Copper(II) Ethylene Polymerization Catalysts: Do They Really Exist?

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The reactions of two types of copper(II) ethylene polymerization catalysts, $[(\mathrm{sal})\mathrm{CuCl}]_2$ (sal = 2-{C(H)=N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}-4,6-^{t}Bu$_2$-phenoxide) and (α-diimine)CuCl$_2$ (α-diimine = [(2,6-^{i}Pr$_2$-C$_6$H$_3$)-N=C(Me)]$_2$), with methylaluminoxane (MAO) and trimethylaluminum (TMA) have been investigated. In both examples, facile and irreversible ligand (L) transfer from copper to TMA present in MAO was observed, resulting in formation of the corresponding (sal)AlMe$_2$ and (imino-amido)AlMe$_2$ complexes. The (imino-amido)AlMe$_2$ complex is formed by α-diimine ligand transfer to aluminum followed by alkylation of one imino moiety in the ligand backbone. Both aluminum complexes were active catalysts for ethylene polymerization with activities similar to their Cu(II) precursors. Simple addition of a neutral salicylaldimine or α-diimine ligand to MAO in the absence of any copper species resulted in the formation of the corresponding LAlMe$_2$ complexes, which are again active for ethylene polymerization. These results indicate that ethylene polymerization does not occur by a migratory insertion mechanism at the copper center, but is the result of ligand transfer to aluminum, and it is the resulting LAlMe$_2$/LAlMe$^+$ complexes that are likely the active species.

Introduction

Early transition metal complexes have long dominated the field of homogeneous ethylene polymerization and have been the subject of numerous reviews.[1] Research into late transition metal systems began in earnest when Brookhart discovered that α-diimine-ligated nickel and palladium systems produced high molecular weight polyethylene with an activity comparable to early transition metal systems.[2] Since this discovery, there has been tremendous research into a variety of late transition metal systems, and this has been the subject of several recent reviews.[3] One general trend that has emerged is to explore the reactivity of transition metals not previously known to polymerize ethylene via a migratory insertion mechanism. Late transition metal species have been especially targeted for the development of catalysts for the copolymerization of ethylene with polar monomers due to their greater functional group tolerance.[4] Direct copolymerization of ethylene with polar monomers remains one of the most sought after goals in the design of new olefin polymerization catalysts. Copper has become an attractive candidate for the homo- and copolymerization of ethylene with functionalized monomers. It was only recently that the first reports of copper complexes being active for the polymerization of ethylene to high molecular weight polyethylene were reported by the groups of Stibrany and Gibson employing either (bisbenzimidazole)CuCl$_2$ systems[5] (**1**) or (α-diimine)CuCl$_2$ (**2**).[6] Since then, several other reports have emerged of LCuCl$_2$ or L$_2$Cu complexes employing salicylaldiminato[7] (**3**), pyrazolylpyrimidine[8] (**4**), and chiral pyrazolylquinoline[9] (**5**) ligands that were also active for ethylene polymerization (Figure 1). Apart from complex **3**, all the reported copper precatalysts maintain a very similar coordination environment about the metal center. In all cases, methylaluminoxane (MAO) was used as a cocatalyst with moderate to very low activities and high polymer molecular weights reported (Table 1). No mechanism for polymerization was deduced, although a coordination/insertion mechanism was postulated in some cases.[5]

We initially intended to investigate the generality of homogeneous Cu(II) systems for ethylene polymerization and the factors that influence both catalyst activity and polymer molecular weight. However, given that no Cu(II) alkyl species has ever been isolated due to rapid reduction at the metal center,[10] it appeared unlikely that ethylene polymerization could occur by a migratory insertion mechanism at the Cu(II) center. While

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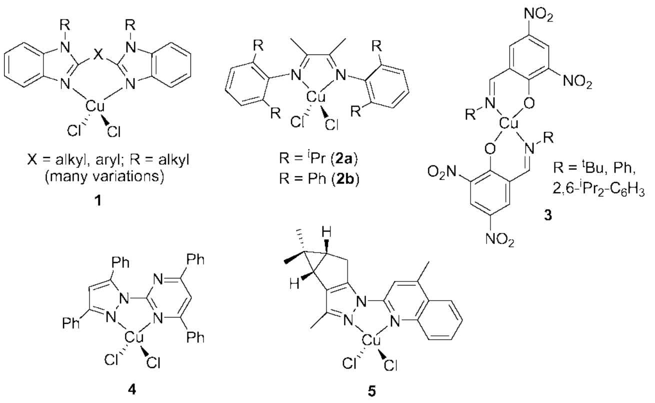


Figure 1. Reported Cu(II) ethylene polymerization precatalysts.

Table 1. Results of Ethylene Polymerization Studies[a]

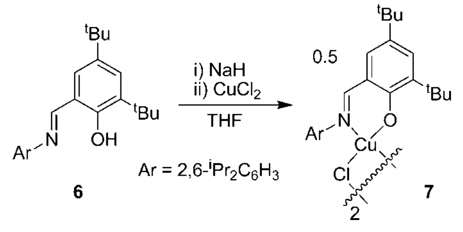
entry	precat.	MAO (equiv)	*P* (atm)	*T* (°C)	yield (g)	activity (g PE/mmol)	M_w	M_w/M_n
1	**6**	200	4.7	70	0.028	1.4	7.2×10^5	3.6
2	**7**	200	4.7	70	0.034	1.7	1.0×10^5	1.5
3	**8**	200	4.7	70	0.046	2.3	1.1×10^6	3.3
4	**9**	200	4.7	70	0.031	1.6	6.7×10^5	2.0
5	**10**	200	4.7	70	0.007	0.35	1.4×10^6	5.5
6	**11**	200	4.7	70	0.030	1.5	4.1×10^5	1.1
7	**2a**	200	4.7	70	0.010	0.5	4.2×10^5	1.1
8[b]		3 mL	4.7	70	0	0		
9[5]	**1**	>200	50	80			"high"	
10[56]	**2a**	500	5.0	70	trace		$>5 \times 10^6$	
11[6]	**2b**	500	4.5	20	0.4	23	$>5 \times 10^6$	
12[7]	**3**	200	80	80	0.11	5.5		
13[7]	**4**	500	10	35	0.7	350		
14[9]	**5**	500	10	35	1.3	650		

[a] Reaction conditions: Fischer-Porter glass reactor, toluene (20 mL), precatalyst (20 μmol), reaction time: 24 h. Average of 2 experiments. Molecular weights determined by GPC at 140 °C. [b] Control experiment performed in the absence of any complex or ligand (3 mL = 200 equiv for entries 1−7). For entries 9−14, results taken from the literature.[5−9]

many Cu(I) alkyl species exist, they are usually unstable at ambient temperatures unless supported by bulky electron-rich phosphine or N-heterocyclic carbene ligands.[11]

We now propose that ethylene polymerization does not occur by a migratory insertion mechanism at the copper center, but in fact ligand transfer occurs from copper to trimethylaluminum (TMA) present in MAO, and it is the resulting aluminum alkyl complexes ($LAlMe_2$/$LAlMe^+$) that are likely the active species for ethylene polymerization. Commercial MAO solutions contain large amounts of trimethylaluminum (30−35%),[12] and aluminum complexes are well known to polymerize ethylene,[13] although the polymerization mechanism in these systems is poorly understood.[14] Facile ligand transfer from nickel to aluminum has been previously reported by Collins et al. employing electron-rich Ni(II) iminophosphonamide complexes in the presence of TMA.[15] Herein we detail ligand transfer studies between copper and aluminum and ethylene polymerization activities of the resulting complexes.

Scheme 1



Results and Discussion

To investigate the reactivity of copper(II) complexes with aluminum alkyl species, we first synthesized a (sal)Cu(II) complex (sal = salicylaldiminato). The particular interest in bulky sal ligands stems from neutral nickel ethylene polymerization catalysts, (sal)Ni(Ph)PPh_3, developed by Grubbs.[16] Reaction of the sodium salt of bulky salicylaldimine **6** with $CuCl_2$ resulted in formation of $[(sal)CuCl]_2$ (**7**) as a paramagnetic ($\mu_{eff} = 2.23\ \mu_B$) dark green solid in 74% yield (Scheme 1). In the IR spectra of **7**, the azomethine band ($\nu_{CN} = 1612$ cm^{-1}) is shifted to lower wavenumber compared to that of the free ligand ($\nu_{CN} = 1622$ cm^{-1}), consistent with coordination through the azomethine nitrogen. Elemental analysis is consistent with the proposed structure for **7**, and a crystal structure determination clearly showed that **7** is a dinuclear chloride-bridged dimer in the solid state, consistent with previously proposed structures for a $[(sal)CuCl]_2$-type complex (Figure 2).[17,18] Somewhat surprisingly, given the near ubiquitous employment of sal ligands across the periodic table, dinuclear four-coordinate chloride-bridged $[(sal)CuCl]_2$ complexes are rare species with no previous characterization by crystallography. The crystal structure of **7** shows that the geometry about each metal center is a distorted square-planar environment, as indicated by N−Cu−O/Cl−Cu−Cl dihedral angles of 18° and 22° for Cu1 and Cu2, respectively. The Cu1···Cu2 distance is 3.330 Å.

Upon activation with MAO, copper complex **7** was active for ethylene polymerization, albeit with low activity (Table 1).

Addition of the neutral salH ligand **6** to MAO *in the absence* of any copper complex resulted in the formation of species that

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(18) X-ray structure determination of **7**: $C_{54}H_{76}Cl_2Cu_2N_2O_2$, M_w 983.15, dark green, crystal size (0.20 × 0.10 × 0.10 mm^3), triclinic, space group $P\bar{1}$, a = 12.7591(6) Å, b = 14.5248(9) Å, c = 17.2981(11) Å, α = 111.594(2)°, β = 100.070(3)°, γ = 104.797(3)°, V = 2750.0(3) Å^3, Z = 2, D_{calc} = 1.187 Mg/m^3, F(000) = 1044, T = 295(2) K, Mo Kα radiation (0.71073 Å, μ 0.908 mm^{-1}). 14 021 collected reflections, 8701 unique (R_{int} = 0.0390); final R indices [$I > 2\sigma(I)$] were R1 = 0.0512, wR2 = 0.1095, R indices (all data): R1 = 0.0832, wR2 = 0.1242; data/restraints/parameters 8701/0/578; GoF = 1.053. Largest peak and hole 0.474 and−0.400 e Å^{-3}.

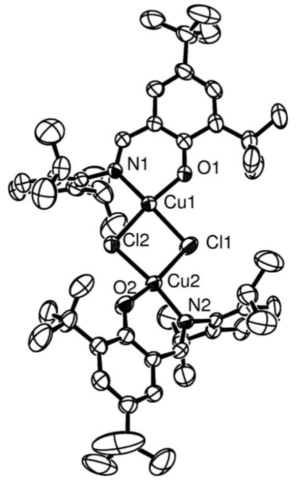
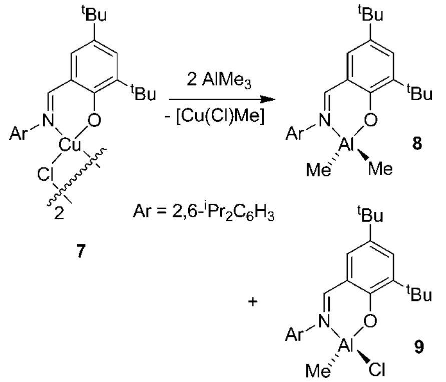


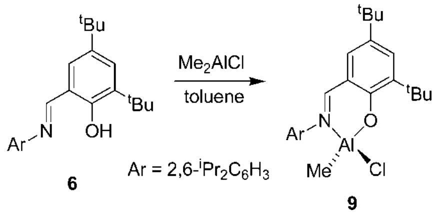
Figure 2. ORTEP plot of **7** at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl(1)−Cu(2) = 2.2590(11), Cl(1)−Cu(1) = 2.3020(12), Cu(1)−O(1) = 1.861(2), Cu(1)−N(1) = 1.954(3), Cu(1)−Cl(2) = 2.2629(10), Cu(2)−Cl(1)−Cu(1) = 93.77(4), O(1)−Cu(1)−N(1) = 94.37(11), O(1)−Cu(1)−Cl(2) = 164.79(9), N(1)−Cu(1)−Cl(2) = 96.07(9), O(1)−Cu(1)−Cl(1) = 86.99(8), N(1)−Cu(1)−Cl(1) = 167.45(10), Cl(2)−Cu(1)−Cl(1) = 85.22(4).

Scheme 2

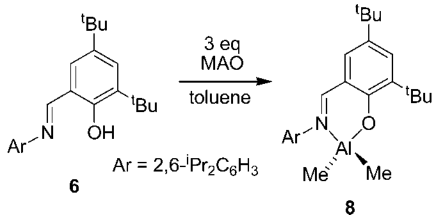


were also active for ethylene polymerization with similar activity to that of **7** (Table 1). Thus, it appeared that copper was not required to initiate ethylene polymerization. To investigate if ligand transfer was occurring from copper to aluminum, stoichiometric reactions of **7** with trimethylaluminum (TMA) were carried out. Commercial MAO solutions contain high amounts of TMA (30−35%)[12] with a significant percentage remaining present in MAO even after distillation.[19] This is due to the fact that TMA in MAO solutions can exist in two distinct forms: first as "free" TMA in its dimeric form, Al_2Me_6, and second as complexed TMA, associated with the various MAO chains.[12] Upon addition of 2 equiv of TMA to **7** in toluene, the dark green solution immediately became pale yellow. After filtration and removal of solvent, a yellow powder was isolated. Analysis by ^{1}H NMR revealed that the reaction of **7** with TMA resulted in ligand transfer to aluminum, yielding two products, (sal)$AlMe_2$ (**8**) and (sal)Al(Cl)Me (**9**), in a 1:1 ratio in 85% isolated yield (Scheme 2). The resulting products showed that not only does sal ligand transfer occur from copper to aluminum but chloride/methyl metathesis also occurs between the two metal centers. The final fate of the copper species was not ascertained.

Scheme 3



Scheme 4



No attempt to separate **8** from **9** was made; however, the identity of both species was further confirmed by comparison to independently synthesized samples of **8** and **9**. The (sal)$AlMe_2$ complex, **8**, has been previously reported by Gibson and is active for ethylene polymerization when activated with $B(C_6F_5)_3$.[13c,d] (Sal)Al(Cl)Me (**9**) is readily synthesized by reaction of the neutral salH ligand **6** with Me_2AlCl in 96% yield (Scheme 3). Both **8** and **9** were active for ethylene polymerization in the presence of MAO and have similar activities (Table 1). SalH ligand **6** was also reacted with 3 equiv of MAO in place of TMA which resulted in formation of (sal)$AlMe_2$ complex **8** in 95% yield (Scheme 4). Using the phosphine method developed by Andrew Barron,[20] the percentage of the total aluminum content existing as TMA in the commercially obtained MAO solution was determined to be 35%. Therefore, 3 equiv of MAO was employed, resulting in approximately 1 equiv of TMA per salH ligand. Control polymerization experiments where MAO was used in the absence of any complex or ligand did not yield any solid polyethylene (Table 1).

Having demonstrated that a copper(II) precatalyst of our own design, upon reaction with TMA or MAO, resulted in facile ligand transfer to aluminum and that these species were active for ethylene polymerization in the absence of copper species, we set about investigating if the same results would be observed with Gibson's (α-diimine)$CuCl_2$ complex, **2a**.

In our hands, precatalyst **2a** was indeed active for ethylene polymerization in the presence of MAO, again with very low activity (Table 1). Addition of the neutral α-diimine ligand **10** to MAO *in the absence* of any copper species resulted in the formation of species that were also active for ethylene polymerization with similar activity to that of **2a** (Table 1). Reaction of (α-diimine)$CuCl_2$ **2a** with TMA resulted in formation of aluminum complex **11**; however, rather than having a neutral diimine coordinated to the aluminum center, alkylation of one of the imino moieties of the ligand backbone occurred, resulting in formation of (imino-amido)$AlMe_2$ complex **11** as the major product (Scheme 5). This reaction did not proceed as cleanly as the analogous reaction for [(sal)$CuCl]_2$ (**7**). One other species was present in the reaction mixture that has not yet been identified. (Formation of the analogous (imino-amido)Al(Cl)Me has been ruled out, as it was independently synthesized and spectral data were compared.) To further confirm the identity of the major product from Scheme 5, α-diimine **10** (the neutral

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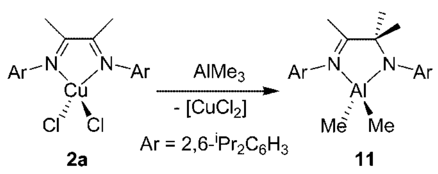
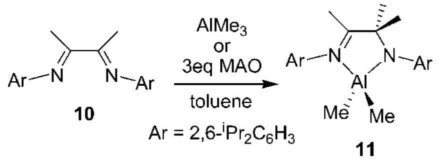
Scheme 5



Scheme 6



ligand from **2a**) was reacted with 1 equiv of TMA in toluene, resulting unequivocally in the formation of **11** in 71% yield (Scheme 6). The alkylation of an imino moiety of a diimine ligand, upon reaction with TMA, has previously been observed for both α-diimine and pyridine-diimine ligands.[13f,21] The ^{1}H NMR spectra for **11** indicated a loss of symmetry in the ligand and formation of a C_s symmetric species with one singlet for the imino-methyl group at 1.42 ppm integrating for three protons and another singlet for the two amino-methyl groups at 1.15 ppm integrating for six protons. Characteristic high-field resonances for the aluminum methyl groups are observed at −0.40 ppm (s, 6H). Single crystals of **11** were obtained from a concentrated toluene solution at −25 °C, thus allowing for an X-ray structure determination (Figure 3).[22] The X-ray data showed that the N1−C1−C2−N2 portion of the imino-amido ligand is almost planar, with a torsional angle of 3.9°. The aluminum atom lies within this plane and adopts a distorted tetrahedral geometry. The Al−Me distances are identical at 1.961(3) Å. As expected, the Al−N bond with the formally negatively charged amido nitrogen N1 is significantly shorter at 1.845(2) Å than the neutral imino nitrogen Al−N2 at 1.980(2) Å.

α-Diimine **10** was also reacted with 3 equiv of MAO in place of TMA, which again resulted in formation of (imino-amido)AlMe$_2$ complex **11** in 78% isolated yield (Scheme 6).

In conclusion, we have shown in two separate examples of copper(II) complexes active for ethylene polymerization in the presence of MAO that the copper itself was not required to initiate polymerization. In both cases, facile ligand transfer takes place from the LCu(II) complexes to trimethylaluminum, resulting in formation of the corresponding LAlMe$_2$ complexes. The same aluminum species can be generated by simple ligand addition to MAO in the absence of any copper species, and the resulting aluminum complexes are all active catalysts for ethylene polymerization, albeit with low activity.

For over a decade now, well-defined aluminum alkyl complexes have been reported to produce polyethylene.[13] While it now appears unlikely that a copper species can be an active catalyst for ethylene polymerization under mild conditions due to ligand transfer to aluminum, it remains unclear what the mechanism for polymerization is for aluminum or even if the aluminum complexes are directly responsible for the observed catalytic activity.[14,23]

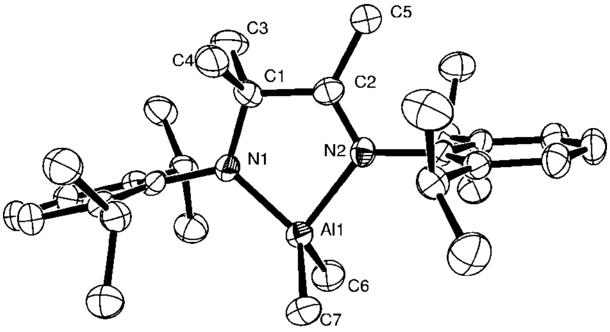


Figure 3. ORTEP plot of **11** at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 1.845(2), Al(1)−C(7) = 1.961(3), Al(1)−C(6) = 1.961(3), Al(1)−N(2) = 1.980(2), N(1)−C(1) = 1.477(3), N(2)−C(2) = 1.303(4), C(7)−Al(1)−C(6) = 108.21(15), N(1)−Al(1)−N(2) = 84.59(10).

Experimental Section

General Information. Unless otherwise stated, all reactions were performed under N$_2$ or vacuum using standard Schlenk techniques or in a N$_2$-filled drybox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated oil baths. All melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm in reference to the residual ^{1}H and ^{13}C resonances of CDCl$_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.24) and C$_6$D$_6$ (^{1}H: δ 7.16). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Elemental analyses for the air-sensitive alkylaluminum complexes **9** and **11** were performed by Midwest Microlabs. IR data was collected by diffuse reflectance spectroscopy. GPC data were obtained from a Viscotek high-temperature GPC. Methylaluminoxane (10 wt % in toluene), dimethylaluminum chloride (1.0 M in hexanes), and trimethylaluminum (2.0 M in toluene) were purchased from the Sigma-Aldrich Chemical Co. The percentage of the total aluminum content existing as TMA in the MAO solution was determined to be 35%.[20] Salicyaldimine (**6**),[13d] (sal)AlMe$_2$ (**8**),[13d] α-diimine (**10**),[2] and (α-diimine)CuCl$_2$ (**2a**)[6] were all synthesized according to literature procedures.

Synthesis of [(sal)CuCl]$_2$ (7). A 100 mL round-bottom flask was charged with salicylaldimine **6** (0.500 g, 1.27 mmol) and THF (20 mL). Two equivalents of NaH (0.062 g, 2.56 mmol) was slowly added, and the suspension was stirred for 1 h and filtered to remove excess NaH. The filtrate then added to a second round-bottom flask containing 1.5 equiv of CuCl$_2$ (0.255 g, 1.89 mmol). The yellow filtrate immediately turned dark brown. The reaction mixture was allowed to stir 24 h, whereupon it was filtered and the solvent removed under vacuum, resulting in a dark green solid. The product was crystallized from a concentrated 1:1 solution of hexane and toluene at −25 °C (0.462 g, 74%). $\mu_{\text{eff}} = 2.23\ \mu_{\text{B}}$. IR (KBr, cm^{-1}): 2960 (s), 2906 (s), 2868 (s), 1612 ν(C=N), 1599 (s), 1585 (s), 1551 (s), 1530 (s), 1462 (s), 1442 (s), 1426 (s), 1384 (s), 1362 (s), 1326 (s), 1272 (s), 1255 (s), 1168 (s), 800 (s), 786 (s), 765 (s).

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[22] X-ray structure determination of **11**: C$_{31}$H$_{49}$AlN$_2$, M_w 476.70, colorless, crystal size (0.12 × 0.12 × 0.03 mm^3), triclinic, space group $P\bar{1}$, a = 8.4373(5) Å, b = 9.7007(5) Å, c = 19.3460(11) Å, α = 82.033(4)°, β = 80.769(3)°, γ = 69.565(3)°, V = 1458.71(14) Å^3, Z = 2, D_{calc} = 1.085 Mg/m^3, F(000): 524, T = 173(2) K, Mo Kα radiation (0.71073 Å; μ 0.090 mm^{-1}). 9900 collected reflections, 5436 unique (R_{int} = 0.0631); final R indices [$I > 2\sigma(I)$] were R1 = 0.0679, wR2 = 0.1354, R indices (all data): R1 = 0.1129, wR2 = 0.1551; data/restraints/parameters 5436/0/321; GoF = 1.033. Largest peak and hole 0.613 and −0.266 e Å^{-3}.

[23] It has been suggested that even ppb levels of transition metals may significantly affect polymerization results: Budzelaar, P. H. M.; Talarico, G. *Struct. Bonding (Berlin)* **2003**, *105*, 141.

Anal. Calcd for $C_{54}H_{76}Cl_2Cu_2N_2O_2$: C 65.97, H 7.79, N 2.85. Found: C 65.63, H 8.01, N 2.71. Mp: 176−178 °C (dec).

Synthesis of (sal)Al(Cl)Me (9). A 100 mL round-bottom flask was charged with salicylaldimine **6** (0.158 g, 0.402 mmol) and toluene (20 mL). Dimethylaluminum chloride (0.40 mL, 1.0 M in hexanes, 0.40 mmol) was added dropwise via syringe and the solution stirred for 24 h at ambient temperatures. The solution was filtered and excess solvent was removed under vacuum, resulting in a yellow solid (0.180 g, 96%). ^{1}H NMR (C_6D_6): δ 7.90 (s, 1H, Ar-N=C*H*-Ar), 7.77 (d, J = 2.6, 1H, NCAr-*H*), 7.12−7.08 (m, 3H, NAr-*H*), 6.92 (d, J = 2.6, 1H, NCAr-*H*), 3.53 (sept, J = 6.7, 1H, C*H*(CH_3)$_2$), 2.97 (sept, J = 6.7, 1H, C*H*(CH_3)$_2$), 1.58 (s, 9H, ^{t}Bu), 1.35 (d, J = 6.7, 3H, CH(CH_3)$_2$), 1.22 (s, 9H, ^{t}Bu), 1.12 (d, J = 6.7, 3H, CH(CH_3)$_2$), 0.87 (d, J = 6.7, 3H, CH(CH_3)$_2$), 0.70 (d, J = 6.7, 3H, CH(CH_3)$_2$), −0.11 (s, 3H, AlCH_3). ^{13}C NMR ($CDCl_3$): δ 175.49 (C=N), 161.92, 143.61, 142.60, 141.36, 141.10, 134.36, 129.12, 128.78, 125.24, 124.07, 118.21, 35.64, 34.39, 31.39, 29.63, 28.84, 28.39, 26.43, 26.40, 23.54, 22.35. Anal. Calcd for $C_{28}H_{41}AlClNO$: C 71.54, H 8.79, N 2.98. Found: C 71.33, H 8.69, N 2.94. EI-MS (*m/z*): calcd for $C_{27}H_{38}AlClNO$ $[M - CH_3]^+$ 454.2, found 454.3.

Ligand Transfer between [(sal)CuCl]$_2$ (7) and AlMe$_3$. A 100 mL round-bottom flask was charged with [(sal)CuCl]$_2$ (**7**) (0.201 g, 0.205 mmol) and toluene (20 mL). Two equivalents of trimethylaluminum (0.23 mL, 2.0 M in toluene, 0.46 mmol) was added dropwise via syringe, and the solution was stirred for 24 h. Upon addition of trimethylaluminum, the dark green solution immediately turned bright yellow. The resulting reaction mixture was filtered and solvent removed under vacuum, resulting in formation of a yellow solid (0.179 g, 85% yield based on 1:1 ratio of **8** and **9**). Only two products were observed by ^{1}H NMR, consisting of a 1:1 mixture of (sal)AlMe$_2$ (**8**) and (sal)Al(Cl)Me (**9**). Identity of products was confirmed by comparison to independently synthesized samples of **8** and **9**.

Synthesis of (sal)AlMe$_2$ (8) from Salicylaldimine (6) and MAO. A 100 mL round-bottom flask was charged with salicylaldimine **6** (0.104 g, 0.265 mmol) and toluene (20 mL). Three equivalents of methylaluminoxane (0.51 mL, 10 wt % in toluene, 0.76 mmol) was added dropwise via syringe and the solution stirred for 24 h. After stirring, the solution was filtered and the solvent was removed under vacuum, resulting in a yellow solid. ^{1}H NMR showed formation of **8** as the only observed species along with residual MAO (0.113 g, 95%). ^{1}H NMR (C_6D_6): δ 7.86 (s, 1H, Ar-N=C*H*-Ar), 7.74 (d, ^4J = 2.4, 1H, NCAr-*H*), 7.15−7.0 (m, 2H, NAr-*H*), 7.05 (s, 1H, NAr-H), 6.91 (d, ^4J = 2.4, 1H, *p*-NCAr-*H*), 3.17 (sept, J = 6.7, 2H, C*H*(CH_3)$_2$), 1.60 (s, 9H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 1.19 (d, J = 6.7, 6H, CH(CH_3)$_2$), 0.81 (d, J = 6.7, 6H, CH(CH_3)$_2$), −0.24 (s, 6H, Al(CH_3)$_2$).

Synthesis of (imino-amido)AlMe$_2$ (11). A round-bottom flask was charged with toluene (20 mL) and α-diimine ligand **10** (0.170 g, 0.421 mmol). Trimethylaluminum (0.22 mL, 2.0 M in toluene, 0.44 mmol) was added dropwise via syringe and the solution stirred for 24 h. The initial bright yellow solution of **10** changed to a pale yellow upon addition of trimethylaluminum. The solution was filtered and solvent removed under vacuum, resulting in formation of a white solid. The product was crystallized from a concentrated toluene solution at −25 °C (0.141 g, 71%). ^{1}H NMR (C_6D_6): δ 7.25 (m, 3H, Ar-*H*), 7.10 (m, 3H, Ar-*H*), 3.93 (sept, J = 6.7, 2H, C*H*(CH_3)$_2$), 3.11 (sept, J = 6.7, 2H, C*H*(CH_3)$_2$), 1.42 (s, 3H, H_3C−C=N), 1.39 (d, J = 6.7, 6H, CH(CH_3)$_2$), 1.31 (d, J = 6.7, 6H, CH(CH_3)$_2$), 1.28 (d, J = 6.7, 6H, CH(CH_3)$_2$), 1.15 (s, 6H, (CH_3)$_2$C−N), 0.96 (d, J = 6.7, 6H, CH(CH_3)$_2$), −0.40 (s, 6H, Al(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 199.09, 151.54, 147.53, 143.03, 141.61, 138.74, 125.19, 124.31, 67.84, 28.58, 28.23, 27.99, 25.13, 24.84, 24.63, 24.54, 18.43, −6.53. Anal. Calcd for $C_{31}H_{49}AlN_2$: C 78.10, H 10.36, N 5.88. Found: C 77.82, H 10.05, N 5.57. EI-MS (*m/z*): calcd for $C_{30}H_{46}AlN_2$ $[M - CH_3]^+$ 461.3, found 461.4.

Ligand Transfer between (α-diimine)CuCl$_2$ (2a) and AlMe$_3$. A round-bottom flask was charged with toluene (20 mL) and (α-diimine)CuCl$_2$ **2a** (0.157 g, 0.291 mmol). Trimethylaluminum (0.201 mL, 2.0 M in toluene, 0.402 mmol) was added dropwise via syringe and the solution stirred for 24 h. The initial dark brown solution changed to a pale orange color upon addition of trimethylaluminum. After stirring, the solution was filtered and the solvent removed, resulting in formation of an orange solid. The ^{1}H NMR showed the presence of (imino-amido)AlMe$_2$ (**11**) as the dominant species; however one other species was also observed by ^{1}H NMR, which has not been identified.

Synthesis of (imino-amido)AlMe$_2$ (11) from α-Diimine 10 and MAO. A 100 mL round-bottom flask was charged with diimine ligand **10** (0.107 g, 0.265 mmol) and toluene (40 mL). Three equivalents of methylaluminoxane (0.58 mL, 10 wt % in toluene, 0.86 mmol) was added dropwise via syringe and the solution stirred for 24 h. After stirring, the solution was filtered and the solvent was removed under vacuum, resulting in a yellow solid. ^{1}H NMR showed formation of **11** as the only observed species along with residual MAO (0.098 g, 78%).

General Ethylene Polymerization Procedure. In a glovebox, the precatalyst (20 μmol) was dissolved in toluene (20 mL) in a Fischer-Porter bottle. The bottle was connected to a valve-polymerization system, sealed, and taken out of the glovebox. The system was connected to a Schlenk line, purged three times with N_2, and filled with 10 psi of ethylene. A 200 equiv amount of MAO (10 wt % in toluene) was added via syringe, and the ethylene pressure increased to 70 psi. The reaction mixture stirred for 24 h while heating at 70 °C. After stirring, the reaction was quenched with 1 M acidified methanol and filtered, and the resulting polymer was washed with 1 M acidified methanol, followed by methanol. The polymer was dried under vacuum. Molecular weights and M_w/M_n were determined using a Viscotek high-temperature GPC at 140 °C.

X-ray Structure Determinations. Data were collected at room temperature for **7** and at −100 °C for **11** on a Nonius Kappa CCD diffractometer, using the COLLECT program.[24] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[25] SIR97[26] was used to solve the structure, and SHELXL97[27] was used to refine the structure. ORTEP-3 for Windows[28] was used for molecular graphics, and PLATON[29] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for all methyl H atoms and 1.2 times U_{eq} of the carrier atom for all other H atoms.

For complex **7**, most of the checkCIF ALERTs occur because the molecule has C atoms that are very rigidly held and others that have very great vibrational and rotational freedom. Thus, the first two A ALERTs come from this wide range of rigidity in the molecule. The third A ALERT (Check Low U_{eq} as compared to Neighbors for C42) occurs because C42 is the central atom of a *tert*-butyl group and is bonded to a phenyl ring, but the three attached methyl groups can rotate and vibrate freely. The first B ALERT occurs because the data were cut at 24.12°. The diffraction pattern became very weak beyond this angle. The other three B ALERTs occur because of the presence of isopropyl and *tert*-butyl groups. The central atom is attached directly to a phenyl ring and has a small U_{eq}, whereas the

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terminal methyl groups have much higher U_{eq}. C11 is a terminal methyl in a *tert*-butyl group. C12 is the central atom of an isopropyl group, and C25 is the central atom of a *tert*-butyl group.

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Supporting Information Available: Full crystallographic data for compounds **7** and **11** are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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