Inorganic Chemistry

Rare-Earth Metal Complexes Supported by Polydentate Phenoxy-Type Ligand Platforms: C–H Activation Reactivity and CO₂/Epoxide Copolymerization Catalysis

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incorporating polydentate bis(imino)phenoxy {N²O}⁻ and bis-(amido)phenoxy {N²O}³⁻ ligands were synthesized by alkane elimination reactions from the tris(alkyl) $M(CH_2SiMe_3)_3(THF)_2$ and $M(CH_2C_6H_4$ -o-NMe₂)₃ (M = Sc, Y) precursors. Complex **1a**-Y was used for the selective C–H activation of 2-phenylpyridine at the 2'-phenyl position affording the corresponding bis(aryl) product **3a-Y**, which was found to be reacted reluctantly with



weak electrophiles (styrene, imines, hydrosilanes). The mechanism of formation of **3a-Y** was established by DFT calculations, which also corroborated high stability of the complex toward insertion of styrene, apparently stemming from the inability to form the corresponding adduct. Copolymerization of cyclohexene oxide and CO₂ promoted by **1a-Y** (0.1–0.5 mol %) was demonstrated to proceed under mild conditions (toluene, 70 °C, $P_{CO2} = 12$ bar) giving polycarbonates with high efficiency (maximal TON of 460) and selectivity (97–99% of carbonate units).

INTRODUCTION

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Phenolate-based ligand platforms constitute a strong and convenient alternative to cyclopentadienyl-type ligands for the modern coordination chemistry of the early transition metals, largely thanks to their remarkable tunability allowing diverse sterico-electronic variations.¹ In particular, these hard, electronegative π -donor ligands are attractive because they offer strong metal-oxygen bonds that are expected to stabilize complexes of highly oxophilic and electropositive metals (e.g., Group 3 metals).² Rare-earth metal alkyl complexes have shown great utility in many 100% atom-economy catalytic reactions involving heteroatom-containing substrates, such as C-H activation/functionalization of anilines, anisoles, amines, and heterocycles,^{3,4} (co)polymerization of polar monomers (lactones, carbonates, epoxides),⁵ and activation of CO_2 .^{6,7} As such, there is continued interest in designing better performing and more stable catalysts that also exhibit improved functional group tolerance.

Herein we report the synthesis and characterization of group 3 metal complexes supported by bulky multidentate bis-(imino)phenolate and bis(anilino)phenolate ligand systems (Scheme 1). The multidentate nature and high coordination abilities of these ligand platforms have initially been anticipated as beneficial for the preparation of dinuclear complexes or formation of dinuclear intermediates in catalytic processes. Special emphasis has been placed on (i) studies of the coordination chemistry of this ligand systems with scandium and yttrium, starting from tris(carbyl) precursors $LnR_3(THF)_{xy}$ in order to achieve selective synthesis of the corresponding





alkyl complexes; (ii) evaluation of potential of the titled alkyl complexes as precatalysts of C–H activation of 2-phenylpyridine and hydroarylation of styrene; (iii) stoichiometric reactions between alkyl complexes and 2-phenylpyridine mimicking the C–H activation step; (iv) evaluation of the efficacy of some complexes obtained during this study in copolymerization reactions of CO_2 with cyclohexene oxide (CHO).

RESULTS AND DISCUSSION

Synthesis of Rare-Earth Metal Complexes Derived from Proligands {N²O}H (1a-H) and {N²O}H₃ (1b-H₃). The

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Scheme 2. Formation of Complexes 1a-M (M = Sc, Y) and 1a-Sc'



proligands, bis(imino)phenol **1a-H** and bis(anilino)phenol **1b-** H_3 , were prepared in good yields (29–60%) using the protocols reported in the literature.⁸ To study the coordination ability of these ligand platforms with group 3 metals (Sc, Y), σ -bond metathesis reactions between the corresponding proligands and metal tris(alkyls) MR₃(THF)₂ were investigated.

The reaction between 1a-H and 1 equiv of Sc- $(CH_2SiMe_3)_3(THF)_2$ in C_6D_6 (Scheme 2), monitored by ¹H NMR spectroscopy, proceeded readily in the -25 to 25 °C range, completely consuming both reagents. However, the final ¹H NMR spectrum (Figure S4) showed two series of resonances corresponding to two different products, monoligand bis(alkyl) 1a-Sc and bis(ligand) monoalkyl 1a-Sc' in a respective \sim 1:0.3 ratio. This observation is in line with that by Piers et al. describing the preferential formation of a related bis(phenoxy-imino) scandium monoalkyl complex { η^2 -1- $[CH=N-Ar]-2-O-3-tBu-C_6H_3\}_2ScCH_2SiMe_3$ (I-Sc) along with small amounts of the monoligand bis(alkyl) congener in the reaction between the equimolar amounts of the corresponding proligand and Sc(CH₂SiMe₃)₃(THF)₂.⁹ In our case, the increased steric bulk of $\{1a\}^-$ contributes to a better stabilization of the monoligand bis(alkyl) species.

More comprehensive NMR data $({}^{13}C{}^{1}H{}^{1}, {}^{1}H{}^{-1}H COSY)$ were collected for this sample that allowed understanding of the solution structures of both products and making assignments of characteristic resonances. For example, for 1a-Sc, the key resonances in the room-temperature ${}^{1}H$ and ${}^{13}C{}^{1}H$ NMR spectra (Figures S4 and S7, respectively) include (a) two broad signals from the two CH=N groups ($\delta_{\rm H}$ 9.20, 8.16 ppm and $\delta_{\rm C}$ 172.5, 158.6 ppm, respectively), (b) two broad signals from the C₆H₂ moiety ($\delta_{\rm H}$ 9.02, 7.35 ppm and $\delta_{\rm C}$ 131.6, 135.2 ppm, respectively), (c) one resonance for the $ScCH_2$ groups $(\delta_{\rm H}$ –0.01 ppm and $\delta_{\rm C}$ 40.4 ppm, respectively), (d) singlet resonance for the SiMe₃ groups ($\delta_{\rm H}$ 0.08 ppm and $\delta_{\rm C}$ 3.3 ppm, respectively). For 1a-Sc', similar key resonances include (a) two sharp signals from the two pairs of the equivalent coordinated and noncoordinated CH=N groups ($\delta_{\rm H}$ 7.93, 7.45 ppm and $\delta_{\rm C}$ 172.5, 156.8 ppm, respectively), (b) two sharp signals from the nonequivalent protons of the two C₆H₂ moieties ($\delta_{\rm H}$ 8.90, 7.19 ppm and $\delta_{\rm C}$ 132.3, 134.8 ppm, respectively), (c) in the ¹H NMR spectrum, two doublets from the diastereotopic ScCHH protons ($\delta_{\rm H}$ 0.67 and -0.25 ppm) and a tiny singlet ($\delta_{\rm C}$ 42.9 ppm) in the ¹³C{¹H} NMR spectrum, (d) singlet resonance for the SiMe₃ groups ($\delta_{\rm H}$ 0.00 ppm and $\delta_{\rm C}$ –0.4 ppm, respectively). Upon increasing the temperature to 72 °C (Figure S5), both products appeared to be stable in solution, and no significant change in the pattern of signals was observed for 1a-Sc'. On the other hand, for 1a**Sc**, substantial broadening was observed for the signals in the aromatic region; thus, suggesting the existence of some fluxional dynamic process probably related to the exchange between the coordinated and pending imino functions.¹⁰ A small amount (15% yield) of pure complex **1a-Sc** was isolated by recrystallization and characterized by X-ray crystallography (vide infra).

Similar NMR scale reaction between 1a-H and 1 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ in C_6D_6 afforded **1a-Y** quantitatively as judged by ¹H NMR spectroscopy. Thus, the scaled-up synthesis was repeated allowing isolation of pure 1a-Y in 67% yield after recrystallization (Scheme 2). Complex 1a-Y was characterized by ¹H and ¹³C NMR spectroscopy and X-ray crystallography. For this compound, a complex fluxional behavior in solution was observed over a broad temperature range. For example, the room-temperature ¹H NMR spectrum of 1a-Y (Figure S8) exhibited a series of broadened signals, only a few of them could be unequivocally assigned: very broad signals at $\delta_{\rm H}$ 9.00–7.50 ppm from the CH=N and C₆H₂ groups, broad multiplet at $\delta_{\rm H}$ 3.18 ppm from the CH(CH₃)₂ protons and singlets at $\delta_{\rm H}$ 0.12 and -0.71 ppm from the $Si(CH_3)_3$ and CH_2 protons, respectively, of the Y-CH₂Si- $(CH_3)_3$ groups. Upon lowering temperature to -40 °C (Figure S9), the broad signals in the aromatic regions split into two pairs of broad singlets, while the resonance from the CH_2 protons in the high-field split into a series of three broad signals. Although more detailed information about the solution structure of 1a-Y could not be obtained, these observations are consistent with the existence of the same exchange processes as those depicted for 1a-Sc and I-Sc.⁹

The molecular structures of 1a-Sc (Figure S1) and 1a-Y (Figure 1) are comparable to those of the penta-coordinate $\{\eta^2 - 1 - [CH = N - Ar] - 2 - O - 3 - tBu - C_6H_3\}Y(CH_2SiMe_3)_2(THF)$ and six-coordinate $\{\eta^2-1-[CH=N-Ar]-2-O-3-tBu-C_6H_3\}Y$ $(CH_2SiMe_3)_2(THF)_2$ complexes, respectively, reported previously.9 Thus, the respective distorted trigonal-bipyramidal and octahedral coordination environments around the metal centers are perfectly reproduced in the structures of 1a-Sc and **1a-Y.** In **1a-Y**, the Y-C(carbyl) and Y-N(1) bond lengths (2.423(2), 2.438(2), and 2.5159(18) Å, respectively) are in the range of those observed in the two yttrium complexes (2.398-2.440 and 2.466-2.661 Å, respectively),⁹ while the Y-O(1) distance (2.1994(15) Å) is only slightly longer (2.121-2.166 Å). In **1a-Sc**, the same bond lengths (2.2100(16), 2.2333(16),2.0198(11), and 2.3502(13) Å, respectively) are shorter than those in the yttrium congener, which is in line with the decrease of the effective ionic radii of the Sc(3+) metal ion.¹¹

In the attempts to synthesize dinuclear complexes, potentially incorporating two M-(CH₂SiMe₃)_x groups united by one multifunctional {N²O}⁻ ligand scaffold, upon reacting



Figure 1. Molecular structure of $\{N^2O\}Y(CH_2SiMe_3)_2(THF)_2$ (1a-Y) (all hydrogen atoms and 2,6-iPr₂ groups are omitted for clarity; thermal ellipsoids drawn at the 50% probability). Selected bond distances (Å) and angles (deg): Y(1)-O(1), 2.1994(15); Y(1)-O(51), 2.3779(18); Y(1)-N(1), 2.5159(18); Y(1)-C(41), 2.423(2); Y(1)-C(45), 2.438(2); Y(1)-O(61), 2.4637(17); O(51)-Y(1)-N(1), 160.20(6); C(45)-Y(1)-O(61), 86.17(7); C(41)-Y(1)-O(61), 168.96(8).

1a-H with 2 equiv of $M(CH_2SiMe_3)_3(THF)_2$, only the formation of **1a-M** together with the unreacted tris(alkyl) precursor took place, as judged by ¹H NMR spectroscopic studies of the corresponding crude reaction mixtures.

In attempts to synthesize dinuclear complexes, in which two metal centers are linked by a single ligand platform, regular alkane elimination reactions of $1b-H_3$ with the corresponding rare-earth metal precursors $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc, Y) in the corresponding 1:2 ratio were studied. However, only alkyl group-free dinuclear bis(ligand) complexes [1b-M]₂ were isolated (Scheme 3). For instance, monitoring by ¹H NMR spectroscopy of the reaction of $1b-H_3$ with 2 equiv of

Scheme 3. Formation of Complexes [1b-M]₂



 $M(CH_2SiMe_3)_3(THF)_2$ confirmed the quantitative formation of these products, while 1 equiv of the tris(alkyl) precursor remained intact in each case. The larger scale syntheses of complexes [**1b-M**]₂ were optimized by using equimolar amounts of the two reagents. Both compounds were found stable in benzene- d_6 or toluene- d_8 solutions at 60 °C for days.

Both complexes featured fluxional behavior in a broad range of temperatures, apparently associated with a restricted rotation of bulky bis(isopropyl)phenyl groups. The roomtemperature ¹H NMR spectra of [**1b-Sc**]₂ and [**1b-Y**]₂ (Figures S12 and S16, respectively) contained in each case a series of resonances consistent with the average C_2 -symmetry of molecules. For [**1b-Sc**]₂, the four broadened characteristic signals from the two pairs of diastereotopic protons of the CH_2N groups were observed at δ_H 5.29, 4.06, 3.85, and 2.97 ppm in the ¹H NMR spectrum and the corresponding two resonances at δ_C 62.8 and 55.8 ppm in the ¹³C NMR spectrum. The same groups in [**1b-Y**]₂ afforded two well-resolved doublets δ_H 5.25 and 3.95 ppm (² $J_{HH} = 14.6$ Hz) and two resonances at δ_C 62.6 and 59.5 ppm at in the corresponding ¹H and ¹³C{¹H} NMR spectra.

The molecular structures of $[1b-Sc]_2$ and $[1b-Y]_2$ are depicted in Figure S3 and Figure 2, respectively. The unit cell



Figure 2. Molecular structure of $[1b-Y]_2$ (all hydrogen atoms and *iPr* groups are omitted for clarity; thermal ellipsoids drawn at the 50% probability). Selected bond distances (Å) and angles (deg): Y(1)-O(1), 2.278(4); Y(1)-O(2), 2.337(4); Y(1)-N(1), 2.212(5); Y(1)-N(2), 2.190(4); O(1)-Y(1)-N(1), 83.12(15); O(2)-Y(1)-N(2), 116.62(18); N(1)-Y(1)-N(2), 106.17(17).

of $[1b-Y]_2$ contains three independent molecules featuring very similar geometrical parameters (bond lengths and angles) and overall organizations, and therefore the structural details of only one of them is discussed hereafter. Isostructural $[1b-Sc]_2$ and $[1b-Y]_2$ exhibit each the two five-coordinated metal atoms whose geometries are best described as distorted trigonal bipyramidal composed by two nitrogen and three oxygen atoms of the two $\{N^2O\}^{3-}$ ligands and one THF molecule.

Scheme 4. Formation of Complex 3a-Y from 1a-Y and 2-Phenylpyridine



Thus, the M–O and M–N bonds (2.090(3)-2.143(3) and 2.006(3)-2.087(3) Å, respectively) with ligand in $[1b-Sc]_2$ are shorter than those in the yttrium analogue (2.278(4)-2.337(4) and 2.190(4)-2.212(5) Å, respectively) by 0.14-0.24 Å, in line with the larger ionic radius of yttrium.¹¹ In addition, the intermetallic M···M distances in these dinuclear molecules (3.4832(12) and 3.9228(16) Å, respectively) are not exceptional¹² and are larger than the sum of the corresponding ionic radii (1.490 and 1.800 Å, respectively).¹¹

Stoichiometric and Catalytic Studies on the Reactivity of Bis(Alkyl) Complex 1a-Y with 2-Phenylpyridine. The C-H bond addition of heterocycles (hydroarylation) to alkenes or imines, catalyzed by alkyl complexes of group 3 metals, is known to follow a multistep mechanism^{3,4} involving the ortho- $C(sp^2)$ -H activation reaction of an aromatic molecule affording aryl intermediate, followed by insertion of the C=Cor C=N bond into the M-aryl bond. Stoichiometric reactivity of group 3 metals alkyls with 2-phenylpyridine has also been the subject of several studies. For example, the formation of different C–H bond activation products incorporating η^2 -N,C-6-phenylpyridyl,¹³ η^2 -N,C-2'-phenylpyridyl,^{13a,14,15} or the 2-phenypyridine-derived biheterocyclic^{13a,b,c,14b} ligands have been reported. In particular, Diaconescu et al.^{13a} observed in the corresponding yttrium and lutetium complexes the slow rearrangement process for the 2-phenylpyridine ligand from the η^2 -N,C-6-phenylpyridyl (three-membered-ring metallocycle) to the more stable η^2 -N,C-2'-phenylpyridyl (fivemembered-ring metallocycle) coordination mode.

In order to assess the potential of bis(alkyl) complex **1a-Y** in $C(sp^2)$ -H activation/hydroarylation reactions, its reactivity with 2-phenylpyridine was preliminarily studied. Monitoring by ¹H NMR spectroscopy of the reaction between equimolar amounts **1a-Y** and 2-phenylpyridine in C_6D_6 at room temperature (Figure S18) showed slow disappearance of the signal at δ_H -0.71 ppm from the CH_2 protons of the Y- $(CH_2Si(CH_3)_3)_2$ groups, and the appearance of a new signal at δ_H -0.28 ppm. The latter apparently belongs to the Y- $CH_2Si(CH_3)_3$ group from a new mixed monoalkyl/aryl species resulted from the C–H activation reaction of 2-phenylpyridine (Scheme 4). Unfortunately, all attempts to isolate and authenticate this putative product failed.

Similar reaction between **1a-Y** and 2 equiv of 2-phenylpyridine after 16 h resulted in a complete consumption of **1a-Y** and in formation of complex **3a-Y** (Scheme 4). Complex **3a-Y** was reprepared on a larger scale and isolated in 54% as dark green crystals. The nature of the compound was authenticated by ¹H and ¹³C NMR spectroscopy and X-ray crystallography. In particular, the room-temperature ¹H NMR spectrum of **3a-**Y was slightly broadened due to fluxional behavior possibly arising from ligand rearrangement. The ¹H and ¹³C{¹H} NMR spectra (Figures S19 and S22) exhibited a single set of resonances, consistent with an average C_s -symmetric species on the NMR time scale, in which the two η^2 -*N*,C-2'-phenylpyridyl fragments are equivalent. In particular, the ¹³C{¹H} NMR spectrum of **3a-Y** (Figure S22) contained only one characteristic doublet (δ_C 190.8 ppm, J_{Y-C} = 41.6 Hz)¹⁴ for the two Y-C carbon nuclei of the two 2-phenyl-pyridyl groups. Upon lowering the temperature to -33 °C (Figure S20), the very broad signal from the CH=N groups split into two single resonances at δ_H of 9.57 to 8.76 ppm, while for many other signals, the pattern did not change significantly. At higher temperature (80 °C), a new series of resonances appeared after 1 h suggesting gradual decomposition of the compound affording unidentified products.

The five-membered-ring metallocyclic ring of complex **3a-Y** exhibiting η^2 -*N*,*C*-2'-phenylpyridyl coordination of the ligand parallels previous results obtained by different groups.^{13a,14,15} It should be also mentioned that the existence of a possible isomerization process in solution similar to that described by Diaconsescu et al.^{13a} and consisting in our case of the change of the mode of coordination of the 2-phenyl-pyridyl ligand in **3a-Y** from η^2 -*N*,*C*-2'-phenylpyridyl to η^2 -*N*,*C*-6-phenylpyridyl type could not be unequivocally established by our experimental techniques.

The molecular structure of **3a-Y** (Figure 3) revealed the yttrium atom in a seven-coordinated environment provided with the oxygen atom and the nitrogen atom of the {N²O}⁻ ligand, the two carbon and two nitrogen atoms of the two monoanionic phenyl-pyridine ligands, and the oxygen atom of the coordinated THF molecule. In **3a-Y**, the Y–O and Y–N distances (2.2225(16) and 2.519(2) Å) for the coordinated phenoxy-imino ligand are very close to those in the parent **1a**-Y. The Y–C(aryl) and Y–N(aryl) bond lengths (2.502(2), 2.505(2), and 2.504(2), 2.583(2) Å, respectively) in the seven-coordinated **3a-Y** are longer than those (2.449–2.480 and 2.453–2.506 Å, respectively) observed for the previously reported five- and six-coordinated yttrium complexes bearing the same η^2 -N,C-2'-phenylpyridyl ligands.^{13–15}

In order to evaluate the feasibility of the alkylation of styrene with 2-phenylpyridine in the presence of **1a-Y**, stoichiometric reactions between complex **3a-Y** and styrene were monitored by ¹H NMR spectroscopy. Unfortunately, no reaction was observed in the temperature range 25-60 °C with 1-10 equiv of styrene. Further increasing of the temperature to 100 °C resulted only in decomposition of **3a-Y**, with no detectable insertion of styrene into the Y-(pyridine-2'-ylbenzene) bond.

To gain a better insight into the mechanism of C-H activation of 2-phenylpyridine with the bis(alkyl) complex 1a-

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Figure 3. Molecular structure of 3a-Y (all hydrogen atoms and iPr groups are omitted for clarity; thermal ellipsoids drawn at the 50% probability). Selected bond distances (Å) and angles (deg): Y(1)-O(1), 2.2225(16); Y(1)-O(2), 2.4167(17); Y(1)-C(47), 2.502(2); Y(1)-C(58), 2.505(2); Y(1)-N(1), 2.519(2); Y(1)-N(3), 2.504(2); Y(1)-N(4), 2.583(2); O(1)-Y(1)-O(2), 85.46(6); O(1)-Y(1)-C(47), 132.75(7); O(1)-Y(1)-N(3), 82.26(7); N(4)-Y(1)-C(58), 66.40(8); N(3)-Y(1)-C(47), 66.73(7).

Y, DFT computations were conducted (Scheme S2). The objectives of these non-exhaustive computations were to assess and compare the energy profiles for several possible concurrent processes: (a) C-H activation reaction of 2-phenyl-pyridine at the 2'-phenyl position resulting in formation of **3a-Y** (E(THF)_x, where x = 1), (b) an alternative C-H activation reaction of 2-phenyl-pyridine at the 6-pyridyl position

Scheme 5. Hydroarylation of Styrene with 2-Phenylpyridine

affording the corresponding isomeric $\mathbf{E}'(\mathrm{THF})_x$ product. In addition, the reactivity of the two products of the *ortho*metalation reactions, bis(aryl) complexes $\mathbf{E}(\mathrm{THF})_x$ and $\mathbf{E}'(\mathrm{THF})_x$ (x = 0, 1), toward styrene was probed computationally, and the role of the presence of coordinated THF molecules on the stability and reactivity of key intermediates was assessed. The computational results were found to be in agreement with the experimental reactivity trends (see SI for details and discussion).

The catalytic performance of 1a-Y, in combination with $B(C_6F_5)_{3,}^{4a}$ [Ph₃C]⁺[$B(C_6F_5)_4$]^{-,4b} or nBu_2NH^{4g} as cocatalysts, was briefly explored in hydroarylation of styrene with 2-phenylpyridine. Each reaction was carried out in a Teflonvalved sealed NMR tube, and the progress of reaction was monitored by ¹H NMR spectroscopy.

For benchmarking purposes, the catalytic performance of several bis(alkyl) complexes of scandium and yttrium CpM^{R4b} and $\{N^4\}M^{R16}$ (Scheme 5) as reference catalyst precursors was explored under our experimental conditions (70-100 °C, C_6D_6 ; Table S2). Among the most successful results, the combination (10 mol %) of $CpSc^{R}$ with $B(C_{6}F_{5})_{3}$ afforded selectively 2-phenyl-6-(2-phenylethyl)pyridine (5) with 53% conversion after 96 h at 70 °C. In addition, the high selectivity in alkylation of 2-phenylpyridine with styrene was achieved with the binary system $\{N^4\}M^R/[Ph_3C]^+[B(C_6F_5)_4]^-$ at 100 $^{\circ}C$ (Table S2, entries 8–10). The catalytic system of CpY^R/ $[Ph_3C]^+[B(C_6F_5)_4]^-$ (2.5 mol %) appeared to be active in ortho-alkylation of anisole with styrene affording quantitatively 1-MeO-2-(2-phenylethyl)benzene after 24 h, which fits well with the result of Hou et al. reported to provide 94% yield under the same conditions.^{4b}

Under the same or modified conditions, poor catalytic results were achieved using complex **1a-Y** as precatalyst (Table S4). For example, only the combination **1a-Y**/[Ph₃C]⁺[B- $(C_6F_5)_4$]⁻ afforded small amounts (6%) of 5 at 100 °C (Table S4, entries 4 and 5). Given that the molecules of **1a-Y** and **3a-Y** both contain coordinated THF molecules, the absence of activity in catalysis, and particularly, reactivity toward styrene, could be attributed to a strong coordination of THF ligand, thus, impeding its displacement by such a poor donor as



styrene. In order to address this issue, several catalytic experiments were conducted in the presence of substoichiometric or stoichiometric amounts of LiCl or AlMe₃ as possible scavengers of THF. However, only in one experiment using AlMe₃ (20 mol %) was formation of only a small amount of 2-(2-(1-phenylethyl)-phenyl)-pyridine (**6**, 5%) observed (Table S4, entry 8). No visible formation of products was detected when other electrophilic substrates (e.g., *N*-R-1-phenylmethanimine (R = Ph, *i*Pr), PhSiH₃, Et₃SiH) were used in the place of styrene.

Studies on Copolymerization of CO₂ with Cyclohexene Oxide. The mononuclear bis(alkyl) 1a-Y and dinuclear alkyl-free complexes $[1b-M]_2$ were then tested as initiators of copolymerization of CO₂ with cyclohexene oxide (Scheme 6). For benchmarking purposes, first the copoly-

Scheme 6. Copolymerization of Cyclohexene Oxide (CHO) and CO₂ Catalyzed by Complex 1a-Y



merization reactions initiated by $\{BDI\}Zn(N(SiMe_3)_2)^{17}$ was studied at 70 °C and 12 bar CO₂ pressure (Table 1, entry 1) affording 10% conversion of monomer after 64 h. The low activity compared with the result reported by Coates et al.,¹⁷ which gave 44% conversion at 50 °C after 2 h, is apparently due to the addition of solvent (toluene), as the copolymerization rate law features a first order dependence on monomer concentration.¹⁸ To our delight, using complex **1a-Y** as catalyst under the same conditions gave 95% conversion and 97% selectivity for polymers (entry 2). The yields remained almost unchanged when the loading of **1a-Y** decreased from 0.5 to 0.2 mol % (entries 3 and 5). Decreasing the concentration of **1a-Y** to 0.1 mol % led to a significantly lower conversion of 57% (entry 12), suggesting high sensitivity of the initiating system to the presence of impurities. Similar observation on the decrease of the polymer conversion upon reducing the catalyst loading to 0.1 mol % was reported for the series of β -diimine bis(alkyl) yttrium complexes.^{7b}

The reaction temperature appeared to have a significant influence on the copolymerization activity. While the experiment conducted at room temperature resulted in no polymer formation (entry 4), at 50 °C, a conversion of 86% was observed after 18 h (entry 6). The highest conversion of 92%, using 500 equiv of CHO (TON of 460), was achieved after 5 h at 70 °C (entry 11). Compared to the reported bis(alkyl) yttrium complex supported by β -diiminate ligand giving TON of 300 at 130 °C and 15 bar CO₂ pressure,^{7b} 1a-Y proved to be one of the most efficient mononuclear rare-earth metal-based catalyst for polycarbonate synthesis. However, the activity of 1a-Y is still lower than those reported for most highly active catalysts systems,¹⁹ such as Lu's bifunctional Co(III)-salen catalysts,^{19a} Rieger's very active dizinc macrocyclic systems,^{19b} La/Zn heteropolymetallic catalysts of Okuda and Mashima,19c Nozaki's porphyrin-based catalysts,^{19d} and Williams's heterobimetallic Mg/Co complexes.¹⁹⁶

In order to determine orders on CHO and catalyst, a series of kinetic studies was undertaken. Kinetic monitoring of copolymerization under regular conditions (Figure S25) did not exhibit a significant induction period, regardless of the catalyst concentration, suggesting rapid initiation with Y-CH₂SiMe₃ groups. The latter fact was corroborated by MALDI-ToF spectroscopy (Figure S31) demonstrating the presence of CH₂SiMe₃ end-groups in the low-molecular-weight polycarbonate sample (Table 1, entry 9). The first-order

Table 1. Copolymerization of CO₂ with CHO Catalyzed by Complex 1a-Y^a

entry	initiator (%)	$T(^{\circ}C)$	time (h) ^b	conversion (%) ^c	polymer ^c	carbonate units ^c	$M_{\rm n,GPC}(M_{\rm n,calc}) \ 10^3 \ { m g \cdot mol}^{-1e}$	\overline{D}^{e}
1	BDIZnNTMS ₂ (0.5)	70	64	10	89	99	-	-
2	1a-Y (0.5)	70	64	95	97	99	8.1 (27.0)	1.49
3	1a-Y (0.5)	70	18	95	97	99	2.4 (27.0)	1.92
4	1a-Y (0.2)	25	18	<1	-	-	-	-
5	1a-Y (0.2)	70	18	95	>99	99	7.9 (67.5)	1.99
6	1a-Y (0.2)	50	18	86	>99	99	10.6 (61.1)	3.30
7	1a-Y (0.2)	70	1	22	>99	99	5.0 (15.6)	2.65
8	1a-Y (0.2)	70	2	41	>99	99	5.4 (29.1)	2.10
9	1a-Y (0.2)	70	3	75	>99	99	6.1 (56.9)	1.78
10	1a-Y (0.2)	70	4	84	>99	99	5.8 (59.7)	1.90
11	1a-Y (0.2)	70	5	92	>99	99	6.6 (65.4)	1.89
12	1a-Y (0.1)	70	18	57	>99	98	12.4 (80.9)	7.75
13 ^f	1a-Y (0.2)	70	18	60	99	99	10.9 (42.6)	8.30
14	$1a-Y/ZnEt_2$ (0.2)	70	18	9	99	99	-	-
15	$1a-Y/MgBu_2$ (0.2)	70	18	8	99	99	-	-
16	$1a-Y/AlMe_3$ (0.2)	70	18	14	95	99	4.1 (10.0)	3.38
17	$[1b-Sc]_2(0.2)$	70	18	14	>99	<1	2.2 (6.86)	2.92
18	$[1b-Y]_2$ (0.2)	70	18	31	>99	<1	3.0 (15.2)	1.72

^{*a*}Reaction conditions: solvent = toluene (1.0 mL); $[CHO]_0 = 4.95 \text{ mol}\cdot\text{L}^{-1}$; 70 °C; $P_{CO2} = 12 \text{ bar}$; $[CO_2]/[CHO] = 5.3$; n.o. = not observed. ^{*b*}Reaction times were not necessarily optimized. ^{*c*}Conversion of product and selectivity were determined by ¹H NMR spectroscopy. ^{*d*}Determined by DSC. ^{*c*}Determined by GPC; $\mathcal{D} = M_w/M_n$. ^{*f*}Experiment conducted in the presence of cyclohexane-1,2-diol (2 equiv vs 1a-Y).

dependence both on the CHO concentration (Figure 4) and on the concentration of catalyst (Figure S26) was determined from the corresponding linear plots, indicating a mononuclear pathway.^{18,20}



Figure 4. Plot of $\ln([CHO]_0/[CHO]_t)$ as a function of time for the copolymerization of CO₂ with CHO catalyzed by complex **1a-Y** (0.05–0.2 mol %); conditions: toluene, $P_{CO2} = 12$ bar, 70 °C, $[CHO]_0 = 4.95$ mol·L⁻¹.

Predominantly alternating polycarbonates rather than cyclic carbonates were isolated in all experiments involving 1a-Y (e.g., entries 6 and 7), regardless of the reaction temperature. The polycarbonate polymers produced were essentially atactic as judged from the corresponding ${}^{13}C{}^{1}H$ NMR data (Figure S29) obtained for the sample of low $M_{\rm p}$ of 8100 g·mol⁻¹ (entry 2). Thus, in the carbonyl region, the intensity pattern of the corresponding key resonances at $\delta_{\rm C}$ 153.8 ppm from the isotactic tetrads ([mmm], [mmr]) and at $\delta_{\rm C}$ 153.1–153.4 ppm ([mrm], [rrm], [rrr], [rmr]) compares well with those reported in the literature for the atactic analogues.²¹ The thermal properties of several copolymer samples (entries 2 and 10) were also examined by DSC analysis revealing the $T_{\rm g}$ values of 88.7 (Figgure S30) and 87.3 °C, respectively. These values are typical for such low-molecular-weight polymers falling in the regular range of those (45.0–118.9 °C) reported for polycarbonates.²² No melting transitions were detected in these cases.

The fact that the experimentally determined by GPC average-number molecular weights are systematically lower than the theoretical values, calculated from the initial monomer-to-initiator ratio and conversion values, is diagnostic of several possible phenomena operating under our conditions: initiation and growing of two polymer chains per one metal center, and occurrence of side transfer reactions, e.g., chain transfer to cyclohexane-1,2-diol generated from CHO in the presence of adventitious protic impurities (H₂O).²³ The latter phenomenon can also be responsible for the broadening of the molecular weight distributions of polymers obtained in the experiments carried out with low amounts of 1a-Y (entry 12). In order to probe this hypothesis, a copolymerization experiment with 2 equiv of cyclohexane-1,2-diol was carried out (entry 13). Thus, the lower CHO conversion (60%) was achieved as compared to that in the experiment without cyclohexane-1,2-diol (95% conversion, entry 5). The PDI value was found to be much broader (8.30 vs 1.99, respectively), which is diagnostic of poorly controlled transfer processes operating under these conditions and/or of multisite behavior of the catalytic system.

Alkyl compounds of main-group metals are known not only to promote the copolymerization of CO_2 with epoxides,²⁴ but also to contribute to the formation of highly active polynuclear systems derived from transition metals.^{6d,19} The effect of the addition of such alkyl metal (Zn, Mg, Al) reagents to **1a-Y** was also investigated in copolymerization (entries 14–16) and, despite our expectations, appeared to be detrimental. The efficiency of the resulting binary systems was found to be much lower than that of the monocomponent **1a-Y**.

Dinuclear alkyl group-free complexes $[1b-Sc]_2$ and $[1b-Y]_2$ were also probed as promoters of copolymerization (entries 17 and 18, respectively). Under identical conditions (70 °C, 18 h), only small amounts of polymers were isolated (14% and 31% conversion, respectively), which were identified by NMR spectroscopy as polyethers (Figure S32),^{7a} homopolymers of CHO. The different nature of initiating groups (alkyl vs phenolate group) may account for the reactivity and selectivity differences in these systems.²⁵ This observation also parallels the results reported by Chakraborty et al. for dinuclear titanium and zirconium complexes, which produced poly-(cyclohexene oxide) polymers in the absence of a nucleophilic cocatalyst.²⁶

CONCLUSIONS

In summary, we investigated complexation of two types of ligand platforms, namely, bis(imino)phenoxy and bis(amido)phenoxy, with group 3 metals. During this study, a series of new complexes of scandium and yttrium were obtained by σ bond metathesis (alkane elimination) and completely characterized. Among them, bis(alkyl) complex {N²O}Y- $(CH_2SiMe_3)_2(THF)_2$ (1a-Y) was used for studies on stoichiometric C-H activation of 2-phenylpyridine selectively affording under mild conditions an original bis(aryl) product, complex {N²O}Y(η^2 -N,C-2'-PhPy)₂(THF) (3a-Y). The latter was found stable in solution under ambient conditions and completely reluctant in reactions with weak electrophiles, such as styrene, imines, and hydrosilanes. This reaction of formation of 3a-Y from 1a-Y and 2-phenylpyridine through a series of C-H activation steps was studied by DFT calculations, and the inactivity of 3a-Y toward styrene was also rationalized. Attempts to use 1a-Y in combination with borane and borate activators for the hydroarylation of styrene and imines were also unsuccessful.

Gratifyingly, **1a-Y** found application as initiator of copolymerization of CO₂ with cyclohexene epoxide under mild conditions (70 °C, 12 bar of CO₂ pressure, toluene). The corresponding polycarbonate polymers were obtained with nearly quantitative conversion over 5 h of polymerization and high selectivity (97–99% of carbonate units). Yet, this system constitutes a rare example of most efficient rare-earth metal alkyl complexes for copolymerization of CO₂ with epoxides (TON of 460) operating under mild conditions. These results again highlight the high potential of group 3 metal alkyl complexes in catalysis. Further studies of the development of new ligand platforms for C–H activation chemistry and CO₂ transformations are ongoing in our laboratories.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et₂O) and Na/K alloy (toluene, pentane) under argon, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene- d_6 , toluene- d_8 , THF- d_8 , >99.5% D, Deutero GmbH and Euroisotop) were vacuum transferred from Na/K alloy into storage tubes. The ligand precursors 1a- H_3^{8a} 1b- H_3^{8b} Me₃SiCH₂Li,²⁷ M(CH₂SiMe₃)₃(THF)₂, M(CH₂C₆H₄-o-NMe₂)₃²⁸ CpSc^{R,4a} CpY^{R,4b} and {N⁴}M^{R16} (M = Sc, Y) were prepared according to the published procedures. Styrene and cyclohexene oxide were distilled from CaH₂ and stored in the fridge at -25 °C. 2-Phenylpyridine, PhOMe, PhNMe₂, PhSiH₃, and Et₃SiH were dried with 4 Å molecular sieves and stored under argon. Other starting materials were purchased from Acros, Strem, and Aldrich, and used as received.

Instruments and Measurements. NMR spectra of complexes were recorded on Bruker AM-400, and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated. ¹H and ${}^{13}C$ chemical shifts are reported in ppm vs SiMe₄ (0.00), as determined by reference to the residual solvent peaks. The resonances of organometallic complexes were assigned from 2D ¹H-¹H COSY, ¹H-¹³C HSQC, and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. DSC measurements were performed on a SETARAM Instrumentation DSC 131 differential scanning calorimeter at a heating rate of 10° /min; first and second runs were recorded after cooling to 30 °C. Size exclusion chromatography (SEC) of polycarbonate samples was performed in THF (1 mL min⁻¹) at 20 °C using a Polymer Laboratories PL50 apparatus equipped with PLgel 5 μ m MIXED-C 300 \times 7.5 mm columns, and combined RI and Dual angle LS (PL-LS 45/90°) detectors. The number-average molecular weights (M_n) and polydispersities (D) of the polymers were calculated with reference to a universal calibration vs. polystyrene standards. The microstructure of polycarbonate was determined by ¹H and ¹³C NMR spectroscopy according to the published procedures.²¹ MALDI-TOF spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). CH₃COONa was added for facilitating ion formation, and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2propenylidene malononitrile was used as matrix.

Reaction between 1a-H and Sc(CH₂SiMe₃)₃(THF)₂. Formation of Complex 1a-Sc. In the glovebox, in a Teflon-valved NMR tube was placed 1a-H (0.026 g, 0.05 mmol), Sc(CH₂SiMe₃)₃(THF)₂ (0.023 g, 0.05 mmol). To this mixture, C_6D_6 (ca. 0.5 mL) was vacuum-transferred in at -25 °C and the tube was shaken for 1 h at room temperature. ¹H NMR spectroscopy indicated quantitative consumption of both reagents and formation of 1a-Sc and 1a-Sc' in ~1:0.3 ratio, respectively. Compound 1a-Sc (some resonances could not be assigned unequivocally): ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ 9.20 (br s, 1H, CH=N), 9.00 (br s, 1H, Ar), 8.16 (br s, 1H, CH= N), 7.35 (br s, 1H, Ar), 3.89 (br m, 4H, α-CH₂, THF), 3.29 (br m, 4H, CH(CH₃)₂), 1.34 (m, 4H, β-CH₂, THF), 1.39-1.26 (m, 24H, CH(CH₃)₂), 1.21 (s, 9H, C(CH₃)₃), 0.08 (s, 18H, Si(CH₃)₃), -0.01 (s, 4H, ScCH₂). ¹³C{¹H} NMR (125 MHz, C₆D₆, 25 °C): δ 172.4 (CH=N), 158.6 (CH=N), 150.9 (Ar), 148.9 (Ar), 140.9 (Ar), 137.4 (Ar), 135.2 (Ar), 131.6 (Ar), 127.1 (Ar), 124.1 (Ar), 122.9 (Ar), 122.3 (Ar), 68.6 (α-CH₂, THF), 40.4 (ScCH₂), 28.6 (CH), 28.2 (CH), 28.1 (CH₃), 25.8 (CH₃), 25.0 (β-CH₂, THF), 23.1 (CH₃), 22.2 (CH_3) , 3.3 $(Si(CH_3)_3)$.

1a-Sc' (Some Resonances Could Not Be Assigned Unequivocally). ¹H NMR (500 MHz, $C_6D_{6^1}$ 25 °C): δ 8.90 (d, ⁴J = 2.6, 2H, Ar), 7.93 (s, 2H, CH=N), 7.45 (s, 2H, CH=N), 7.30-7.19 (m, 10H, Ar), 7.19 (d, ⁴J = 2.6, 2H, Ar), 6.93 (d, J = 7.5, 2H, Ar), 6.82 (d, J = 7.5, 2H, Ar), 6.57 (t, J = 7.5, 2H, Ar), 3.22 (q, J = 6.8, 2H, CH(CH_3)_2), 3.10 (q, J = 6.8, 4H, CH(CH_3)_2), 2.63 (q, J = 6.8, 2H, CH(CH_3)_2), 1.18 (s, 18H, C(CH_3)_3), 1.00-0.82 (m, 48H, CH-(CH_3)_2), 0.67 (d, ²J_{HH} = 12.7, 1H, ScCH₂), 0.08 (s, 18H, Si(CH₃)₃), -0.25 (d, ²J_{HH} = 12.7, 1H, ScCH₂). ¹³C{¹H} NMR (125 MHz, C₆D₆, 25 °C): δ 172.5 (CH=N), 164.2 (Ar), 164.1 (Ar), 156.8 (CH=N),

150.9 (Ar), 150.7 (Ar), 148.1 (Ar), 140.1 (Ar), 140.0 (Ar), 139.9 (Ar), 139.8 (Ar), 136.6 (Ar), 134.8 (Ar), 132.3 (Ar), 126.9 (Ar), 126.0 (Ar), 123.9 (Ar), 123.4 (Ar), 123.0 (Ar), 122.6 (Ar), 42.9 (ScCH₂), 33.8 (CH), 30.8 (CH), 29.8 (CH), 28.1 (CH), 25.1 (CH₃), 23.3 (CH₃), 22.4 (CH₃), 22.0 (CH₃), 21.9 (CH₃), -0.4 (Si(CH₃)₃).

All volatiles were removed in vacuum and hexane (1 mL) was added. Colorless crystals of **1a-Sc** (0.0070 g, 15%), suitable for X-ray diffraction study, were isolated after the solution was kept for 7 days at -25 °C.

Synthesis of Complex 1a-Y. A solution of 1a-H (0.525 g, 1.0 mmol) in hexane (5.0 mL) was added quickly to a solution of $Y(CH_2Si(CH_3)_3)_3(THF)_2$ (0.495 g, 1.0 mmol) in hexane (5.0 mL) at -25 °C. The resulted reaction mixture was stirred at room temperature for 2 h. Green crystals of 1a-Y were obtained (0.623 g, 67%) after the solution was kept for 2 days at -25 °C. ¹H NMR (500 MHz, C_7D_8 , 25 °C): δ 8.70–8.02 (br m, 4H, CH=N + Ar), 7.20– 7.14 (m, 6H, Ar), 3.79 (s, 8H, α-CH₂ THF), 3.20 (br m, 4H, $CH(CH_3)_2$, 1.36–1.25 (m, 52H, β -CH₂ (THF) + CH(CH₃)₂ + $C(CH_3)_3$, 0.12 (s, 18H, Si(CH₃)₃), -0.71 (s, 4H, YCH₂). ¹³C{¹H} NMR (125 MHz, C7D8, 25 °C) (many aromatic signals were not observed due to fluxional dynamics and overlapping): δ 165.4 (C= N), 151.0 (C=N), 139.1 (Ar), 133.9 (Ar), 123.6 (Ar), 70.4 (α-CH₂, THF), 34.1 (CHCH₃), 32.3 (br s, YCH₂), 31.4 (CHCH₃), 28.6 (CH₃), 25.4 (CH₃), 23.9 (β-CH₂, THF), 4.4 (Si(CH₃)₃). Anal. Calcd for C₅₂H₈₅N₂O₃Si₂Y: C, 67.06; H, 9.20; N, 3.01. Found: C, 67.30; H, 9.46: N. 2.92

Reaction between 1b-H₃ and Sc(CH₂SiMe₃)₃(THF)₂. Formation of Complex [1b-Sc]₂. Using a similar procedure, described for 1a-Y, complex [1b-Sc]₂ was prepared from 1b-H₃ (0.053 g, 0.1 mmol) and Sc(CH₂SiMe₃)₃(THF)₂ (0.045 g, 0.1 mmol). Colorless crystals of $[1b-Sc]_2$ (0.029 g, 45%) were obtained after the solution was kept for 3 days at -25 °C. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 7.39 (br m, 6H, Ar), 7.32-6.74 (br m, 8H, Ar), 6.74 (br m, 2H, Ar), 5.60 (br m, 2H, CH₂N), 5.29 (br m, 2H, CH₂N), 4.41 (br m, 2H, $CH(CH_3)_2$), 4.06 (br m, 2H, CH_2N), 4.00 (br m, 4H, α - CH_2 , THF), 3.85 (br m, 2H, CH₂N), 3.53 (br m, 6H, α -CH₂, THF + CH(CH₃)₂), 2.97 (br m, 4H, CH(CH₃)₂), 1.77 (br m, 6H, C(CH₃)₃), 1.60-0.70 (br m, 62H, CH(CH₃)₂ + β -CH₂ (THF) + C(CH₃)₃), 0.43 (br m, 6H, $C(CH_3)_3$). ¹³C{¹H} NMR (125 MHz, C_6D_{64} 25 °C) (due to a strong fluxional dynamics some of the aromatic signals could not be observed): δ 153.7 (Ar), 152.2 (Ar), 145.3 (Ar), 123.6 (Ar), 71.6 (α-CH₂, THF), 62.8 (CH₂N), 55.8 (CH₂N), 31.1 (CHCH₃), 29.3 (CHCH₃), 28.1 (CH₃), 26.8 (CH₃), 23.8 (β-CH₂, THF), 22.6 (CH₃). Anal. Calcd for C72H98N4O2Sc2: C, 75.76; H, 8.65; N, 4.91. Found C, 75.84; H, 8.69; N, 4.73.

Reaction between 1b-H₃ and Y(CH₂SiMe₃)₃(THF)₂. Formation of Complex [1b-Y]2. Using a similar procedure, described for 1a-Y, complex $[1b-Y]_2$ was prepared from $1b-H_3$ (0.053 g, 0.1 mmol) and Y(CH₂Si(CH₃)₃)₃(THF)₂ (0.050 g, 0.1 mmol). Yellow crystals of $[1b-Y]_2$ (0.024 g, 39%) were obtained after the solution was kept for 7 days at -25 °C. ¹H NMR (500 MHz, toluene- d_8 , 25 °C): δ 7.20– 6.96 (m, 16H, Ar), 5.25 (d, ${}^{2}J_{HH}$ = 14.6, 4H, CH₂N), 3.95 (d, ${}^{2}J_{HH}$ = 14.6, 4H, CH₂N), 3.80-3.00 (br m, 16H, α -CH₂ THF + $CH(CH_3)_2$), 1.34–1.11 (m, 74H, β - CH_2 (THF) + $CH(CH_3)_2$ + $C(CH_3)_3$). ¹³C{¹H} NMR (125 MHz, toluene- d_8 , 25 °C): δ 152.5 (Ar), 145.2 (Ar), 131.8 (Ar), 128.1 (Ar), 127.8 (Ar), 127.2 (Ar), 125.3 (Ar), 124.3 (Ar), 123.4 (Ar), 122.6 (Ar), 70.7 (α-CH₂, THF), 62.6 (CH₂N), 59.5 (CH₂N), 33.5 (CHCH₃), 31.6 (CHCH₃), 31.3 (CHCH₃), 28.2 (CH₃), 25.2 (β-CH₂, THF), 24.9 (CH₃), 22.8 (CH₃). Anal. Calcd for C72H98N4O2Y2: C, 70.34; H, 8.04; N, 4.56. Found C, 70.05; H, 8.40; N, 4.03.

Synthesis of Complex **3a-Y**. To a solution of **1a-Y** (0.093 g, 0.10 mmol) in hexane (2.0 mL) was added 2-phenylpyridine (28.4 μ L, 0.20 mmol) in hexane (1.0 mL) at -25 °C. The solution was stirred at room temperature for 3 h. Dark green crystals of **3a-Y** (0.053 g, 54%) were obtained after the solution was kept for 7 days at -25 °C. ¹H NMR (500 MHz, toluene- d_8 , 25 °C): δ 8.74 (br m, 2H, CH=N), 8.57 (d, J = 4.8, 1H, Ar), 8.46 (d, J = 4.8, 2H, PhPy), 8.11 (d, 2H, J = 7.6, PhPy), 7.81 (br m, 2H, PhPy), 7.61 (d, 2H, J = 4.8, PhPy), 7.45 (d, 2H, J = 7.8, PhPy), 7.27 (m, 3H, Ar), 7.20 (d, 1H, J = 8.0, Ar),

7.18–7.12 (m, 4H, Ar), 6.95 (t, 3H, J = 7.6, PhPy), 6.70 (dd, J = 4.8, 7.6, 1H, Ar), 6.23 (t, J = 6.2, 2H, PhPy), 3.42 (br m, 4H, α -CH₂, THF), 3.14 (br m, 4H, CH(CH₃)₂), 1.43–1.10 (m, 16H, β -CH₂ (THF) + CH(CH₃)₂), 0.94–0.87 (m, 9H, C(CH₃)₃). ¹³C{¹H} NMR (125 MHz, toluene- d_8 , 25 °C) (some of the quaternary aromatic signals could not be observed): δ 190.8 (d, $J_{Y-C} = 41.6$, Y-C(PhPy)), 166.6 (C=NH), 165.7 (PhPy), 157.1 (C=NH), 149.5 (PhPy), 149.2 (PhPy), 145.7 (PhPy), 139.6 (Ar), 139.6 (PhPy), 138.2 (Ar), 137.8 (Ar), 137.4 (Ar), 135.8 (Ar), 129.9 (PhPy), 128.8 (Ar), 128.2 (Ar), 126.8 (Ar), 124.5 (Ar), 123.1 (PhPy), 121.5 (Ar), 119.5 (Ar), 118.6 (PhPy), 68.5 (α -CH₂, THF), 33.7 (CH(CH₃)₂), 31.6 (CH₃), 31.1 (C(CH₃)), 28.4 (CH₃), 24.8 (CH(CH₃)₂), 23.5–22.7 (br m, β -CH₂ (THF) + CH(CH₃)₂ + C(CH₃)). Anal. Calcd for C₆₂H₇₀N₄O₂Y: C, 75.06; H, 7.11; N, 5.65. Found C, 75.18; H, 7.39; N, 5.77.

Crystal Structure Determination of Complexes 1a-M, 2a-M, [1b-M]₂, and 3a-Y (M = Sc and Y). Diffraction data were collected at 150(2) K using a Bruker APEX CCD diffractometer with graphitemonochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix leastsquares refinement based on F2 (programs SIR97 and SHELXL-97).²⁹ Many hydrogen atoms could be located from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom positions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S1. Crystal data, details of data collection, and structure refinement for all compounds (CCDC 2016816-2016822, respectively) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Computational Studies. The calculations were performed using the Gaussian 09^{30} program employing B3PW91³¹ functional, and using a standard double- ζ polarized basis set, namely, the LANL2DZ set, augmented with a single polarization *f* function on yttrium (0.835) and a single polarization *d* function on silicon (0.296). The solvent effects, in our case for toluene, were taken into account during all the calculations by means of the SMD model.³² All stationary points were fully characterized via analytical frequency calculations as either true minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). The IRC procedure was used to confirm the nature of each transition state connecting two minima.³³ Zero-point vibrational energy corrections (ZPVE) were estimated by a frequency calculation at the same level of theory, to be considered for the calculation of the total energy values at *T* = 298 K in the same way as in the approach used by Castro et al.³⁴

Typical Procedure for Hydroarylation of Styrene with 2-Phenyl-Pyridine in the Presence of Group 3 Metal Complexes. In a typical experiment (Table S1, entry 4), in the glovebox, into a Teflon-valved NMR tube was placed 1a-Y (0.0093 g, 0.01 mmol), 2phenylpyridine (14.20 μ L, 0.10 mmol), and styrene (11.50 μ L, 0.10 mmol), and C₆D₆ (0.5 mL) was added at -25 °C. The tube was sealed at room temperature and the mixture was heated at the required temperature for the desired time. Progress of the reaction was monitored by ¹H NMR spectroscopy.

Typical Procedure for Copolymerization of CO₂ with CHO. In a typical experiment (Table 1, entry 5), in the glovebox, a Schlenk tube was charged with CHO (1.0 mL, 9.9 mmol), **1a-Y** (0.02 g, 0.05 mmol), and toluene (1.0 mL). The mixture was transferred to an autoclave equipped with a magnetic stirring bar under argon and then pressurized at CO₂ (12 bar). The reaction mixture was stirred vigorously at the required temperature for the desired time. After cooling to room temperature, CO₂ was released, and a small amount of the resulting mixture was analyzed by ¹H NMR spectroscopy to determine the conversion and selectivity. The reaction mixture was quenched by the addition of MeOH/HCl, and then poured into a large amount of MeOH to precipitate the polymer, which was dried under vacuum at 40 °C and weighed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02112.

Crystallographic data; representative NMR and MALDI-TOF spectra of complexes and polymers; DSC curves; DFT computations (PDF)

Accession Codes

CCDC 2016816–2016822 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

The authors declare no competing financial interest.

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