⁶⁹ 5-Bromo-2isopropylaniline was synthesized from 2-nitrocumene using literature procedures for 5-bromo-2,6-dimethylaniline.⁷⁰

NMR spectra were recorded on Bruker ADVANCE II+ 500 and DRX 400 spectrometers at room temperature unless otherwise specified. ¹H and ¹³C chemical shifts are reported relative to SiMe₄ and internally referenced to residual ¹H and ¹³C solvent resonances. The baselines of the ¹H NMR spectra for the paramagnetic compounds were spline-corrected. Peak integrations for the spectra of the paramagnetic compounds were unreliable, and only δ and $v_{1/2}$ values for the resonances are reported.

MALDI-TOF-TOF-MS spectra were collected on a Bruker Ultraflextreme instrument using dithranol as the matrix. Highresolution accurate mass spectra (HRA-MS) were recorded on an Agilent 6224 TOF-MS instrument in mixed (ESI/APCI) mode. While the expected $[M - Br]^+$ ion was observed by MALDI-TOF-TOF-MS for all metal complexes, ions of the form $[M - xBr + yCl]^+$ were instead observed by by HRA-MS, with $[M - 4Br + 3Cl]^+$ being the most prevalent. We attribute this phenomenon to the formation of Cl⁻ ions during ionization, originating from the CH₂Cl₂ solvent used for analysis. The observed isotope patterns closely matched isotope patterns calculated using envipat 2.2 Web and are reported in the Supporting Information for each metal complex.⁷¹ The reported m/zvalue corresponds to the most intense peak in the isotope pattern. Xray-quality crystals of (1)Zn₂Br₄·4C₂H₄Cl₂, ${(1)Co_2Br_4}{(1)Co_2Br_4}$. $0.23H_2O$ $(2)Zn_2Br_4 \cdot 5C_2H_4Cl_2$, (2) $Co_2Br_4 \cdot 6C_2H_4Cl_2$, and (3)Fe₂Br₄·4C₂H₄Cl₂ were grown by diffusion of hexanes into a 1,2dichloroethane solution (1/1) of each compound at room temperature over 2 days. Thermal ellipsoids are drawn at the 50% probability level.

Elemental analyses were performed by Midwest Microlab. In most cases the ligands and metal complexes did not combust well and significant deviations in C% (3-5%) but accurate H% and N% values (typically within $\pm 0.4\%$) were observed. The elemental analysis results are included for completeness.

3-Amino-4-methylphenylboronic Acid Pinacol Ester (Scheme 2). 5-Bromo-2-methylaniline (6.49 g, 34.9 mmol, 1

Scheme 2. Synthesis of 3-Amino-4-R-phenylboronic Acid Pinacol Esters (R = Me, ⁱPr)



equiv), B₂pin₂ (9.74 g, 38.4 mmol, 1.1 equiv), PdCl₂(dppf) (684 mg, 1 mmol, 3 mol %), and KOAc (14.8, 105 mmol, 3 equiv) were placed in a side-armed round-bottom flask under an N₂ purge. Dioxane (90 mL) was added by syringe. A condenser was attached, and the reaction mixture was refluxed for 3 h. The reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. The crude black solid was dissolved in EtOAc/CH₂Cl₂ (1/9), filtered through Celite, and chromatographed on silica gel to yield 3-amino-4-methylphenylboronic acid pinacol ester as a white solid. Yield: 4.16 g, 51.1%. ¹H NMR (CDCl₃, 400 MHz): δ 7.16 (d, ³J_{HH} = 7.4 Hz, 1H, Ar-H⁵), 7.12 (s, 1H, Ar-H²), 7.07 (d, ³J_{HH} = 7.2 Hz, 1H, Ar-H⁶), 3.57 (s, 2H, -NH₂), 2.18 (s, 3H, Ar-CH₃), 1.33 (s, 12H, B-

O-C- $(CH_3)_2$). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 144.2, 130.1, 126.0, 125.4, 121.2, 83.7 (B-O-C- $(CH_3)_2$), 25.0 (B-O-C- $(CH_3)_2$), 17.7 (Ar-CH₃); the B-C resonance was not observed. ESI/APCI-TOF HRA-MS (*m*/*z*): [M + H]⁺ calcd for C₁₃H₂₁BNO₂⁺ 234.1660; found 234.1667.

3-Amino-4-isopropylphenylboronic Acid Pinacol Ester (Scheme 2). This compound was synthesized by the procedure for 3-amino-4-methylphenylboronic acid pinacol ester using 5-bromo-2isopropylaniline (3.50 g, 16.4 mmol, 1 equiv), B₂pin₂ (4.57 g, 18.0 mmol, 1.1 equiv), PdCl₂(dppf) (401 mg, 0.49 mmol, 3 mol %), and KOAc (4.81 g, 49.0 mmol, 3 equiv). The crude product was chromatographed on silica gel using EtOAc/CH₂Cl₂ (0.5/9) to yield 3-amino-4-isopropylphenylboronic acid pinacol ester as a white solid. Yield: 2.89 g, 67.0%. ¹H NMR (CDCl₃, 400 MHz): δ 7.25 (dd, ${}^{3}J_{HH} =$ 9.5 Hz, ${}^{4}J_{\rm HH}$ = 1.3 Hz, 1H, Ar-H⁶, overlapped with solvent resonance), 7.17 (d, ${}^{3}J_{HH} = 9.5$ Hz, 1H, Ar-H⁵),7.14 (d, ${}^{3}J_{HH} = 1.3$ Hz, Ar-H²), 3.64 (s, 2H, -NH₂), 2.92 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 1H, Ar-CH(CH₃)₂), 1.33 (s, 12H, B-O-C-(CH₃)₂), 1.26 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6H, Ar-CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 142.9, 136.3, 125.7, 125.0, 122.2, 83.7 (B-O-C-(CH₃)₂), 27.9 (Ar-CH(CH₃)₂), 25.0 (B-O-C- $(CH_3)_2$), 22.3 (Ar-CH $(CH_3)_2$); the B-C resonance was not observed. ESI/APCI-TOF HRA-MS (m/z): $[M + H]^+$ Ccalcd for C15H25BNO2+ 262.1973; found 262.1977.

4',**5'**-Dimethyl-[**1**,**1'**:**2'**,**1''**-terphenyl]-**3**,**3''**-diamine (Scheme 3). 2,5-Dibromo-*o*-xylene (2.79 g, 10.5 mmol, 1 equiv), 3-

Scheme 3. Synthesis and Atom-Labeling Scheme of 4,4''-R₂-4',5'-Dimethyl-[1,1':2',1''-terphenyl]-3,3''-diamines (R = H, Me, ⁱPr)



aminophenylboronic acid pinacol ester (4.83 g, 22.1 mmol, 2.1 equiv), Pd(PPh₃)₄ (345 mg, 0.30 mmol, 3 mol %), and K₂CO₃ (5.80 g, 42.0 mmol, 4 equiv) were place in a side-armed round-bottom flask under N₂. Dioxane (25 mL) and degassed H₂O (25 mL) were added by syringe. A condenser was attached, and the reaction mixture was refluxed for 16 h. The mixture was cooled to room temperature, and the dioxane was removed under vacuum, yielding a slurry of a yellow solid in a colorless supernatant. CH2Cl2 (25 mL) was added, and the biphasic mixture was stirred until the solid dissolved. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL), and the combined organic layers were washed with saturated aqueous NaHCO₃ (3×15) mL), dried with MgSO₄, and filtered. The solvent was removed under vacuum. The crude red oil was dissolved in EtOAc/hexanes (3/1) and chromatographed on silica gel to yield 4',5'-dimethyl-[1,1':2',1''terphenyl]-3,3"-diamine as a white solid. Yield: 2.51 g, 83.0%. ¹H NMR (CDCl₃, 500 MHz): δ 7.19 (s, 2H, H_e), 6.98 (t, ${}^{3}\tilde{J}_{HH}$ = 7.9 Hz, 2H, H_c), 6.53 (m, 6H, H_a , H_{b_1} , H_d), 3.54 (s, 4H, $-NH_2$), 2.33 (s, 6H, terphenyl-CH₃). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 145.9, 142.9, 138.2, 135.7, 131.9, 128.7, 120.8, 116.8, 113.3, 19.5 (terphenyl-CH₃). ESI/APCI-TOF HRA-MS (m/z): $[M + H]^+$ calcd for $C_{20}H_{21}N_2^-$ 289.1699; found 289.1706.

4,4',4'',5'-Tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (Scheme 3). This compound was synthesized by the procedure for 4',5'-dimethyl-[1,1':2',1''-terphenyl]-3,3''-diamine using 2,5-dibromo-o-xylene (2.49 g, 9.43 mmol, 1 equiv), 3-amino-4-methylphenylboronic acid pinacol ester (4.50 g, 19.3 mmol, 2.1 equiv), Pd(PPh₃)₄ (327 mg, 0.28 mmol, 3 mol %), and K₂CO₃ (5.02 g, 36.3 mmol, 4 equiv). The crude red oil was dissolved in EtOAc/hexanes (1/1) and chromatographed on silica gel to yield 4,4',4'',5'tetramethyl-[1,1':2',1'''-terphenyl]-3,3''-diamine as a white solid. Yield: 2.11 g, 71.0%. ¹H NMR (CDCl₃, 500 MHz): δ 7.10 (s, 2H, H_e), 6.86 (d, ³J_{HH} = 7.6 Hz, 2H, H_c), 6.51 (d, ³J_{HH} = 1.6 Hz, 2H, H_a), 6.43 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.7 Hz, 2H, H_d), 3.54 (s, 4H, -NH₂), 2.30 (s, 6H, H_b), 2.11 (s, 6H, terphenyl-CH₃). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 144.7, 141.1, 138.3, 135.7, 132.1, 130.0, 120.6, 120.6, 116.4, 19.4 (terphenyl-CH₃), 17.2 (C-H_b). ESI/APCI-TOF HRA-MS (*m*/*z*): [M + H]⁺ calcd for C₂₂H₂₄N₂⁺ 317.2012; found 317.2006.

4,4"-Diisopropyl-4',5'-tetramethyl-[1,1':2',1"-terphenyl]-**3**,3"-diamine (Scheme 3). This compound was synthesized by the procedure for 4',5'-dimethyl-[1,1':2',1''-terphenyl]-3,3''-diamine using 2,5-dibromo-*o*-xylene (2.90 g, 11.0 mmol, 1 equiv), 3-amino-4-isopropylphenylboronic acid pinacol ester (6.0 g, 23.0 mmol, 2.1 equiv), Pd(PPh₃)₄ (379 mg, 0.33 mmol, 3 mol %), and K₂CO₃ (6.04 g, 43.7 mmol, 4 equiv). The crude red oil was dissolved in EtOAc/ Hex (3/7) and chromatographed on silica gel to yield 4,4"diisopropyl-4',5'-tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine as a pale yellow solid. Yield: 3.13 g, 76.5%. ¹H NMR (CDCl₃, 500 MHz): δ 7.12 (s, 2H, H_d), 6.96 (d, ³J_{HH} = 7.8 Hz, 2H, H_b), 6.51 (m, 4H, H_a and H_c), 3.58 (s, 4H, $-NH_2$), 2.86 (sept, ³J_{HH} = 6.8 Hz, 2H, Ar-CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 126 MHz): δ 143.5, 140.6, 138.2, 135.7, 132.2, 131.0, 125.0, 120.8, 117.3, 27.8 (Ar-CH(CH₃)₂), 2.2.4 (Ar-CH(CH₃)₂), 19.4 (terphenyl-CH₃). ESI/APCI-TOF HRA-MS (*m*/*z*): [M + H]⁺ calcd for C₂₆H₃₃N₂⁺ 373.2638; found 373.2633.

Compound 1. 4-*tert*-Butyl-2,6-diacetylpyridine (701 mg, 3.20 mmol, 1 equiv), 4',5'-dimethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (924 mg, 3.20 mmol, 1 equiv), *p*-TsOH (120 mg, 10 mol %), and PhMe (40 mL) were placed in a round-bottom flask. A Dean–Stark trap and condenser were attached, and the reaction mixture was refluxed for 6 h. The mixture was cooled to room temperature, and the PhMe was removed under vacuum. MeOH (25 mL) was placed in the flask, and the brown suspension was stirred for 5 min. The beige solid was collected on a sintered-glass frit and washed with MeOH (2 × 20 mL) and Et₂O (2 × 5 mL) to yield 1 as a white solid. Yield: 982 mg, 65.0%. The labeling scheme for 1 is shown in Figure 6. ¹H NMR



Figure 6. Atom labeling scheme for 1-3.

 $\begin{array}{l} (\mathrm{CD}_2\mathrm{Cl}_2, 500 \ \mathrm{MHz}) : \delta \ 8.28 \ (s, 4H, m-\mathrm{py}), 7.29 \ (t, {}^3J_{\mathrm{HH}} = 7.7 \ \mathrm{Hz}, 4H, \\ \mathrm{H}_c), 7.27 \ (s, 4H, \mathrm{H}_e), 6.94 \ (d, {}^3J_{\mathrm{HH}} = 7.7 \ \mathrm{Hz}, 4H, \ \mathrm{H}_d), 6.68 \ (d, {}^3J_{\mathrm{HH}} = 7.7 \ \mathrm{Hz}, 4H, \ \mathrm{H}_d), 6.56 \ (s, 4H, \ \mathrm{H}_a), 2.34 \ (s, 12H, \ \mathrm{terphenyl-CH}_3), 2.06 \ (s, 12H, \ \mathrm{N} ==\!\!C-\mathrm{CH}_3), 1.37 \ (s, 18H, \ ^{\mathrm{Bu}}). \ ^{13}\mathrm{C}\{^{1}\mathrm{H}\} \ \mathrm{NMR} \ (\mathrm{CD}_2\mathrm{Cl}_2, 126 \ \mathrm{MHz}) : \delta \ 168.2 \ (\mathrm{N=C}), 161.2 \ (p-\mathrm{py}), 155.5 \ (o-\mathrm{py}), 151.8 \ (\mathrm{C-N=C}), 143.2 \ (C_{\mathrm{terphenyl}}\ \mathrm{C}_{\mathrm{aniline}}), 138.5 \ (C_{\mathrm{terphenyl}}\ \mathrm{C}_{\mathrm{aniline}}), 136.2 \ (\mathrm{terphenyl}\ C-\mathrm{CH}_3), 131.9 \ (C-\mathrm{H}_e), 129.1 \ (C-\mathrm{H}_c), 125.1 \ (C-\mathrm{H}_d), 121.0 \ (C-\mathrm{H}_a), 119.4 \ (m-\mathrm{py}), 117.5 \ (C-\mathrm{H}_b), 35.6 \ (-\mathrm{C}(\mathrm{CH}_3)_3), 30.8 \ (-\mathrm{C}(\mathrm{CH}_3)_3), 19.5 \ (\mathrm{terphenyl-CH}_3), 16.7 \ (\mathrm{N=C-CH}_3). \ \mathrm{MALDI-TOF-TOF} \ (\mathrm{dithranol}) \ (m/z) : \ [\mathrm{M} + \mathrm{H}]^+ \ \mathrm{calcd} \ \mathrm{for} \ \mathrm{C}_{66} \ \mathrm{H}_{67} \ \mathrm{N}_6^+ : 943.542, \ \mathrm{found} \ 943.5418. \ \mathrm{Anal. \ Calcd} \ \mathrm{for} \ \mathrm{C}_{66} \ \mathrm{H}_{66} \ \mathrm{N}_6 : \ \mathrm{C}, \\ 84.04; \ \mathrm{H}, \ 7.05; \ \mathrm{N}, \ 8.91. \ \mathrm{Foundie} \ \mathrm{C}, \ 81.89; \ \mathrm{H}, \ 6.99; \ \mathrm{N}, \ 8.56. \end{array}$

Compound 2. This compound was synthesized by the procedure for 1 using 4-*tert*-butyl-2,6-diacetylpyridine (701.0 mg, 3.20 mmol, 1 equiv), 4,4',4'',5'-tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (1.01 g, 3.20 mmol, 1 equiv), *p*-TsOH (120 mg, 10 mol %), and PhMe (40 mL). The crude solid was washed with MeOH (20 mL)

and hexanes (10 mL) to yield **2** as a white solid. Yield: 840 mg, 52.5%. The labeling scheme for **2** is shown in Figure 6. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.36 (s, 4H, *m*-py-H), 7.19 (s, 4H, H_e), 7.15 (d, ³J_{HH} = 7.7 Hz, 4H, H_d), 6.86 (d, ³J_{HH} = 7.7 Hz, 4H, H_c), 6.44 (s, 4H, H_a), 2.32 (s, 12H, terphenyl-CH₃), 2.06 (s, 12H, Me_b), 1.98 (s, 12H, N= C-CH₃), 1.37 (s, 18H, ¹Bu). ¹³C{¹H} MMR (CD₂Cl₂, 126 MHz): δ 167.6 (N=C), 161.1 (*p*-py), 155.3 (*o*-py), 150.3 (*C*-N=C), 140.8 (C_{terphenyl}-C_{aniline}), 138.5 (C_{terphenyl}-C_{aniline}), 135.9 (terphenyl C-CH₃), 131.9 (C-H_e), 130.4 (C-H_d), 125.3 (C-C(H_b)₃), 124.9 (C-H_c), 120.2 (C-H_a), 119.3 (*m*-py), 35.5 (-C(CH₃)₃), 30.8 (-C(CH₃)₃), 19.5 (terphenyl-CH₃), 17.5 (C-Me_b), 16.7 (N=C-CH₃). MALDI-TOF-TOF (dithranol) (*m*/*z*): [M + H]⁺ calcd for C₇₀H₇₅N₆ 999.61, found 999.61. ESI/APCI-TOF HRA-MS (*m*/*z*): [M + H]⁺ calcd for C₇₀H₇₅N₆ * 999.6048, found 999.6041. Anal. Calcd for C₇₀H₇₄N₆: C, 84.13; H, 7.46; N, 8.41. Found: C, 83.99; H, 7.66; N, 8.21.

Compound 3. This compound was synthesized by the procedure for 1 using 4-tert-butyl-2,6-diacetylpyridine (701.0 mg, 3.20 mmol, 1 equiv), 4,4"-diisopropyl-4',5'-tetramethyl-[1,1':2',1''-terphenyl]-3,3"-diamine (1.19 g, 3.20 mmol, 1 equiv), p-TsOH (120 mg, 10 mol %), and PhMe (40 mL). The crude solid was washed with MeOH $(2 \times 10 \text{ mL})$ and hexanes (10 mL) to yield 3 as a yellow solid. Yield: 840 mg, 52.5%. The labeling scheme for 3 is shown in Figure 6. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.32 (s, 4H, *m*-py), 7.23 (d, ³J_{HH} = 7.9 Hz, 4H, H_c), 7.19 (s, 4H, H_e), 6.93 (dd, ${}^{3}J_{HH} = 7.9$ Hz, ${}^{4}J_{HH} = 1.3$ Hz, 4H, H_d), 6.45 (d, ${}^{3}J_{HH} = 1.3$ Hz, 4H, H_a), 2.92 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 4H, -CH(CH₃)₂), 2.31 (s, 12H, terphenyl-CH₃), 2.04 (s, 12H, N=C-CH₃), 1.36 (s, 18H, ^tBu), 1.15 (d, ${}^{3}J_{HH} = 6.8$ Hz, 24H, $-CH(CH_3)_2$). ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz): δ 167.3 (N=C), 161.4 (p-py), 155.7 (o-py), 149.1 (C-N=C), 140.4 (C_{terphenyl}-C_{aniline}), 138.4 (Cterphenyl-Caniline), 136.5 (C-CH(CH₃)₂), 135.9 (terphenyl C-CH₃), 132.1 (C-H_d), 125.7 (C-H_b), 125.5 (C-H_c), 120.2 (C-H_a), 119.3 (*m*-py), 35.4 ($-C(CH_3)_3$), 30.8 ($-C(CH_3)_3$), 28.7 ($-CH_3$) (CH₃)₂), 22.9 (-CH(CH₃)₂), 19.5 (terphenyl-CH₃), 16.9 (N=C-CH₃). MALDI-TOF-TOF (dithranol) (m/z): $[M + H]^+$ calcd for C₇₀H₇₅N₆⁺ 1111.73, found 1111.73. ESI/APCI-TOF HRA-MS (m/ z): calcd for $C_{70}H_{75}N_6^+$ [M + H]⁺ 1111.7300, found 1111.7303. Anal. Calcd for C₇₈H₉₀N₆: C, 84.28; H, 8.16; N, 7.56. Found: C, 81.84; H, 8.10; N, 7.30.

(1)Zn₂Br₄. A vial was charged with ZnBr₂ (67.6 mg, 0.106 mmol, 2 equiv) and THF (5 mL). The suspension was stirred for ca. 5 min, resulting in a pale yellow solution. 1 (50.0 mg, 0.053 mmol, 1 equiv) was added in one portion. The pale yellow suspension was stirred for 16 h at room temperature. The solvent was removed under vacuum, and the solid was suspended in Et₂O (10 mL). The solid was collected on a glass frit and washed with Et₂O (2 × 5 mL) and hexanes (5 mL). The solid was dried under vacuum for 2 days at 100 °C to yield (1)Zn₂Br₄ as a pale yellow solid. Yield: 65.4 mg, 88.6%. The atom-labeling schemes for (1)Zn₂Br₄ for fast and slow PDI exchange are shown in Figures 7 and 8, respectively. ¹H NMR (CD₂Cl₂, 500 MHz, room temperature, intermediate PDI exchange): δ 8.07 (br s, 4H, *m*-py), 7.23 (br s, 16H, H_b, H_c, H_d), 6.65 (br s, 4H,



Figure 7. Atom-labeling scheme for $(1-3)M_2Br_4$ under conditions of fast PDI exchange.



Figure 8. Atom labeling scheme for $(1-3)M_2Br_4$ under conditions of slow PDI exchange.

H_a), 2.31 (br s, 24H, N=C-CH₃, H_e), 1.46 and 1.33 (two br s, total integral 18H, -C(CH₃)₃). ¹H NMR (CD₂Cl₂, 500 MHz, -78 °C, slow PDI exchange): major isomer, δ 8.09 (s, 2H, H_f), 7.83 (s, 2H, H_{f}'), 7.77 (s, 2H, H_{a}), 7.41 (d, J = 7.2 Hz, H_{c}), 7.37 (s, 2H, H_{e}), 7.34 $(d, J = 7.1 \text{ Hz}, H_d), 7.03 (s, 2H, H_e'), 6.96 (t, {}^{3}J = 7.3 \text{ Hz}, H_c'), 6.60 (d, {}^{3}J = 7.5 \text{ Hz}, 2H, H_b'), 6.56, {}^{3}J = 6.8 \text{ Hz}, 2H, H_b), 6.48 (d, {}^{3}J = 7.3 \text{ Hz}, 2H, H_b')$ Hz, H_{d}'), 6.42 (s, 2H, H_{a}'); minor isomer, δ 8.15 (s, 2H, H_{f}), 7.97 (s, 2H, H_f'), 7.77 (s, 2H, H_a, coincident with major isomer), 7.29 (s, 2H, $H_{e'}$), 7.13 (s, 2H, $H_{e'}$), 6.32 (s, 2H, $H_{a'}$). By COSY, the rest of the aromatic resonances for the minor isomer overlap with those of the major isomer at δ 7.77, 7.41, 6.96, and 6.60. The terphenyl-Me, imine-Me, and ^tBu resonances for the major and minor isomers are overlapped: δ 2.54 (s, 6H), 2.52 (s, 3H), 2.39 (s, 14H), 2.20 (s, 8H), 2.00 (s, 6H), 1.38 (s, 14H, ^tBu), 1.34 (s, 5H, ^tBu), 1.31 (s, 11H, ^tBu). ¹H NMR ($C_2D_2Cl_4$, 400 MHz, 100 °C, fast PDI exchange): δ 8.09 (s, 4H, m-py), 7.25 and 7.00 (overlapping br s, total integral 20 H, H_a, H_b, H_c. H_d, and H_e), 2.37 (br s, 12 H, H_e), 2.33 (br s, 12H, N=C- CH_3), 1.54 (s, total integral 18H, $-\tilde{C}(CH_3)_3$). ¹³ $C{^1H}$ NMR (CD₂Cl₂, 126 MHz): δ 163.7 (br s, N=C-CH₃). 148.7 (br s), 146.9 (br s), 142.5 (br s), 137.8 (br s), 137.3 (br s), 136.7 (br s), 132.2 (br s, C-H_e), 128.9 (br s, C-H_b, C-H_c, or C-H_d), 128.1 (br s, C-H_b, C-H_c, or C-H_d), 127.2 (br s, C-H_b, C-H_c, or C-H_d), 125.5 (br s), 124.0 (br s, m-py), 123.6 (br s, m-py), 118.9 (br s, C-H_a), 36.6 (br s, $(-C(CH_3)_3)$, 30.6 $(-C(CH_3)_3)$, 19.6 (terphenyl-CH₃), 17.8 (N= C-CH₃). A total of 16 ¹³C resonances are expected for (1)Zn₂Br₄ assuming fast exchange. A total of 19 are observed, which is due to the slower NMR time scale of ¹³C versus ¹H. MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for $C_{66}H_{66}N_6Zn_2Br_3^+$ 1313.14, found 1313.14. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^{-1}$ calcd for $C_{66}H_{66}N_6Zn_2Cl_3^+$ 1179.2956, found 1179.2981; $\lceil M - 3Br + 1179.2981 \rceil$ 2Cl]⁺ calcd for C₆₆H₆₆N₆Zn₂BrCl₂⁺ 1223.2451, found 1223.2467. Anal. Calcd for C666H66N6Zn2Br4: C, 56.88; H, 4.77; N, 6.03. Found: C, 55.98; H, 5.06; N, 6.01.

(1) Co_2Br_4 . A vial was charged with $CoBr_2$ (23.2 mg, 0.106 mmol, 2 equiv) and THF (5 mL). The suspension was stirred for ca. 5 min, resulting in a blue solution. 1 (50.0 mg, 0.053 mmol, 1 equiv) was added in one portion, resulting in a brown solution. The mixture was stirred for 16 h. Et₂O (10 mL) was added to the brown suspension, and the mixture was stirred for ca. 5 min. The suspension was filtered through a sintered-glass frit, and the brown solid was washed with Et_2O (2 × 5 mL) and hexanes (5 mL) and dried under vacuum overnight to yield $(1)Co_2Br_4$ as a pale brown solid. Yield: 60.2 mg, 82.2%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 119.2 ($v_{1/2}$ = 1000 Hz), 97.0 $(v_{1/2} = 1000 \text{ Hz}), 17.2 (v_{1/2} = 2000 \text{ Hz}), 5.2 (v_{1/2} = 80 \text{ Hz}), 3.8 (v_{1/2} = 2000 \text{ Hz}), 5.2 (v_{1/2} = 2000 \text{ Hz}), 3.8 (v_{1/2} = 2000 \text{ Hz}), 5.2 (v_{1/2} = 2000 \text{ Hz}), 3.8 (v_{1/2} = 2000 \text{ Hz}), 5.2 (v_{1/2} = 2000$ = 30 Hz), 2.1 ($v_{1/2}$ = 30 Hz), 1.9 ($v_{1/2}$ = 20 Hz), 1.3 ($v_{1/2}$ = 30 Hz), 0.9 ($v_{1/2}$ = 30 Hz), 0.1 ($v_{1/2}$ = 200 Hz), -17.7 ($v_{1/2}$ = 1000 Hz), -20.1 ($v_{1/2} = 1000$ Hz), -42.7 ($v_{1/2} = 1000$ Hz), -55.4 ($v_{1/2} = 1000$ Hz), -85.6 ($v_{1/2}$ = 1000 Hz). MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for $C_{66}H_{66}N_6Co_2Br_3^+$ 1301.15, found 1301.15. ESI/ APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for $C_{66}H_{66}N_6Co_2Cl_3^+$ 1167.3064, found 1167.3084; $[M - 3Br + 2Cl]^+$ calcd for $C_{66}H_{66}N_6Co_2BrCl_2^+$ 1211.2556, found 1211.2572; [M - 2Br

+ Cl]⁺ calcd for $C_{66}H_{66}N_6Co_2Br_2Cl^+$ 1255.2050, found 1255.2034. Anal. Calcd for $C_{66}H_{66}N_6Co_2Br_4$: C, 57.41; H, 4.82; N, 6.09. Found: C, 54.33; H, 5.33; N, 5.93. μ_{eff} (Evans method): 7.8(7) μ_B .

(1) Fe_2Br_4 . A vial was charged with $FeBr_2$ (22.9 mg, 0.106 mmol, 2 equiv) and THF (10 mL). The suspension was stirred for 5 min, resulting in a yellow solution. 1 (50.0 mg, 0.053 mmol, 1 equiv) was added in one portion. The dark blue solution was stirred for 16 h. Et₂O (10 mL) was added, and the mixture was stirred for ca. 5 min. The blue suspension was filtered through a sintered-glass frit, and the solid was washed with Et_2O (2 × 5 mL) and hexanes (5 mL) and dried under vacuum overnight to yield (1)Fe₂Br₄ as a dark blue solid. Yield: 54.1 mg, 74.2%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 11.3 ($v_{1/2}$ = 140 Hz), 6.0 ($v_{1/2}$ = 630 Hz), 3.7 ($v_{1/2}$ = 19.1), 2.2 ($v_{1/2}$ = 50 Hz), 1.2 $(v_{1/2} = 160 \text{ Hz})$, $-15.1 (v_{1/2} = 82 \text{ Hz})$, $-21.7 (v_{1/2} = 340 \text{ Hz})$. MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for C66H66N6Fe2Br3+ 1295.16, found 1295.16. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for C₆₆H₆₆N₆Fe₂Cl₃⁺ 1161.3103; found 1161.3108. Anal. Calcd for C666H66N6Fe2Br4: C, 57.67; H, 4.84; N, 6.11. Found: C, 51.76; H, 5.06; N, 5.08. μ_{eff} (Evans method): 8.4(7) $\mu_{\rm B}$.

(2)Zn₂Br₄. A vial was charged with ZnBr₂ (67.6 mg, 0.300 mmol, 2 equiv) and THF (10 mL). The suspension was stirred for ca. 5 min, resulting in a pale yellow solution. 2 (150.0 mg, 0.150 mmol, 1 equiv) was added in one portion. The yellow solution was stirred for 16 h. Et₂O (10 mL) was added, and the mixture was stirred for ca. 5 min. The suspension was filtered through a sintered-glass frit, and the yellow solid was washed with Et_2O (3 × 10 mL) and hexanes (10 mL) and dried under vacuum for 2 days at 100 °C to yield (2)Zn₂Br₄ as a yellow solid. Yield: 181.6 mg, 83.0%. The atom-labeling scheme for (2)Zn₂Br₄ is shown in Figure 8. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.16 (s, 2H, H_f), 7.96 (s, 2H, H_f'), 7.36 (s, 2H, H_e'), 7.27 (m, 6 H, $H_{a'}H_{c'}$, $H_{d'}$), 7.01 (s, 2H, H_{e}), 6.85 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 2H, H_{c}), 6.50 $(dd, {}^{3}J_{HH} = 7.8 Hz, {}^{4}J_{HH} = 1.2 Hz, 2H, H_{d}), 6.42 (s, 2H, H_{a}'), 2.36 (s, 2H, H_{a}'), 2$ 6H, N=C-CH₃), 2.31 (s, 6H, terphenyl-Me'), 2.24 (s, 6H, terphenyl-Me), 2.19 (s, 6H, Me_b'), 2.04 (s, 6H, Me_b), 2.03 (s, 6H, N=C-CH₃'), 1.49 (s, 9H, 'Bu), 1.44 (s, 9H, 'Bu'). $^{13}C{^{1}H}$ NMR $(CD_2Cl_2, 126 \text{ MHz}): \delta 164.2 \text{ (N=C')}, 163.6 \text{ (N=C)}, 149.0, 148.1,$ 146.4, 145.6, 141.2, 138.5, 137.6, 137.4, 136.7, 136.0, 132.1 (C-H_e), 132.0 (C-H_e'), 130.4 (C-H_a or C-H_c'' or C-H_d'), 129.6 (C- H_b), 127.6 (C-H_d), 126.6, 126.1 (C-H_a' overlapped with C-H_a or C-H_c' or C-H_d'), 125.2, 123.9 (C-H_a or C-H_c' or C-H_d'), 123.6 (C-H_f and C-H_f'), 36.5 $(-C(CH_3)_3)$, 36.2 $(-C(CH_3)_3')$, 30.60 $(-C(CH_3)_3)$, 30.58 $(-C(CH_3)_3')$ 19.5 (terphenyl-CH₃'), 19.4 (terphenyl-CH₃), 18.4 (Me_b'), 17.9 (Me_b), 17.8 (N=C-CH₃'), 17.4 (N=C-CH₃). In total, 32 resonances are observed in ¹³C{¹H} NMR and 36 are expected. On the basis of the expected chemical shift, the 4 missing resonances correspond to the two sets of o-py and p-py quaternary carbons. This is due to a low signal in ${}^{13}C{}^{1}H$ NMR due to the poor solubility of (2) Zn_2Br_4 in $C_2D_2Cl_4$. MALDI-TOF-TOF (dithranol) (m/z): [M – $Br]^{+}$ calcd for $C_{70}H_{74}N_{6}Zn_{2}Br_{3}^{+}$ 1369.21; found 1369.20. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for $C_{70}H_{74}N_6Zn_2Cl_3^+$ 1235.3584, found 1235.3634. Anal. Calcd for C70H74N6Zn2Br4: C, 57.99; H, 5.15; N, 5.80. Found: C, 56.68; H, 5.06; N, 5.71.

(2)Co₂Br₄. This compound was synthesized by the procedure for (1)Co₂Br₄ using CoBr₂ (65.6 mg, 0.300 mmol, 2 equiv), 2 (150.0 mg, 0.150 mmol, 1 equiv), and THF (10 mL) The crude brown solid was washed with Et_2O (3 × 10 mL) and hexanes (10 mL) and dried under vacuum overnight to yield $(2)Co_2Br_4$ as a pale brown solid. Yield: 187.4 mg, 87.0%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 108.6 ($v_{1/2}$ = 200 Hz), 104.5 ($v_{1/2}$ = 130 Hz), 20.5 ($v_{1/2}$ = 71 Hz), 13.5 ($v_{1/2}$ = 61 Hz), 12.0 ($v_{1/2} = 100 \text{ Hz}$), 7.2 ($v_{1/2} = 71 \text{ Hz}$), 5.9 ($v_{1/2} = 130 \text{ Hz}$), -2.0 $(v_{1/2} = 56 \text{ Hz}), -4.8 (v_{1/2} = 71 \text{ Hz}), -5.9 (v_{1/2} = 59 \text{ Hz}), -7.6 (v_{1/2} = 50 \text{ Hz})$ = 110 Hz), -10.0 ($v_{1/2}$ = 59 Hz), -20.0 ($v_{1/2}$ = 210 Hz), -23.2 ($v_{1/2}$ = 93 Hz), -28.6 ($v_{1/2}$ = 190 Hz), -73.1 ($v_{1/2}$ = 300 Hz). MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for $C_{70}H_{74}N_6Co_2Br_3^+$ 1357.22; found 1357.21. ESI/APCI-TOF HRA-MS (*m*/*z*): [M - 4Br + 3Cl]⁺ calcd for C₇₀H₇₄N₆Co₂Cl₃⁺ 1223.3692, found 1223.3702; [M - 3Br + 2Cl]⁺ calcd for C₇₀H₇₄N₆Co₂BrCl₂⁺ 1267.3184, found 1267.3164. Anal. Calcd for C70H74N6C02Br4: C, 58.51; H, 5.21; N, 5.87. Found: C, 57.85; H, 5.12; N, 5.86.

(2)Fe₂Br₄. This compound wassynthesized by the procedure for (1)Fe₂Br₄ using FeBr₂ (64.7 mg, 0.300 mmol, 2 equiv), 2 (150.0 mg, 0.150 mmol, 1 equiv), and THF (10 mL). The crude blue solid was washed with Et₂O $(3 \times 10 \text{ mL})$ and hexanes (10 mL) and dried under vacuum overnight to yield (2)Fe₂Br₄ as a dark blue solid. Yield: 154.3 mg, 72.0%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 79.0 ($v_{1/2}$ = 69 Hz), 75.0 ($v_{1/2}$ = 59 Hz), 12.5 ($v_{1/2}$ = 29 Hz), 11.6 ($v_{1/2}$ = 29 Hz), 9.8 $(v_{1/2} = 100 \text{ Hz})$, 8.3 $(v_{1/2} = 37 \text{ Hz})$, 8.0 $(v_{1/2} = 53 \text{ Hz})$, 7.8 $(v_{1/2} = 100 \text{ Hz})$ 100 Hz), 5.0 ($v_{1/2}$ = 24 Hz), 4.0 ($v_{1/2}$ = 20 Hz), 0.6 ($v_{1/2}$ = 24 Hz), $-1.43 (v_{1/2} = 36 \text{ Hz}), -8.3 (v_{1/2} = 250 \text{ Hz}), -12.3 (v_{1/2} = 29 \text{ Hz}),$ $-17.6 (v_{1/2} = 32 \text{ Hz}), -23.2 (v_{1/2} = 70 \text{ Hz}), -25.8 (v_{1/2} = 76 \text{ Hz}).$ MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for C₇₀H₇₄N₆Fe₂Br₃⁺ 1351.22; found 1351.19. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for $C_{70}H_{74}N_6Fe_2Cl_3^+$ 1217.3731, found 1217.3750. Anal. Calcd for C₇₀H₇₄N₆Fe₂Br₄: C, 58.77; H, 5.21; N, 5.87. Found: C, 58.05; H, 5.31; N, 5.68.

(3)Zn₂Br₄. This compound was synthesized by the procedure for (2)Zn₂Br₄ using ZnBr₂ (60.8 mg, 0.270 mmol, 2 equiv), 3 (150.0 mg, 0.135 mmol, 1 equiv), and THF (10 mL). The crude solid was washed with Et₂O $(3 \times 10 \text{ mL})$ and hexanes (10 mL) and dried under vacuum for 2 days at 100 °C to yield (3)Zn₂Br₄ as a bright yellow solid. Yield: 157.1 mg, 74.5%. The atom-labeling scheme for (3)Zn₂Br₄ is shown in Figure 8. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.23 (s, 2H), 8.01 (br s, 2H), 7.44 (br s, 4H), 7.35 (s, 3H), 7.06 (d, ${}^{3}J_{HH} = 7.9$ Hz, 3H), 6.94 (br s, 2H), 6.71 (br s, 2H), 6.34 (br s, 2H), 2.89 (br s, 2H), 2.47 (s, 6H), 2.29 (s, 6H), 2.23 (s, 8H), 2.12 (br s, 4H), 1.52 (s, 9H), 1.43 (s, 9H), 1.18 (m, 24H). ¹H NMR (C₂D₂Cl₄, 500 MHz, 100 °C): δ 8.30 (s, 2H, H_f), 8.08 (s, 2H, H_f'), 7.57 (d, ³J_{HH} = 8.0 Hz, 2H, H_c), 7.49 (d, ${}^{3}J_{HH}$ = 8.0 Hz, 2H, H_d), 7.39 (s, 2H, H_a), 7.34 (s, 2H, H_e), 7.11 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 2H, H_c'), 6.99 (s, 2H, H_e'), 6.85 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 2H, H_d'), 6.33 (s, 2H, H_a'), 2.75 (br s, 4H, $-CH(CH_3)_2$, 2.54 (s, 6H, N=C-CH₃), 2.36 (s, 6H, Me_b), 2.31 (s, 6H, Me_b'), 2.24 (s, 6H, N=C-CH₃'), 1.63 (s, 9H, ^tBu), 1.52 (s, 9H, ^tBu'), 1.27 (m, 24H, -CH(CH₃)₂). ¹³C{¹H} NMR (C₂D₂Cl₄, 500 MHz, 100 °C): δ 164.4 (C-H_f), 148.6, 148.0, 144.3, 142.6, 140.8, 138.6, 137.0, 136.3, 136.2, 136.0, 135.7, 135.5, 132.4 (C-He'), 132.0 (C-H_a), 128.0 (C-H_d'), 127.4 (C-H_d), 126.9 (C-H_c), 124.9 (C-H_c'), 123.5 (C-H_e'), 123.2 (C-H_e), 36.3 ($-C(CH_3)_3$), 36.1 ($-C(CH_3)_3$ '), 30.4 (-C(CH₃)₃), 30.2 (-C(CH₃)₃'), 27.6 (-CH(CH₃)₂), 27.4 $(-CH(CH_3)_2)$, 24.9 $(-CH(CH_3)_2)$, 24.4 $(-CH(CH_3)_2')$, 23.6 $(-CH(CH_3)_2)$, 23.4 $(-CH(CH_3)_2')$, 18.83 (Me¹), 18.80 (Me¹'), 17.84 (Me²), 17.80 (Me²). In total, 35 resonances are observed by $^{13}C{^{1}H}$ NMR and 38 resonances are expected. One N=C resonance is not observed. The other missing resonances correspond to the substituted aromatic carbons: $C_{\text{terphenyl}}$ - C_{aniline} , $C_{\text{terphenyl}}$ - C_{aniline} , and/or *o*-py and/or *p*-py. This is due to a low signal in ¹³C{¹H} MMR due to the poor solubility of $(3)Zn_2Br_4$ in $C_2D_2Cl_4$. MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for $C_{78}H_{90}N_6Zn_2Br_3^+$ 1481.33; found 1481.33. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for C₇₈H₉₀N₆Zn₂Cl₃⁺ 1347.4839, found 1347.4892; [M - 3Br + 2Cl]⁺ calcd for C₇₈H₉₀N₆Zn₂BrCl₂⁺ 1393.4320, found 1393.4376. Anal. Calcd for C₇₈H₉₀N₆Zn₂Br₄: C, 59.98; H, 5.81; N, 5.38. Found: C, 51.50; H, 5.46; N, 4.48.

(3) Co_2Br_4 . This compound was synthesized by the procedure used for (1)Co₂Br₄ using CoBr₂ (59.1 mg, 0.270 mmol, 2 equiv), 3 (150.0 mg, 0.270 mmol, 1 equiv), and THF (10 mL). The crude solid was washed with Et₂O (3 \times 10 mL) and hexanes (10 mL), and dried under vacuum overnight to yield $(3)Co_2Br_4$ as a pale brown solid. Yield: 170.1 mg, 81.3%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 119.0 ($v_{1/2}$ = 170 Hz), 108.7 ($v_{1/2}$ = 100 Hz), 18.2 ($v_{1/2}$ = 110 Hz), 16.4 ($v_{1/2}$ = 72 Hz), 14.8 ($v_{1/2}$ = 30 Hz), 14.4 ($v_{1/2}$ = 70 Hz), 6.6 ($v_{1/2}$ = 90 Hz), 4.0 ($v_{1/2}$ = 34 Hz), 0.93 ($v_{1/2}$ = 77 Hz), -5.0 ($v_{1/2}$ = 42 Hz), -5.1 $(v_{1/2} = 32 \text{ Hz}), -5.5 (v_{1/2} = 30 \text{ Hz}), -14.0 (v_{1/2} = 60 \text{ Hz}), -14.1$ $(v_{1/2} = 31 \text{ Hz}), -19.8 (v_{1/2} = 30 \text{ Hz}), -23.0 (v_{1/2} = 130 \text{ Hz}), -28.1$ $(v_{1/2} = 290 \text{ Hz}), -30.2 (v_{1/2} = 160 \text{ Hz}), -49.7 (v_{1/2} = 290 \text{ Hz}),$ $-63.1 (v_{1/2} = 270 \text{ Hz}), -87.9 (v_{1/2} = 290 \text{ Hz}).$ MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for $C_{78}H_{90}N_6Co_2Br_3^+$ 1469.34; found 1469.33. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for C₇₈H₉₀N₆Co₂Cl₃⁺ 1335.4948, found 1335.4988. Anal. Calcd

for $C_{78}H_{90}N_6Co_2Br_4$: C, 60.48; H, 5.86; N, 5.43. Found: C, 66.47; H, 6.58; N, 5.90. μ_{eff} (Evans method): 7.9(8) μ_B .

(3)Fe₂Br₄. This compound was synthesized by the procedure for (1)Fe₂Br₄ using FeBr₂ (58.2 mg, 0.270 mmol, 2 equiv), 3 (150.0 mg, 0.135 mmol, 1 equiv), and THF (10 mL). The crude blue solid was washed with $Et_2O(3 \times 10 \text{ mL})$ and hexanes (10 mL) and dried under vacuum overnight to yield (3)Fe2Br4 as a dark blue solid. Yield: 153.8 mg, 73.8%. ¹H NMR (CD₂Cl₂, 500 MHz): δ 76.8 ($v_{1/2}$ = 130 Hz), 74.7 ($v_{1/2}$ = 190 Hz), 13.8 ($v_{1/2}$ = 150 Hz), 12.2 ($v_{1/2}$ = 96 Hz), 7.0 $(v_{1/2} = 180 \text{ Hz}), 5.3 (v_{1/2} = 130 \text{ Hz}), 4.3 (v_{1/2} = 150 \text{ Hz}), 2.7 (v_{1/2} = 120 \text{ Hz}), 2.7$ 80 Hz), 1.6 ($v_{1/2}$ = 49 Hz), -0.2 ($v_{1/2}$ = 80 Hz), -2.9 ($v_{1/2}$ = 140 Hz), $-5.2 (v_{1/2} = 160 \text{ Hz})$, $-10.1 (v_{1/2} = 100 \text{ Hz})$, $-16.4 (v_{1/2} = 490 \text{ Hz})$ Hz), $-17.2 (v_{1/2} = 110 \text{ Hz})$, $-17.3 (v_{1/2} = 280 \text{ Hz})$, $-18.7 (v_{1/2} = 280 \text{ Hz})$ 240 Hz), 18.9 ($v_{1/2}$ = 240 Hz), -24.4 ($v_{1/2}$ = 290 Hz), -28.7 ($v_{1/2}$ = 190 Hz). MALDI-TOF-TOF (dithranol) (m/z): $[M - Br]^+$ calcd for C₇₈H₉₀N₆Fe₂Br₃⁺ 1463.35; found 1463.34. ESI/APCI-TOF HRA-MS (m/z): $[M - 4Br + 3Cl]^+$ calcd for $C_{78}H_{90}N_6Fe_2Cl_3^+$ 1329.4987, found 1329.5024. Anal. Calcd for C78H90N6Fe2Br4: C, 60.72; H, 5.88; N, 5.45. Found: C, 58.63; H, 5.69; N, 5.50. μ_{eff} (Evans method): $8.9(5) \mu_{\rm B}$

Low-Pressure Ethylene Oligomerization. Ethylene oligomerization/polymerization reactions at 2 bar were performed in a 200 mL Fischer-Porter bottle equipped with a 2 in. long Teflon-coated magnetic stir bar and a stainless-steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, a safety check valve, and a pressure gauge. In a N2-filled glovebox, the Fischer-Porter bottle was charged with PhMe (46.5 mL) and a catalyst stock suspension in PhMe (1.0 mL). The apparatus was removed from the glovebox, connected to a stainless-steel doublemanifold vacuum/ethylene line, placed in a room-temperature water bath, and stirred at 370 rpm. The N₂ atmosphere was replaced with ethylene by three evacuation-refill cycles. The solution was equilibrated at 2 bar of ethylene pressure for 15 min. A stock solution of the appropriate Al activator in PhMe (2.5 mL) was added via a gastight syringe. The ethylene pressure was kept constant by feeding ethylene on demand. Ethylene consumption was measured using a Brooks Instruments 5860i Mass Flow Sensor. The total ethylene consumption was determined by numerical integration of the mass flow curve using the LabView software package. After 30 min, the ethylene line was closed, the Fischer-Porter bottle was vented, and MeOH (50 mL) was added to quench the reaction. o-Xylene (100 μ L) was added as an internal standard, and the solution was analyzed by GC-MS using an Aglient 6890/5973N GC-MS instrument. The masses of the oligomers were determined by GC-MS using predetermined response factors.

High-Pressure Ethylene Polymerization Reactions. Ethylene polymerizations at 20 bar were performed using a stainless-steel Parr 300 mL autoclave, which was equipped with a magnetically driven 1.5 in. diameter four-blade propeller stirrer, thermocouple, water cooling loop, and a Parr 4842 controller. In a N2 glovebox, a 200 mL glass autoclave liner was charged with PhMe (39.0 mL) and a stock suspension of the catalyst in PhMe (1.0 mL) and placed in the autoclave. The autoclave was sealed, removed from the glovebox, and attached to the ethylene line. A stock solution of the appropriate Al activator in PhMe (2.5 mL) was transferred to a 10 mL stainless-steel injection port and diluted with PhMe (7.5 mL). The mixture was stirred (400 rpm), pressurized to 15 bar of ethylene, and stirred at the desired reaction temperature for 15 min. The injection line was attached, and the activator solution was injected at 20 bar. The ethylene pressure was kept constant by feeding ethylene on demand. After 30 min the ethylene line was closed, and the autoclave was vented. Methanol (50 mL) was added to precipitate the polymer, which was characterized as described below.

Polymer Analysis. DSC measurements were performed on a TA Instruments 2920 differential scanning calorimeter. Samples (5 mg) were annealed by heating to 250 °C at 15 C/min, cooled to 0 °C at 10 °C/min, and analyzed by heating to 250 °C at 15 °C/min. ¹H and ¹³C{¹H} NMR spectra of PE samples were obtained at 100 °C in dry degassed CDCl₂CDCl₂ solvent using a Bruker Advance 500 NMR instrument. ¹³C{¹H} NMR spectra of PE samples were internally

referenced to the main-chain CH₂ resonance at δ 30.0. Gel permeation chromatography (GPC) was performed on a Polymer Laboratories PL-GPC 200 instrument at 150 °C with 1,2,4-trichlorobenzene (stabilized with 125 ppm of BHT) as the mobile phase. Three PLgel 10 μ m Mixed-B LS columns were used. The molecular weights were calibrated using narrow polystyrene standards with a 10-point calibration of M_n from 570 Da to 5670 kDa and were corrected for linear polyethylene by universal calibration by using the following Mark–Houwink parameters: polystyrene, $K = 1.75 \times 10-2$ cm³ g⁻¹, $\alpha = 0.67$; polyethylene, $K = 5.90 \times 10^{-2}$ cm³ g⁻¹, $\alpha = 0.69$.⁷²

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00211.

NMR and mass spectra for compounds, GPC and NMR of polymers, and X-ray crystallography details (PDF)

Accession Codes

CCDC 1991375–1991379 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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(43) A total of 18 and 22 resonances are respectively expected in the ¹H NMR spectra of (2)M₂Br₄ and (3)M₂Br₄ for *C_s*-symmetric structures under conditions of slow exchange of the (PDI)M units. Sixteen and seventeen ¹H resonances are observed for (2)Co₂Br₄ and (2)Fe₂Br₄, respectively. The unobserved resonances are most likely broadened into the baseline. The¹H NMR spectrum of (3)Co₂Br₄ contains the expected 22 resonances. The¹H NMR spectrum of (3) Fe₂Br₄ contains 20 resonances due to overlapping of several resonances at δ –17.2 and 18.7.

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