Mitigating Chain-Transfer and Enhancing the Thermal Stability of Co-Based Olefin Polymerization Catalysts through Sterically Demanding Ligands

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ABSTRACT: Sterically demanding Fe- and Co-based olefin polymerization catalysts **2-Fe** and **2-Co** bearing 2,6-bis(biphenyl-methyl)-4-methylaniline substituted bis(imino)pyridine ligands were synthesized and evaluated for ethylene polymerization. The late-transition metal complexes were characterized by X-ray diffraction, NMR spectroscopy, and HRMS, while their resultant polymers were characterized by size-exclusion chromatography and ¹H NMR spectroscopy. While catalyst **2-Fe** was inactive, catalyst **2-Co** was found to polymerize ethylene and avoid any detectable chain-transfer to aluminum events that are known to plague other Fe- and Co-based catalyst

systems and to limit molecular weight. Furthermore, **2-Co** displays virtually perfect thermal stability up to 80°C and shows greatly enhanced thermal stability at 90°C as compared to previously reported analogues. These observations are attributed to the extreme steric demand imposed by the ligand which mitigates catalyst transfer, deactivation, and decomposition reactions. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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INTRODUCTION The development of well-defined, homogeneous olefin polymerization catalysts remains a vital area of research within industry and academia alike. In particular, homogeneous single-site catalysts have enabled researchers to gain tremendous insight into the mechanistic underpinnings of olefin polymerization and the identity of their catalytically active species.^{1–5} This information has enabled researchers to intimately examine how ligand sterics, ligand electronics, and transition metal choice influence overall catalytic activity, reactivity, and selectivity, which has in turn lead to enhanced polymerization control.^{3,5–11}

For many years, researchers focused heavily on single-site catalysts that use early transition metals such as Ti, Zr, and Hf.⁵ However, in the late 1990s, it was discovered that late transition metal catalysts using metals such as Ni, Pd, Fe, and Co were also capable of producing high-molecular-weight polyolefins.¹² This capability was enabled through careful ligand design and use of sufficiently bulky substituents that effectively block the axial sites of the active metal center and prevent undesirable associative displacement of the growing polymer chain by monomer.^{3,12}

Despite their appeal, late transition metal-based catalysts often suffer from many limitations that can include: (1) poor

thermal stability, which is well documented for many Niand Pd-based α -diimine catalysts and (2) a notable propensity to undergo deleterious chain transfer events, which has been well-documented for Fe- and Co-based bis(imino)pyridine catalysts.^{13–18} Recent work by our group has addressed a portion of these issues by demonstrating that Ni(II) α diimine catalysts bearing sterically demanding 2,6-dibenzhydryl-4-methylaniline moieties exhibit greatly enhanced thermal stability (at temperatures as high as 90 °C) and virtually no detectable chain transfer events.^{19,20} Furthermore, these moieties have also been used to enhance Pd(II) α -diimine and Ni(II) salicylaldimine catalysts as well.²¹⁻²⁴

The enhanced performance of these, Ni catalysts are believed to arise due to restricted *N*-aryl rotations within the ligand, which in turn mitigates deleterious catalyst decomposition and deactivation reactions.^{14,18,25–31} We hypothesized that such sterically demanding dibenzhydryl moieties may also enhance the performance of related Fe and Co bis(imino)pyridine catalysts **1-Co** and **1-Fe** (Fig. 1).^{32–34}

Late transition metal precatalysts **1-Co** and **1-Fe** drew considerable attention as they use earth abundant and inexpensive metal precursors.^{35,36} They are known to produce

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FIGURE 1 Comparison of previously reported Co and Fe precatalysts **1** and the symmetrically substituted Co and Fe precatalysts **2** bearing dibenzhydryl moieties.

highly linear polyethylene at low ethylene feed pressures, which is in stark contrast to their Ni- and Pd-based counterparts that often produce branched polyethylene via a chainwalking mechanism.³⁷ However, despite these advantages, precatalysts **1-Co** and **1-Fe** are limited in that they often produce lower molecular weight polyethylene due to their propensity to undergo chain transfer to aluminum. The presence of these aluminum species stems from the use of methylaluminoxane (MAO), which is required for the activation of **1-Co** and **1-Fe**.³² Furthermore, although these catalysts have been reported to be active at elevated temperatures, no systematic determination of their time-resolved thermal stability has ever been reported, to the best of our knowledge.

Toward this goal, herein, we describe the synthesis and polymerization behavior of symmetric, dibenzhydryl-substituted precatalysts **2-Co** and **2-Fe**. We will show that precatalyst **2-Co** is highly active for ethylene polymerization, while **2-Fe** is virtually inactive. Furthermore, we will compare the susceptibility of precatalysts **1-Co** and **2-Co** to chain-transfer to aluminum as well as evaluate their time-resolved thermal stability.

EXPERIMENTAL

General Methods and Materials

All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System and degassed via three freeze-pump-thaw cycles. CDCl₃ was dried over activated molecular sieves (4 Å). The compounds 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine, 2,6-bis[1-(2,6-diisopropylphenyl-imino)ethyl] pyridine cobalt(II)bromide, 2,6-bis-(diphenylmethyl)-4-methylaniline, and **2-Fe** were prepared as reported previously.^{18,20,32,38} MAO was received as a gift from Albemarle Corp. and used as received. All other reagents were purchased from commercial vendors and used without further purification.

¹H and ¹³C spectra were recorded at ambient temperature on a Varian VNMRS 500 MHz narrow-bore broadband system. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. Gel permeation chromatography was performed at 145 °C in 1,2,4-trichlorobenzene at 1.0 mL/min on a Malvern Viscotek HTGPC equipped with refractive index, viscometer, and two-angle light-scattering detectors. Polymer melting transition temperatures ($T_{\rm m}$ s) were measured on a TA Instruments Q2000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min. High resolution mass spectrometry was obtained using a direct inject, positive ion mode with an electrospray ionization onto a Thermo Scientific Exactive Plus Orbitrap mass spectrometer.

Synthesis of 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4methylaniline)] pyridine (3)

To a solution of 2,6-diacetylpyridine (185 mg, 1.14 mmol) in absolute ethanol (20 mL) was added 2,6-bis(diphenylmethyl)-4-methylaniline (1.00 g, 2.28 mmol). A few drops of glacial acetic acid were added and the solution was refluxed overnight. Upon cooling to room temperature, the product crystallized from the ethanol solution. The product was washed with ethanol and dried under vacuum overnight to give **3** as an off-white solid (787.2 mg) in 69.5% yield.

¹H NMR (CDCl₃, 500 MHz): δ 8.12 (d, 2 H), δ 7.78 (t, 1 H), δ 7.26–7.02 (m, 40 H), δ 6.71 (d, 4 H), δ 5.30 (s, 4 H), δ 2.19 (s, 6 H), δ 0.91 (s, 6 H). ¹³C NMR (CDCl₃, 75 Hz) 170.1, 154.8, 146.0, 143.8, 142.6, 136.4, 132.2, 131.6, 129.8, 129.4, 128.6, 127.9, 126.0, 121.9, 121.9, 77.2, 76.7, 51.9, 21.3, 16.8. HRMS C₇₅H₆₃N₃ (H⁺ adduct) = 1006.5056 *m/z*; HRMS^{expt} C₇₅H₆₃N₃ (H⁺ adduct) = 1006.5076 *m/z*.

Synthesis of 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4methylaniline)] pyridine cobalt(II)bromide (2-Co)

A solution of **3** (400 mg, 0.40 mmol) in tetrahydrofuran (20 mL) was added to cobalt(II) dibromide hydrate (83.1 mg, 0.38 mmol) in a Schlenk flask and stirred overnight at room temperature. Diethyl ether (10 mL) was then added to the reaction to precipitate the complex and the resulting solids were filtered in air, washed using diethyl ether and pentane, and dried *in vacuo* to yield complex **2-Co** as a brown powder (268.8 mg) in 67.2% yield.

¹HNMR (DMSO-d₆, 500 MHz) δ 8.18 (d, 2 H), δ 7.98 (m, 1 H), δ 7.27–6.95 (m, 40 H), δ 6.64 (s, 4 H), δ 5.21 (s, 4 H), δ 2.21 (s, 6 H), δ 0.80 (s, 6 H). HRMS^{calc} C₇₅H₆₃N₃Br₂Co (H⁺ adduct) = 1224.2700 *m/z*; HRMS^{expt} C₇₅H₆₃N₃Br₂Co (H⁺ adduct) = 1224.5700 *m/z*.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes

The well-known cobalt precatalyst **1-Co** and **1-Fe** were synthesized as reported previously.³² Precatalysts **2-Co** and **2-Fe** were synthesized according to Scheme 1 in which 2,6-dibenzhydryl-4-methylaniline was synthesized as described previously via electrophilic aromatic substitution of *p*-toluidine using benzhydrol and catalytic ZnCl₂.^{19,20} This substituted aniline was condensed onto 2,6-diacetylpyridine to provide the target ligand 2-[1-(2,6-dibenzhydryl-4-methyl-phenyl-imino)ethyl]-6-[1-arylimino)eth-yl]-pyridine (**3**) in good overall yield (69.5%). Ligand **3** was metallated using the appropriate Co or Fe precursor in THF to provide precatalysts **2-Co** and **2-Fe**.



SCHEME 1 Synthesis of precatalysts 2-Co and 2-Fe.

NMR spectroscopy confirmed that both precatalysts **2-Co** and **2-Fe** display paramagnetic behavior, which was expected for high-spin Fe and Co complexes. Single crystals of precatalyst **2-Co** suitable for X-ray diffraction analysis were obtained by vapor diffusion of hexanes into a saturated dichloromethane (DCM) solution (Fig. 2). Complex **2-Co** displayed a distorted square-pyramidal geometry in which the Co center is pushed out of the chelating [*N*,*N*,*N*]-ligand plane. This observation is believed to be due to ligand sterics, which has also been noted for analogous complexes.^{17,18,32} As a note, we were unable to obtain suitable crystals of **2-Fe** for analysis by X-ray diffraction.

Ethylene Polymerization Using 2-Co and 2-Fe

Both precatalysts **1-Co** and **1-Fe** are known to be highly active for ethylene polymerization, and have been detailed in the literature.³² In contrast, initial ethylene polymerizations quickly revealed that while **2-Co** is active for ethylene polymerization, precatalyst **2-Fe** is essentially inactive, yielding only trace amounts of polymer. Although we are not certain



FIGURE 2 An ORTEP representation of precatalyst **2-Co** with thermal ellipsoids drawn at 30% probability. Hydrogens are omitted for clarity. [Color figure can be viewed at wileyonline-library.com]

TABLE 1 Ethylene polymerization results for precatalyst 2-Co^a

Entry	T _{rxn} (°C)	Yield (mg)	Prod. ^b (kg/mol)	<i>M</i> w ^c (kg/mol)	а	7m ^d (°C)
1	20	75	14.9	33	4.58	134.0
2	40	139	27.8	23	3.06	133.9
3	60	211	42.2	13	3.62	130.5
4	80	271	54.1	10	1.21	129.5
5	90	312	62.4	4.3	1.49	127.8
6	100	282	56.5	3.0	1.25	121.9
7 ^e	40	757	151	57	1.96	133.4
8 ^e	80	1240	247	29	2.84	132.0
9 ^e	100	707	141	10	1.84	130.6

 a Polymerization conditions: [2-Co] = 5 $\mu mol,$ 50 mL toluene, 30 psi ethylene, 300 equiv MAO, 30 min.

Productivity = kilogram of ethylene/mol cat.

 $^{\circ}$ Determined using gel permeation chromatography at 145 $^{\circ}\mathrm{C}$ in 1,2,4-trichlorobenzene.

^d Determined via differential scanning calorimetry, second heating cycle.

^e Polymerizations performed at 100 psi of ethylene.

of the origins of inactivity of **2-Fe**, it agrees strongly with related studies by Sun and coworkers and may potentially be due to the instabilities of the MAO activated Fe species.^{17,18,35} Because of the inactivity of **2-Fe**, the remainder of this work will only focus on the cobalt containing precatalysts **1-Co** and **2-Co** so as to make a direct comparison of the effects of ligand sterics on catalytic behavior.

To evaluate the catalytic behavior of 2-Co, ethylene polymerizations were conducted at temperatures ranging from 20 to 100 °C (Table 1). It was found that each polyethylene sample produced was highly linear, as evidenced by their high $T_{\rm m}$ (121.9–134 °C), and a decreasing trend in $T_{\rm m}$ was observed as a function of increasing temperature (Table 1, entries 1-6). For comparison, perfectly linear polyethylene is generally regarded to have a $T_{\rm m} = 137 \,{}^{\circ}\text{C.}^{39}$ Similarly, molecular weight was also found to decrease as a function of increasing temperature (33 \rightarrow 3 kg/mol) which can be attributed to either the decreased solubility of ethylene gas in the reaction solvent (toluene) or increased rates of chain transfer at elevated temperatures (Table 1, entries 1-6).^{13,40,41} However, we will provide evidence in the following sections of this work that ethylene solubility is the likely cause. Finally, polymerizations conducted at or below 60 °C yielded polymer dispersity values (D) that are significantly broader than those obtained at higher polymerization temperatures. This is due to the presence of a high-molecular-weight shoulder in their respective GPC chromatograms (Supporting Information), but which is virtually eliminated for all polymerizations conducted at or above 80 °C.

Polymerizations conducted under an ethylene feed pressure of 30 psi (Table 1, entries 1–6) show a steady increase in polyethylene productivity as polymerization temperature is increased, reaching a maximum of 62.4 kg/mol at 90 °C (Table 1, entry



TABLE 2 Evaluating the effects of [AI] for precatalysts 1-Co and 2-Co^a

Entry	Cat.	Al:cat	Yield (mg)	Prod. ^b (kg/mol)	<i>M</i> w ^c (kg/mol)	а
1	1-Co	100:1	4383	876	23	1.3
2	1-Co	300:1	5160	1032	10	1.4
3	1-Co	500:1	4868	973	8.3	2.1
4	1-Co	1000:1	5879	1176	6.7	1.2
5	1-Co	1500:1	6263	1253	5.6	1.9
6	2-Co	100:1	295	59	39	3.4
7	2-Co	300:1	774	155	57	4.4
8	2-Co	500:1	764	153	61	3.2
9	2-Co	1000:1	1302	260	67	2.4
10	2-Co	1500:1	1068	214	64	2.0

 a Polymerization conditions: [cat] = 5 $\mu mol,~50$ mL toluene, 100 psi, 40 °C, 30 min.

^b Productivity = kilogram ethylene/mol cat.

 $^{\rm c}$ Determined using gel permeation chromatography at 145 $^{\circ}{\rm C}$ in 1,2,4-trichlorobenzene.

5). However, further increasing the polymerization temperature to 100 °C resulted in a slight drop in productivity suggesting that some degree of catalyst decomposition or deactivation may be occurring at this temperature (Table 1, entry 6). This drop in productivity at 100 °C was also observed for polymerizations conducted at higher ethylene feed pressure (100 psi) (Table 1, entries 7–9), which partially suggests that catalyst **2-Co** may potentially be thermally unstable at this temperature. Additionally, polymerizations conducted at 100 psi of ethylene feed pressure produced polymers with significantly higher molecular weights and increased melting temperatures relative to those conducted at 30 psi. We attribute both of these observations to increased monomer concentration in solution, which increases polymerization rates and decreases the propensity of the catalyst to undergo any chain-walking events.³⁷

It was noted that the productivity of catalyst **2-Co** was consistently lower than observed when using catalyst **1-Co** under identical conditions (62.4 kg/mol versus 264 kg/mol, respectively) (Supporting Information). We attribute the decreased productivity of **2-Co** to the greatly increased ligand sterics surrounding the open coordination site of the activated Co center, which thereby hinders ethylene coordination and insertion. Polymerizations conducted at 100 psi of ethylene feed pressure showed that productivity of **2-Co** can be greatly enhanced (54.1 \rightarrow 247 kg/mol) by increasing ethylene feed pressure (Table 1, entries 4 and 8). This suggests that rate of chain propagation of catalyst **2** is heavily dependent on ethylene concentration.

Comparing the Effects of [Al] for 1-Co and 2-Co

As mentioned previously, the ratio of MAO activator to catalyst (Al:cat) can have a strong influence on the activity of the propagating catalyst, particularly in regards to polymer yield, molecular weight (M_w), and molecular weight dispersity (D).

This is particularly true for precatalyst **1-Co** and its Fe-based analogue, which are known to produce lower molecular weight polymers when using high Al:cat ratios. This effect has been directly attributed to chain transfer to Al during polymerization.³² Therefore, to evaluate the propensity of precatalyst **2-Co** toward chain transfer to Al, varying ratios of Al:cat were screened and compared with analogous polymerizations using **1-Co** (Table 2).

As expected, polymerizations using catalyst **1-Co** showed a slightly increasing trend in productivity as a function of increasing Al:cat ratio. However, a corresponding notable decrease in $M_{\rm w}$ was also observed (23 \rightarrow 5.6 kg/mol) (Table 2, entries 1–5) as the Al:cat ratio was increased, which supports previous reports that **1-Co** undergoes deleterious chain transfer from cobalt to aluminum. Furthermore, analysis of these samples via ¹H NMR spectroscopy also revealed the presence of olefinic end groups (Supporting Information Figs. S12 and S13) that is indicative of β -hydride transfer events, which may result due to β -hydride elimination followed by dissociation or chain-transfer to monomer (Table 2).

In contrast to catalyst **1-Co**, the productivity of catalyst **2-Co** was found to increase steadily up to an Al:cat ratio of 1000:1, reaching a maximum productivity of 260 kg/mol (Table 2, entry 9). Further increasing the Al:cat ratio to 1500:1 resulted in a decrease in productivity; however, it did not alter the molecular weight of the resultant polyethylene (Table 2, entry 10). The absence of associative chain transfer events is further supported by the lack of olefinic end groups via ¹H NMR spectroscopy (Supporting Information Figs. S14 and S15).

These observations suggest that while activity of catalyst **2-Co** is directly dependent on Al:cat ratio, it is not readily susceptible to deleterious chain transfer to Al events, as is observed for catalyst **1-Co**. We hypothesize that chain transfer to Al is avoided due to the extreme steric bulk of the dibenzhydryl substituted ligand and effective steric congestion of the active Co-center's axial coordination sites.

Evaluating the Thermal Stability of 1-Co and 2-Co

To evaluate the thermal stability of precatalysts **1-Co** and **2-Co**, ethylene polymerizations were conducted at 80, 90, and 100 °C under constant ethylene feed pressure (30 psi). Although catalyst **2-Co** displays optimal productivity when using an Al:cat ratio of 1000:1, a lower ratio of 300:1 was chosen for this study so that chain-transfer to aluminum is minimized when studying comparative polymerizations using precatalyst **1-Co**. Furthermore, although the exact deactivation pathways for Fe- and Co-based bis(imino)pyridine catalysts are not fully known,⁴² we suspected that chain transfer to aluminum could be a potential source of catalyst deactivation and ultimately complicate a direct comparison between the temporal thermal stability profiles of catalyst **1-Co**.

To study the temporal thermal stability of precatalysts **1-Co** and **2-Co**, polyethylene productivities were monitored as a function of time. In these studies, a linear increase in



FIGURE 3 Plot of polyethylene productivity versus time for precatalyst **1-Co**. Polymerization conditions: [**1-Co**] = 5 μ mol, 30 psi ethylene, 50 mL toluene, 300 equiv MAO. [Color figure can be viewed at wileyonlinelibrary.com]

productivity versus time is expected if the catalyst is stable at a given temperature. Each reaction was equilibrated at the desired temperature (80, 90, or 100 °C) and ethylene pressure (30 psi) before being activated by injection of 300 equivalents of MAO. The polymerizations were stopped at the prescribed time interval by injecting methanol into the polymerization reactor, and the polymer samples were stirred in acidic methanol for 24 h to dissolve any polymeric MAO-based contaminants before being isolated and dried before analysis.

The results of this study are shown in Figure 3, where catalyst **1-Co** clearly shows little or no polyethylene productivity after the first ~ 20 min of polymerization, which clearly suggests deactivation of the catalyst. This same result was observed at each elevated temperature studied (80, 90, and 100 °C), and in each case catalyst **1-Co** was virtually inactive after just 30 min of polymerization time. Polymer molecular weights decreased as temperature was increased; however, no observable trends in polymer dispersity or molecular weight were observed as a function of time, which was expected for this non-living polymerization catalyst.



FIGURE 4 Plot of productivity versus time for precatalyst **2-Co.** Polymerization conditions: **[2-Co]** = 5 μ mol, 30 psi ethylene, 50 mL toluene, 300 equiv MAO. [Color figure can be viewed at wileyonlinelibrary.com]

In contrast, polymerizations using catalyst **2-Co**, which bears sterically demanding dibenzhydryl moieties, shows a perfectly linear increase in productivity as a function of time at 80 °C (Fig. 4). This suggests that catalyst 2-Co is thermally stable at 80 °C for the entire time period studied (70 min). Ethylene polymerizations at even higher temperatures revealed that polyethylene productivity deviates from linearity at 90 °C and shows significant deviation from linearity at 100 °C, which we attribute to decomposition or deactivation of the active catalytic species. Although catalyst 2-Co is not perfectly stable at 90 °C, it shows only slightly diminished productivity after 1 h of polymerization and is far more stable at this temperature than catalyst **1-Co** which is virtually inactive after 50 min. In similarity to catalyst 1-Co, polymer molecular weights generally decreased as temperature was increased; however, no observable trends in polymer dispersity or molecular weight were observed as a function of time, which again was expected for this non-living polymerization catalyst.

Although the detailed decomposition pathways of bis(imino)pyridine-ligated Fe- and Co-based catalysts are not fully understood, we attribute the enhanced thermal stability of catalyst **2-Co** (at 80 °C and 90 °C), relative to **1-Co**, to the bulky dibenzhydryl *N*-aryl moieties of the ligand backbone. We hypothesize that the extreme steric demand of **2-Co** ligand severely inhibits *N*-aryl rotations and rigidifies the catalyst structure. This rigid ligand effectively blocks the axial coordination sites of the active Co metal center and prevents deleterious reactions that lead to the premature deactivation or decomposition of catalyst **2-Co**.^{15,20}

Finally, several structural parameters have been previously proposed to influence catalyst thermal stability. These include the presence of short metal to nitrogen bond lengths, and the presence of a firm/rigid ligand framework.³³ Catalyst **2-Co** clearly represents a complex in which ligand rigidity is enhanced due to steric constraints, and based upon the trends presented herein support those hypotheses.

CONCLUSIONS

In sum, we synthesized and evaluated the ethylene polymerization behavior of catalysts **2-Fe** and **2-Co**. Upon activation with MAO, catalyst **2-Fe** was found to be essentially inactive for ethylene polymerizations while catalyst **2-Co** showed good polymerization activity and was used for the fundamental studies presented herein. Specifically, the timeresolved thermal stability of catalyst **2-Co**, and its sensitivity to Al:cat ratio were investigated relative to the extensively studied catalyst **1-Co**.

Through these investigations, it was found that catalyst **2-Co** displays virtually no deleterious chain transfer to Al events, which is in stark contrast to the results obtained for **1-Co**. Furthermore, catalyst **2-Co** demonstrates near perfect time-resolved thermal stability at 80 °C and greatly enhanced thermal stability at 90 °C as compared to catalyst **1-Co**. We attribute this enhancement in thermal stability and decrease in



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deleterious chain transfer to Al events to sterically demanding dibenzhydryl substituted ligand framework of catalyst **2**-**Co**. These bulky substituents are proposed to restrict *N*-aryl rotations and effectively block the axial coordination sites of the active metal center. We hypothesize that this steric protection mitigates any unwanted reactions that lead to premature catalyst transfer, deactivation, and/or decomposition.

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