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Square-Planar Cu(II) Diketiminate Complexes in Lactide Polymerization

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Supporting Information

ABSTRACT: Cu(O*i*Pr)$_2$ was reacted with several β-diketimine ligands, *nacnac*^{R}H. Sterically undemanding ligands with *N*-benzyl substituents afforded the dimeric heteroleptic complexes [*nacnac*^{Bn}Cu(μ-O*i*Pr)]$_2$ and [3-Cl-*nacnac*^{Bn}Cu(μ-O*i*Pr)]$_2$ (Bn = benzyl). With sterically more demanding amines, dimerization was not possible, and the putative *nacnac*CuO*i*Pr intermediate underwent ligand exchange to the homoleptic bisdiketiminate complexes Cu(*nacnac*^{ipp})$_2$ and Cu(*nacnac*^{Naph})$_2$ (ipp = 2-isopropylphenyl, Naph = 1-napthyl). Homoleptic complexes were also prepared with *N*-benzyl ligands to yield Cu(*nacnac*^{Bn})$_2$ and Cu(3-succinimido-*nacnac*^{Bn})$_2$. All complexes were characterized by single-crystal X-ray diffraction. Even bulkier ligands with *N*-anthrylmethyl, *N*-mesitylmethyl, or *N*-methylbenzyl substituents failed to react with Cu(O*i*Pr)$_2$. In the case of *nacnac*^{dipp}CuO*i*Pr, putative *nacnac*^{dipp}CuO*i*Pr decomposed by β-hydride elimination. Heteroleptic complexes [*nacnac*^{Bn}Cu(μ-O*i*Pr)]$_2$ and [3-Cl-*nacnac*^{Bn}Cu(μ-O*i*Pr)]$_2$ are very highly active *rac*-lactide polymerization catalysts, with complete monomer conversion at ambient temperature in solution in 0.5−5 min. In the presence of free alcohol, the homoleptic complexes seem to be in equilibrium with small amounts of the respective heteroleptic complex, which are sufficient to complete polymerization in less than 60 min at room temperature. All catalysts show high control of the polymerization with polydispersities of 1.1 and below. The obtained polymers were essentially atactic, with a slight heterotactic bias at ambient temperature and at −17 °C.

INTRODUCTION

With the increasing use of plastics, concerns about the accumulation of plastic debris in the environment favor the use of polymers that are 100% biodegradable. One such polymer is polylactic acid (PLA), the condensation polymer of lactic acid.[1] PLA is currently marketed, albeit on a small scale for commodity polymers. It is biodegradable given the right conditions, since hydrolysis yields easily metabolized lactic acid. An additional advantage stems from the fact that lactic acid can be obtained by fermentation of natural products and does not depend—directly—on fossil fuels.[2]

Industrial production of PLA currently relies on the polymerization of lactide, the dimeric anhydride of lactic acid, using a nonselective tin catalyst, in particular Sn(Oct)$_2$, at elevated temperatures. Although only isotactic PLA is currently of commercial interest, the use of an unselective catalyst is possible since lactic acid is obtained from fermentation of natural products in enantiopure form. The polymerization of lactide has attracted in the past two decades considerable attention in the scientific community. This interest is fuelled partly by the potential of commercial applications, and partly by the lack of catalysts which combine properties such as correct stereocontrol, stability, activity, and polymer molecular weight control.

Establishing clear structure−reactivity relationships for lactide polymerization catalysts, which would enable rational catalyst design, is handicapped by the overall reversibility of the reaction, the presence of two important transition states for insertion and ring-opening of comparable energy,[3] the multitude of possible reaction pathways given the chirality of the catalyst, the polymer chain and the monomer, and interfering side reactions, such as chain transfer between catalyst centers or transesterification. While the existing literature is already too vast to be easily summarized,[4] some very general trends with regard to the central metal and typical coordination geometries can be seen: Following Spassky's initial work, five- or six-coordinated aluminum complexes can provide high stereocontrol toward either isotactic or heterotactic monomer enchainment, but suffer from reduced activities.[5] Indium (or gallium) analogues show in general higher activity. No highly isospecific and active catalyst has yet been reported,[6] but high selectivity for heterotactic enchainment can be achieved.[7] Group 3 and rare earth catalysts with a variety of coordination geometries are among the most active catalysts known and can yield highly heterotactic to moderately isotactic polymer.[8] Alkaline and earth alkaline compounds, again with a variety of coordination geometries, show low to high activities and in rare cases a moderate preference for isotactic monomer enchainment.[9] Group 4 metal catalysts, mostly of octahedral geometries, can show moderate amounts of isospecificity, but have in general low to moderate activity.[10]

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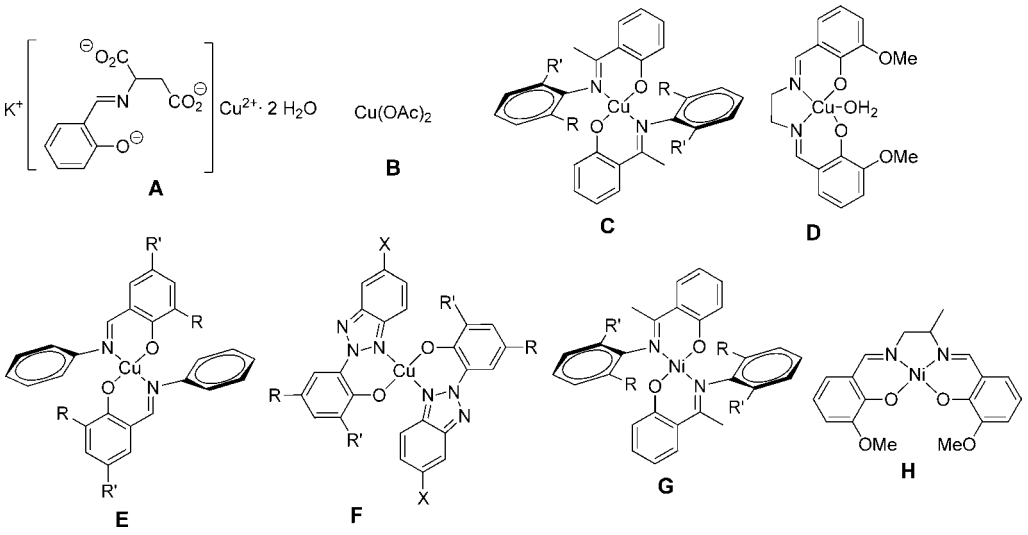


Figure 1. A: 97%, 24 h, 130 °C, molten monomer, lactide/Cu = 200.[14a] **B**: 97%, 8 h, 145 °C, molten monomer, lactide/Cu = 200.[14e] **C**: 76%, 4 h, 160 °C, molten monomer, lactide/Cu = 200.[14b] **D**: 52%, 24 h, 130 °C, molten monomer, lactide/Cu = 1000.[14d] **E**: 80%, 35 h, 70 °C, toluene, lactide/Cu = 50.[14c] **F**: >92%, 6 h, 110 °C, toluene, lactide/Cu = 400.[14f] **G**: no polymerization, 160 °C, molten monomer.[14b] **H**: 78%, 24 h, 130 °C, molten monomer, lactide/Cu = 1000.[15]

Tetrahedral Mg and Zn complexes have been investigated widely, following the seminal work of Coates et al.,[11] and show moderate to high activities.[12] They tend to produce heterotactic PLA by a chain-end control mechanism with high stereocontrol. Only in rare cases were low isospecificities observed.[13]

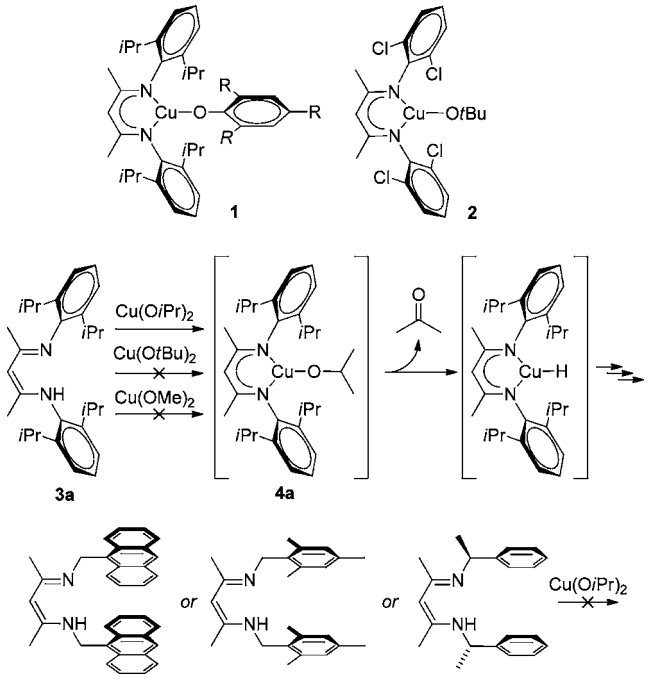
Despite the number of investigations into metal-catalyzed lactide polymerization, the use of catalysts with square-planar geometry was somewhat neglected. We are aware only of a limited number of examples reported for lactide polymerization based on copper(II)[14] and nickel(II) (Figure 1),[14b,15] and none for Cr(II), Pd(II), Pt(II), Rh(I), or Ir(I). The initial literature survey on copper(II) catalyzed lactide polymerization seems less than promising. While several catalysts were able to provide decent molecular weight control, they all required high temperatures, typically in molten monomer and showed only low activities even under those conditions.

A serendipitous choice of the right spectator ligand, however, showed that square-planar copper complexes can indeed be interesting candidates for lactide polymerization, and we recently reported preliminary results that $[(nacnac^{Bn}Cu(\mu\text{-}OiPr)]_2$ is highly active in lactide polymerization, reaching complete conversion of monomer in less than 1 min at room temperature ($nacnac^{Bn}$ = *N*,*N*-dibenzyl-pentane-2,4-diiminato, lactide/Cu = 300).[16] In the present manuscript, we extend these investigations to other *N*-alkyl and *N*-aryl copper(II) diketiminate complexes.

RESULTS AND DISCUSSION

Complex Syntheses. Only two examples of Cu(II) diketiminate alkoxide or aryloxide complexes have been reported in the literature. Tolman and co-workers prepared $nacnac^{dipp}CuOAr$, **1**, (dipp = 2,6-diisopropylphenyl, Scheme 1) from the reaction of $nacnac^{dipp}CuCl$ with thallium aryl oxides.[17] Warren and co-workers obtained $nacnac^{Ar}CuOtBu$, **2**, by oxidation of the respective Cu(I) complex with *tert*-butyl peroxide.[18] Since aryl oxides, as well as *tert*-butoxide groups tend to give slow polymerization initiation, our interest was focused on more reactive alkoxides, such as isopropoxide. We thus reacted $nacnac^{dipp}H$, **3a**, with $Cu(OiPr)_2$ in an attempt to prepare $nacnac^{dipp}CuOiPr$, **4a**, by a protonation route. Upon addition of the ligand, green $Cu(OiPr)_2$ solubilized and the color changed to brown, indicating that the ligand did indeed react with $Cu(OiPr)_2$. However, no isolable product could be obtained. Analysis of the volatiles of the reaction showed the presence of acetone. We speculate that **4a** was indeed formed as an intermediate, analogous to the reported three-coordinated complexes **1** and **2**. The latter do not contain β-hydrogen atoms on the alkoxide ligand and could be isolated. **4a**, on the other hand, undergoes β-H elimination to yield acetone and a putative Cu(II) hydride which, unsurprisingly, is unstable (Scheme 1). Direct hydride transfer to the diketiminate ligand following a Meerwein–Ponndorf–Verley mechanism would likewise yield acetone,[19] but seems less likely in this case.

Scheme 1



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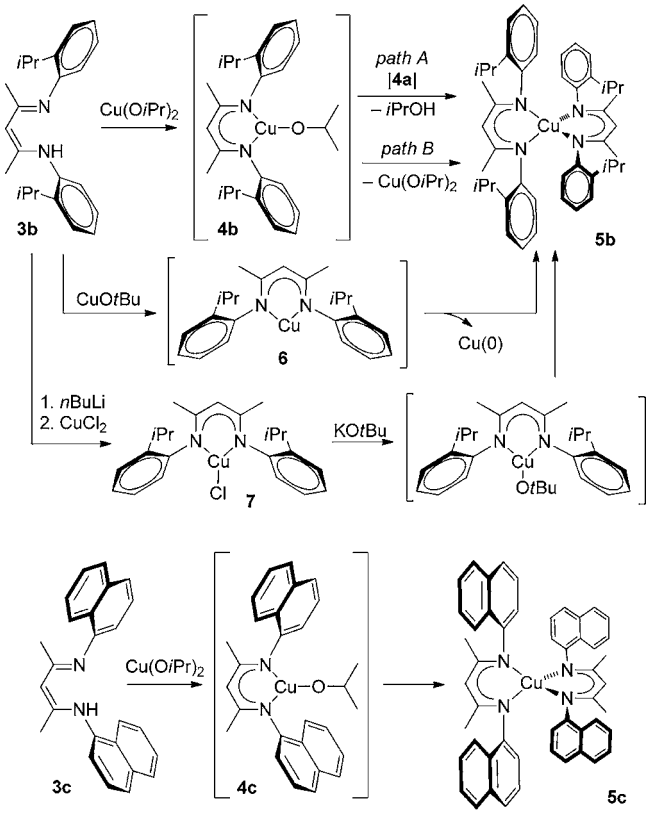
Alternative routes to *nacnac*^{dipp}CuOR likewise failed: Probably because of steric hindrance, *nacnac*^{dipp}H failed to react with Cu(O*t*Bu)$_2$ even at 100 °C (toluene), and only starting materials were observed. Surprisingly, Cu(OMe)$_2$ was unreactive as well. Other bulky diketimine ligands, such as *nacnac*^{An}H (An = 9-antrhylmethyl), *nacnac*^{Mes}H (Mes = mesitylmethyl), or *S,S-nacnac*^{R*}H (R* = α-methylbenzyl), failed to react even with Cu(O*i*Pr)$_2$.

Given the lack of reactivity with sterically encumbered diketimines, monosubstituted *nacnac*^{ipp}H, **3b**, (ipp = 2-isopropylphenyl, Scheme 2) was reacted with Cu(O*i*Pr)$_2$.

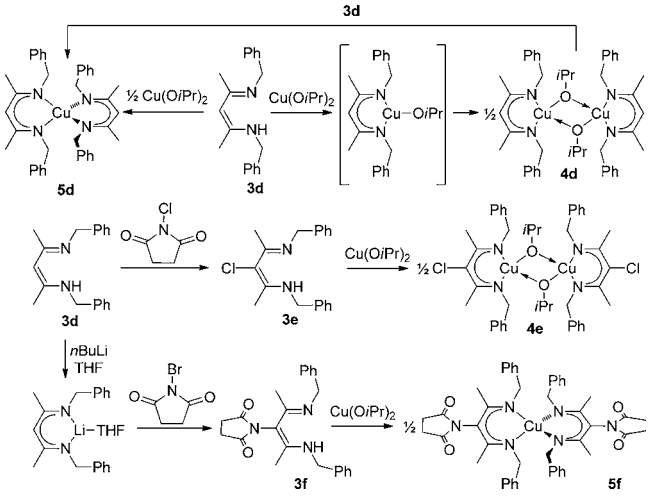
Scheme 2



However, instead of heteroleptic *nacnac*^{ipp}CuO*i*Pr, **4b**, the homoleptic bisdiketiminate complex (*nacnac*^{ipp})$_2$Cu, **5b**, was obtained, at a variety of reaction conditions. For comparison purposes, **5b** was prepared independently by reaction of 2 equiv of **3b** with Cu(O*i*Pr)$_2$. Attempts to obtain *nacnac*^{ipp}CuO*t*Bu by a route similar to the one used by Warren and co-workers for **2** failed because of the instability of the respective Cu(I) complex **6**, which disproportionated into Cu(0) and **5b**. An increased tendency for decomposition by disproportionation has been observed previously for Cu(I) diketiminate complexes with *N*-alkyl ligands, which required stabilization with an ancillary ligand.[20] Monosubstituted *N*-aryl diketimines seem to suffer from similar stability problems. Reaction of the lithiated ligand *nacnac*^{ipp}Li with $CuCl_2$[17] yielded the respective copper(II) chloride complex, **7**, but subsequent reaction with KOtBu did not yield the heteroleptic complex. Instead homoleptic **5b** was obtained again. The latter reaction provided some indications with regard to the inaccessibility of **4b**. In protonations of Cu(O*i*Pr)$_2$ with **3b**, the putative intermediate **4b** might either be kinetically labile, given that it might be more reactive toward a second protonation than insoluble Cu(O*i*Pr)$_2$ (Scheme 2, path A) or it is thermodynamically labile and undergoes ligand exchange to **5b** and Cu(O*i*Pr)$_2$ without further participation of **3b** (Scheme 2, path B). The fact that changing reaction conditions, that is, order of addition, reagent concentrations, or temperature, did not affect the reaction outcome already indicated that **4b** might rather be thermodynamically labile. This was confirmed in the salt metathesis reaction of **7** with KOtBu, since there is no possible pathway in which **5b** can be obtained as the kinetic product. Heteroleptic Cu(II) alkoxides with monosubstituted *N*-aryl substituents thus seem to be inherently labile toward ligand redistribution to form homoleptic, four-coordinate complexes. With the disubstituted *N*-aryl ligand **3a**, formation of a homoleptic bis(diketiminate) complex (*nacnac*^{dipp})$_2$Cu was most likely not possible because of the increased steric bulk of the disubstituted *N*-aryl, and decomposition of the intermediate **4a** via β-H elimination is presumed. A reactivity similar to that of **3b** was observed with *nacnac*^{Naph}H, **3c** (Naph = 1-naphthyl, Scheme 2), which also yielded the homoleptic complex (*nacnac*^{Naph})$_2$Cu, **5c**, upon reaction with Cu(O*i*Pr)$_2$.

Reaction of Cu(O*i*Pr)$_2$ with *nacnac*^{Bn}H, **3d**, finally afforded the heteroleptic complex (*nacnac*^{Bn}CuO*i*Pr)$_2$, **4d** (Scheme 3).[16]

Scheme 3



In Cu(I) chemistry, diketiminate ligands with primary *N*-alkyl ligands have been shown to be sterically significantly less bulky than those with *N*-aryl substituents.[20b,c] Given the propensity of *nacnac*CuOR to undergo ligand exchange to the homoleptic complexes, isolation of **4d** with a sterically undemanding spectator ligand was counterintuitive. It seems unlikely that formation of the homoleptic complex Cu(*nacnac*^{Bn})$_2$, **5d**, should not be possible with an *N*-benzyl substituent. Indeed, **5d** could not only be prepared from the reaction of 2 equiv of **3d** with Cu(O*i*Pr)$_2$, but was also formed in the reaction of **4d** with a second equivalent of **3d** (Scheme 3).[21] Given the easy access to **5d**, an additional mechanism has thus to be responsible for the stabilization of **4d**. The solid-state structure of **4d** yielded further insights. Contrary to **1** and **2**, complex **4d** crystallized as an alkoxide-bridged dimer in the solid state (vide infra). A UV/vis study of **4d** confirmed that the dimeric structure is most likely retained in solution: UV/vis-spectra of **4d** in toluene did not change notably and obeyed the Beer–Lambert law over a concentration range of 0.050–6.5 mM

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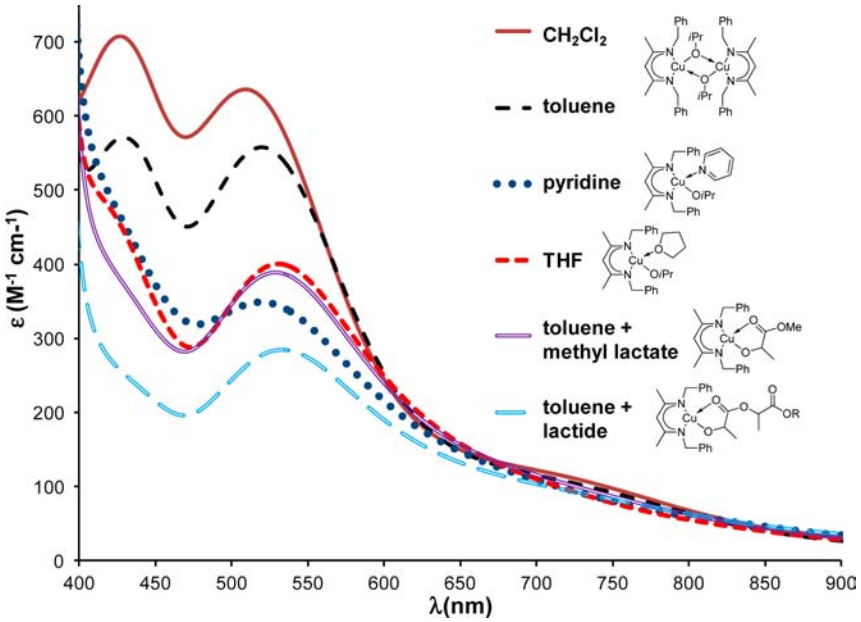

Figure 2. UV/vis spectra of **4d** in different solvents or after addition of methyl lactate or lactide, respectively.

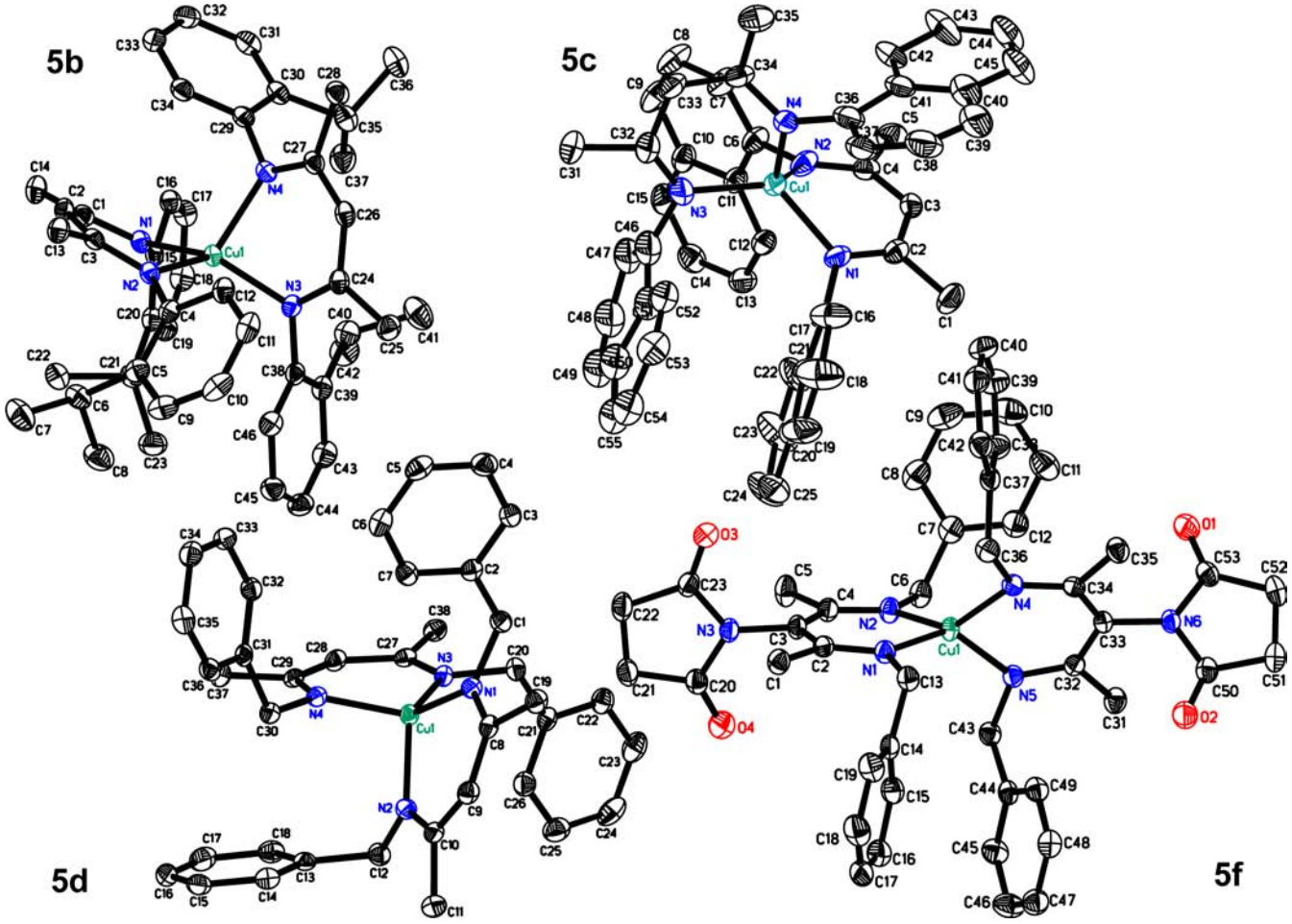

Figure 3. X-ray structure of compounds **5b**–**d** and **5f**. Hydrogen atoms and disordered atoms in **5c** are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

(Supporting Information, Figure S1), indicating the absence of any monomer–dimer equilibria in this concentration range. Likewise, addition of 0.25–10 equiv of pyridine did not affect the UV/vis spectra of **4d** in toluene (Supporting Information, Figure S2). Subtle, but more notable changes were observed between UV/vis spectra of **4d** in noncoordinating solvents,

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Table 1. Selected Geometric Data for Homoleptic Complexes 5b, 5c, 5d, and 5f[a]

	5b	5c	5d	5f	$nacnac^{Me}{}_2Cu$[23c,d]	$nacnac_2Cu$[23]
Cu−N_A	1.943(1), 2.016(1)	1.952(3), 1.967(3)	1.946(1), 1.951(1)	1.945(1), 1.958(1)	1.95	1.93−1.99
Cu−N_B	1.947(1), 2.019(1)	1.909(5)− 1.975(3)	1.974(1), 1.976(1)	1.945(1); 1.958(1)	1.95	
Δ(Cu−N)	0.07	0.02−0.06	0.02	0.01	<0.01	0−0.02
N_A−Cu−N_A,	90.99(6),	92.21(12),	95.21(6),	94.04(6),	95	95−98
N_B−Cu−N_B,	91.69(6)	91.9(3), 94.74(16)	95.58(6)	93.31(6)		
N_A−Cu−N_B	104.29(6)−147.23(6)	98.78(13)−128.5(3)	101.74(6)−135.41(6)	100.82(6)−134.23(6)	135	98−137
$(N_A)_2Cu/(N_B)_2Cu$[b]	68	73, 81	67	62	62	60−67
θ_M[c]	29, 32	13, 25, 31	7, 9	5, 9	3	1−7
$\Delta\theta_x/\Delta\theta_y/\Delta\theta_z$	15/9/67	4/3/82, 8/9/72	3/5/64	3/0/59	0/1/60	
orientation N-R[d]	syn, syn	syn, anti	syn, anti	anti, anti		

[a] $\Delta\theta_z$ given for deviations from square-planar geometry (Scheme 4). N_A and N_B denote the nitrogen atoms in the first and in the second diketiminate ligand, respectively. [b] Angle between the planes formed by the N atoms of each diketiminate and Cu, roughly comparable to θ_z. [c] Bending of Cu out of the ligand mean plane, described as the angle between the N_2Cu plane and the plane formed by the two nitrogen and the two α-carbon atoms of the diketiminate ligand. [d] Relative orientation of either the N−CH_2-R or the N−Ar substituents.

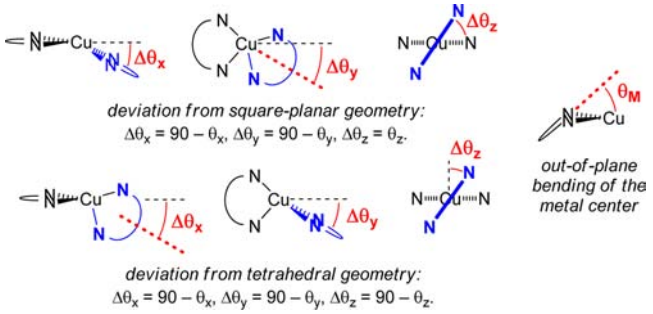
such as dichloromethane or toluene, and coordinating solvents, such as tetrahydrofuran (THF) or pyridine (Figure 2). Spectra similar to those obtained in coordinating solvents were obtained in toluene after addition of 1 equiv of methyl lactate or 10 equiv of lactide. Based on these UV/vis studies, it appears that **4d** is dimeric in solution in the absence of strong donors without any noticeable dissociation. In the presence of intermolecular or intramolecular Lewis bases, the dimer can break apart to yield a tetracoordinated monomeric species (Figure 2).

Since *N*-benzyl diketimines were the only ligands which yielded a heteroleptic copper(II) complex, we attempted to slightly vary the electronic and steric nature of the ligand by substitution in the 3-position. Reaction of **3d** with *N*-chlorosuccinimide afforded the expected 3-chlorosubstituted ligand **3e** (Scheme 3). Reaction of the lithiated ligand $nacnac^{Bn}Li(THF)$ with *N*-bromosuccinimide, on the other hand, afforded the 3-succinimido substituted ligand **3f**, probably by reaction of the initially formed 3-bromosubstituted ligand with lithium succinimide.[20a] Despite their minor differences, both ligands reacted differently. Reaction of **3e** with $Cu(OiPr)_2$ yielded the heteroleptic complex **4e**, while reaction of **3f** with $Cu(OiPr)_2$ afforded homoleptic **5f**, at least under the conditions applied here.

Solid State Structures. Crystal structures were obtained for the homoleptic complexes **5b**−**5d**, and **5f** (Figure 3, Table 1). The coordination geometry in $(L^{\wedge}L)_2M$ complexes can be described using the θ angles introduced by White and co-workers,[22] where $\theta_x = \theta_y = \theta_z = 90°$ represent ideal tetrahedral coordination and $\theta_x = \theta_y = 90°$, $\theta_z = 0°$ ideal square-planar geometry (Scheme 4). All bisdiketiminate copper complexes, $Cu(nacnac)_2$, described here or elsewhere,[23] show distorted geometries with $\theta_z \approx 60°$ (Table 1). Distortion from ideal geometry might occur for electronic reasons in tetrahedral copper complexes because of their d^9 electron configuration and for steric reasons in square-planar complexes because of the in-plane interactions of the *N*-substituents. (Pseudo)tetrahedral Cu(II) complexes are not uncommon and the fact that the value of θ_z does not correlate with the steric demand of the *N*-substituent would argue to assign the coordination geometries as distorted tetrahedral. However, complexes electronically very similar to $Cu(nacnac)_2$, that is, $Cu(acac)_2$ and $Cu(acnac)_2$ (acnac = 4-imino-penta-2-nonate), show square-planar geometries. Closer inspection of the structure of the sterically least encumbered bisdiketiminate complex, $Cu(nacnac^{Me})_2$,[23c,d] shows that $\theta_z \approx 60°$ actually represents the closest sterically possible approach to square-planar symmetry, even for *N*-substituents as small as methyl. Coordination geometries in **5b**−**d** and **5f** (Figure 3) are thus best described as distorted square-planar, even though the θ_z-values are closer to a tetrahedral geometry. In **5b**, steric demands of the *N*-isopropylphenyl substituent lead to further distortion from ideal geometry. Although some of the steric strain is released (as often encountered in sterically demanding diketiminate complexes) by a strong bending of the Cu metal out of the mean plane of the diketiminate ligand ($\theta_M \approx 30°$, Scheme 4, Table 1), coordination around Cu in **5b** is highly unsymmetrical with differences in Cu−N bond lengths of 0.07 Å, $\Delta\theta_x = 15°$ and $\Delta\theta_y = 9°$ (Table 1). The *N*-naphthyl substituent in **5c** likewise introduces strong distortions. Interligand π-stacking between naphthyl substituents and between naphthyl and diketiminate is observed in **5c**, which was absent in **5b** probably because of the isopropyl substituent. While θ_z values remain ≈60°, reduction of the steric impact of the *N*-substituent reduces additional distortions caused by steric interactions. Complexes **5d** and **5f** thus display only small differences in Cu−N bond lengths (Δ = 0.01−0.02 Å), a much smaller bending of the Cu atom out of the ligand mean plane ($\theta_M = 5$−9°), and a symmetry much closer to the (crystallographic) C_2 symmetry observed for $Cu(nacnac^{Me})_2$ ($\Delta\theta_x < 3°$, $\Delta\theta_y < 5°$).

The alkoxide complexes **4d** and **4e** crystallize as oxygen-bridged dimers (Figure 4). Their coordination geometry is best

Scheme 4



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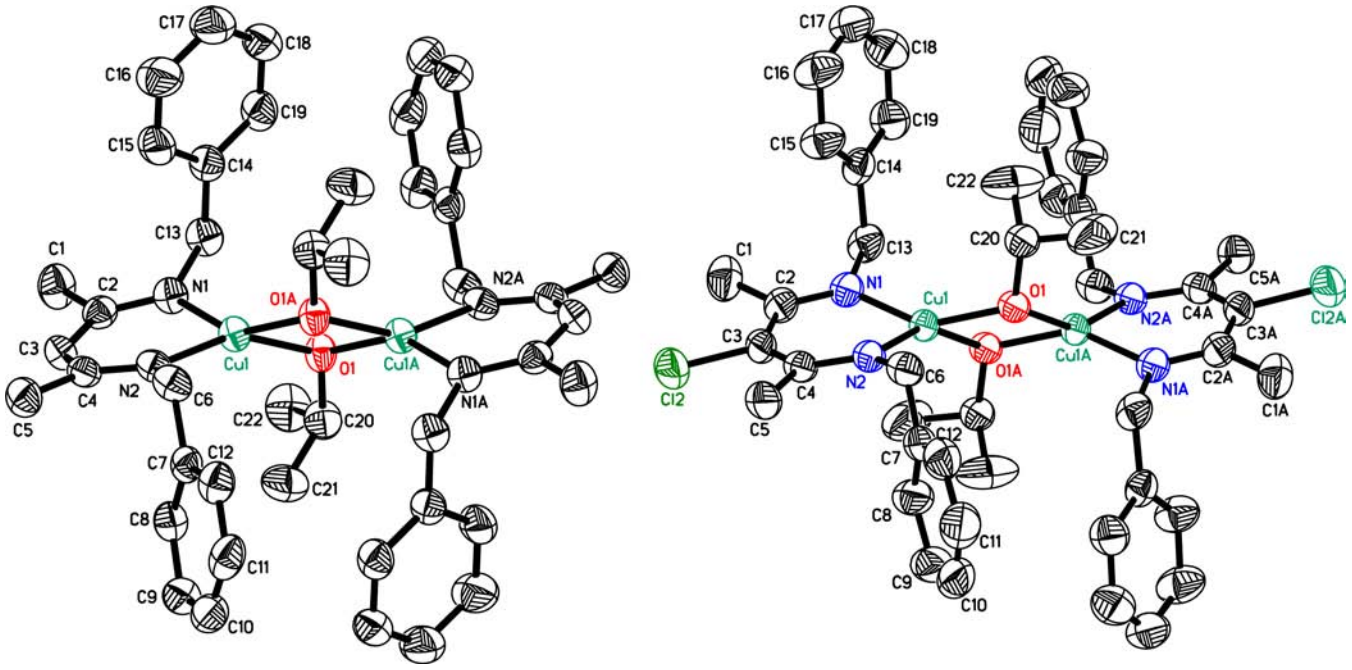

Figure 4. X-ray structure of **4d**[16] (left) and **4e** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 2. Selected Geometric Data for Heteroleptic Alkoxide Complexes 4d,[16] and 4e

	4d[16]	**4e**	*nacnac*^{diip}CuOAr[17]	*nacnac*^{Ar}CuO*t*Bu[18a]
Cu−N	1.921(3), 1.951(3); 1.923(3), 1.946(3)	1.917(3), 1.932(2)	1.86−1.90	1.88−1.89
Cu−O	1.951(2), 1.979(2); 1.954(2), 1.982(2)	1.948(2), 1.977(2)	1.75−1.82	1.78−1.79
N−Cu−N	95.19(12); 94.92(11)	94.63(10)	96−97	96
N−Cu−O	96.14(11)−152.75(11)	98.46(9)−149.23(9)	129−135	118−146
N_2Cu/Cu_2O_2[a]	41, 43	45		
θ_M[b]	13, 14	15	0−6	1−10
$\Delta\theta_x/\Delta\theta_y/\Delta\theta_z$	2/4/35	0/2/40		
orientation N-R	anti	anti		

[a]Angle between the planes formed by the N atoms of the diketiminate and Cu and by the $Cu_2(\mu\text{-}O)_2$ core. [b]Bending of the Cu out of the ligand mean plane, described as the angle between the N_2Cu plane and the plane formed by the two nitrogen and two α-carbon atoms of the diketiminate ligand. [c]Relative orientation of the N−CH_2-R substituents.

described as distorted square-planar, with a distortion from planarity ($\Delta\theta_z$ = 50−55) because of unfavorable steric interactions of the alkoxide ligands with the *N*-substituents. Cu−N distances are slightly longer than those in monomeric *nacnac*^{diip}CuOAr[17] or *nacnac*^{Ar}CuO*t*Bu[18a] (Table 2) and the bending of Cu out of the ligand mean plane (θ_M, Table 2) is slightly more pronounced. Introduction of a chloride substituent in the 3-position of the ligand has barely noticeable steric consequences. Interaction between the chloride substituent and the ligand methyl groups, leads to a slight (1°) widening of the C_β-C_α-C_{Me} angles in the ligand (when compared to **4d**), which in turn very slightly increases the steric pressure in the front of the complex. Even this minor effect seems to be absent in the case of a succinimido substituent since structures **5d** and **5f** are practically identical.

Lactide Polymerization. Performance in *rac*-lactide polymerization was first investigated using heteroleptic **4d** and **4e** (Table 3). Preliminary results on the surprisingly high activity of **4d** (Table 3), given the generally low activity reported for copper(II) complexes in lactide polymerization,[14a−e] have been reported recently.[16] Structurally very similar **4e** was also highly active in lactide polymerization. With 1 mM **4d** or **4e** in dichloromethane at room temperature, polymerizations reached completion in <1 or 3 min, respectively. Polymerizations with both catalysts were highly controlled and narrow polydispersities below 1.1 were obtained, indicating fast activation and the absence of side reactions. ^{1}H NMR spectra showed signals at the position and with the intensities expected for an isopropoxy end group. Intensities were too low, however, to provide a reliable polymer molecular weight estimate from NMR spectroscopy. The obtained polymers were atactic, with a slight heterotactic bias (P_r = 0.56 for **4d**, 0.53 for **4e**. P_r = probability of alternating monomer insertion). Tetrahedral magnesium alkoxide complexes, carrying the same ligands as **4d** and **4e**, showed a slight isotactic preference for lactide polymerization at low temperatures.[13c,24] In the case of square-planar **4d** and **4e**, polymerizations at −17 °C led only to a slight increase of the heterotactic bias. Despite very narrow polydispersities, the observed polymer molecular weight sometimes differed from expectations (e.g., Table 3, #1). Although experimental errors, such as weighing errors and catalyst decomposition, are more likely to be responsible for the

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Table 3. Polymerization of rac-Lactide with Heteroleptic and Homoleptic Copper Complexes

#	catalyst	Cu: lactide (: BnOH)[a]	[Cu]/ mM[a]	conversion	time (min)	P_r	M_n mol/g	M_n (exp.)/ M_n[b]	M_w/M_n	k_{obs} min
1[d]	**4d**	1:300	2	90−98%	1−3	0.56−0.57	27 400−62 300	0.7−1.5	1.04−1.07	3.6(4)−4.4(5)
2	**4d**, −17 °C	1:300	2	80−98%	30	0.60−0.61	37 400[b]	1.1	1.06	
3	**4d**	1:300:1 (**3d**)	2	36%	90	0.64	53 300	0.5	1.06	$5.1(1) \times 10^{-3}$
4	**4e**	1:300	2	95−98%	3−11	0.53−0.54	29 400[b]	1.4	1.04	0.8(1)−1.3(2)
5	**4e**, −17 °C	1:300	2	95−98%	60−175	0.53−0.54	30 300[b]	1.4	1.04	
6	**5d**	1:300	2	10%	10					$\approx 10^{-2}$
7	**5d**	1:300:1[c]	2	95%	45	0.60	26 400	1.6	1.04	$11.2(1) \times 10^{-2}$
8	**5d**	1:300:1	2	95%	40	0.59	29 900	1.4	1.03	$9.6(2) \times 10^{-2}$
9	**5d**	1:300:1 (*i*PrOH)	2	75%	40	0.60	41 600	0.8	1.04	$3.8(1) \times 10^{-2}$
10	**5d**	1:300:1 (*i*PrOH)	2	97%	125	0.58	46 400	0.9	1.03	$4.4(1) \times 10^{-2}$
11	**5b**	1:300	2	80%	85	0.63	487 700	0.07	1.12	
12	**5b**	1:300:1[c]	2	98%	60	0.59	30 500	1.4	1.48	$12.0(4) \times 10^{-2}$
13	**5b**	1:300:1	2	95%	60	0.60	35 300	1.2	1.07	$6.7(3) \times 10^{-2}$
14	**5b**	1:300:25	2	98%	60	0.57	1400	1.3	1.12	$17.2(9) \times 10^{-2}$
15	**5c**	1:300	2	7%	60		56 000	0.06	1.06	
16	**5c**	1:300:1	2	95%	60	0.52	4300	4.8	1.08	$6.4(3) \times 10^{-2}$
17	**5f**	1:300	2	10%	60		79 300	0.06	1.14	
18	**5f**	1:300:1	2	95%	60	0.57	4300	4.8	1.53	$12.7(5) \times 10^{-2}$

If a range is provided: minimum and maximum values of three experiments. Conditions: CH_2Cl_2, ambient temperature. P_r determined from decoupled ^{1}H NMR by $P_r = 2 \cdot I_1/(I_1+I_2)$, with I_1 = 5.20−5.25 ppm (*rmr, mmr/rmm*), I_2 = 5.13−5.20 ppm (*mmr/rmm, mmm, mrm*). M_n and M_w determined by size exclusion chromatography vs polystyrene standards, with a Mark−Houwink correction factor of 0.58. [a]Concentrations and ratios provided per Cu atom, that is, for (putative) monomeric complexes. [b]GPC analysis was performed only on selected examples. M_n(expected) = [lactide]/([Cu] + [ROH])·conversion·$M_{lactide}$ + M_{ROH}. [c]Alcohol added after 10 min polymerization time. [d]Values taken from ref 16.

observed discrepancies than transesterification reactions, changes in P_r over time were investigated. (Because of the overlap of rr-triads, formed during transesterification, with mm-triads, transesterification results in an artificially low P_r value if the latter is determined from homonuclear decoupled NMR.) Thus, *rac*-lactide was polymerized with **4d** (>95% conversion after 1 min) and kept for 12 h under polymerization conditions to allow transesterification of the formed polymer. Analysis of a polymer sample showed that the P_r value of the polymer decreased slightly, indicating a very low amount of transesterification over a time period 1000× longer than the polymerization time. In a similar experiment, *S,S*-lactide was polymerized by **4d** to isotactic PLA and kept for 12 h without quenching under polymerization conditions. No change in the P_r value was observed. **4d** thus does not catalyze polymer epimerization. In both cases, addition of additional monomer confirmed that **4d** remained active.[16]

Given that only homoleptic diketiminate complexes were obtained with ligands **3b**, **3c**, and **3f**, their activity in *rac*-lactide polymerization was verified. Polymerization with **5d** under conditions identical to **4d** yielded, unsurprisingly, a very low activity because of the absence of a suitable initiator group, and only 10% conversion was observed after 10 min (Table 4, Supporting Information, Figure S3). Addition of benzyl alcohol increased the activity by an order of magnitude. The polymerization was completely controlled with polydispersities below 1.05 and showed the molecular weight expected from the amount of added alcohol. The pseudo-first order rate constant $k_{obs} = 9 \times 10^{-2}$ min^{-1} was, however, 50× lower than the rate observed for the heteroleptic complex **4d**, although the same active species should have been obtained after the first monomer insertion. We thus assume that protonation of a diketiminate ligand by benzyl alcohol is unfavorable and that polymerization occurs under immortal polymerization conditions catalyzed by about 2% of heteroleptic complex present in the equilibrium under these conditions (Scheme 5). The latter mechanism is supported by the fact that **4d** is stable under immortal polymerization conditions,[16] that UV/vis titrations of **4d** with ligand **3d** yield the homoleptic complex **5d**, and that addition of 1 equiv of **3d** to *rac*-lactide polymerizations with **4d** reduced activities drastically by 3 orders of magnitude (Table 3, #3). If isopropanol instead of benzyl alcohol is employed as cocatalyst, a notably longer induction period and an overall lower activity was observed (Table 3, Supporting Information, Figure S3). While the induction period can be explained by the lower acidity of isopropanol compared to benzyl alcohol, activity is governed by the acidity of the polymeryl alcohol and should be independent of the starting alcohol, once all catalyst initiated. We have at the moment no explanation for this behavior.

Polymerizations with homoleptic **5b** in the absence of any cocatalyst again proceeded sluggishly. A positive curvature of the conversion/time plot up to 60 min (Supporting Information, Figure S4) and a polymer weight of 500 000 g/mol indicate slow activation of small amounts of **5b**, most likely by impurities in the monomer. It should be noted that although only 5% of **5b** were active in polymerization with an extremely slow initiation, and although polymerization had to be quenched at 80% when the solution became too viscous to stir, the obtained polymer still showed a very narrow polydispersity of 1.12. Addition of benzyl alcohol as a cocatalyst reduced the induction period to about 10 min and yielded an activity approximately half as high as that of **5d**. In the presence of 25 equiv of benzyl alcohol, the induction period disappeared and activity increased by a factor of 2−3, in agreement with the mechanism proposed in Scheme 5.

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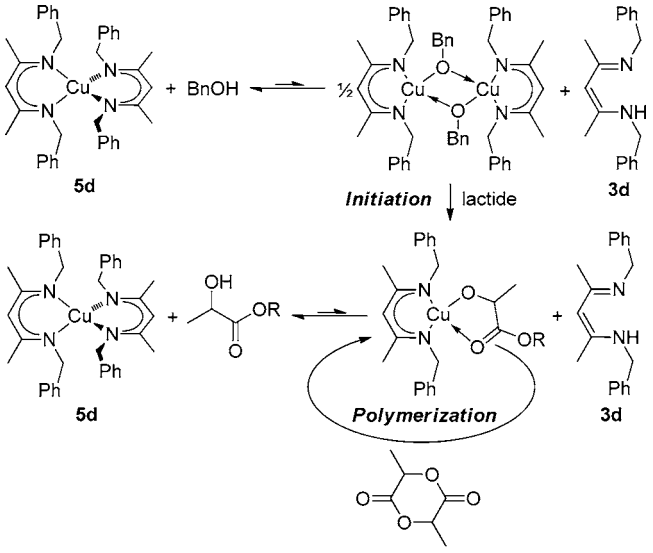
Table 4. Details of X-ray Diffraction Studies

	4e	5b	5c	5d	5f
formula	$C_{44}H_{54}Cl_2Cu_2N_4O_2$	$C_{46}H_{58}CuN_4$	$C_{50}H_{42}CuN_4$	$C_{38}H_{42}CuN_4$	$C_{46}H_{48}CuN_6O_4{\cdot}CH_2Cl_2$
M_w (g/mol); $d_{calcd.}$ (g/cm^3)	868.89; 1.400	730.50; 1.194	762.41; 1.291	618.29; 1.302	897.37;
T (K); $F(000)$	150; 908	100; 1564	100; 798	100; 654	150; 1876
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
unit cell:					
a (Å)	13.6092(14)	16.6129(5)	12.0601(13)	9.5454(6)	11.2594(4)
b (Å)	10.2310(10)	10.4872(3)	12.1002(13)	11.3169(7)	17.7065(7)
c (Å)	14.8126(16)	23.5375(7)	16.0178(18)	15.0776(10)	21.5097(8)
α (deg)			78.080(4)	93.248(3)	
β (deg)	91.846(5)	97.799(2)	75.677(4)	103.821(3)	91.886(2)
γ (deg)			60.513(5)	92.335(3)	
V (Å^3); Z	2061.4(4); 2	4062.8(2); 4	1961.5(4); Z	1576.57(18); 2	4285.9(3); 4
μ (mm^{-1}); abs. corr.	2.786; multiscan	1.018; multiscan	1.089; multiscan	1.219; multiscan	2.283; multiscan
θ range (deg); completeness	4−70; 0.99	3−71; 0.99	3−72; 0.97	3−70; 0.98	3−70; 1.00
collected reflections; R_σ	39607; 0.023	58938; 0.026	54014; 0.026	35571; 0.028	100806; 0.063
unique reflections; R_{int}	3895; 0.059	7830; 0.046	7430; 0.048	5844; 0.043	8180;
R1(F) ($I > 2\sigma(I)$)	0.047	0.037	0.076	0.037	0.036
wR(F^2) (all data)	0.145	0.103	0.1948	0.102	0.101
GoF(F^2)	1.04	1.03	1.04	1.06	1.04
residual electron density	0.35; −0.82	0.44; −0.40	1.25; −1.18	0.71; −0.36	0.45; −0.39

Scheme 5



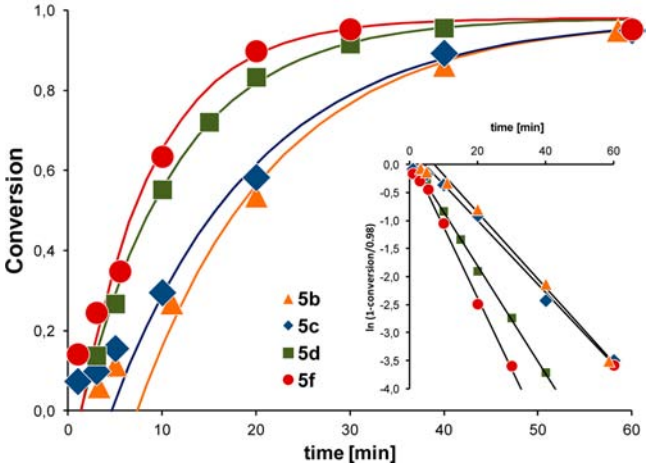


Figure 5. Conversion−time plots for *rac*-lactide polymerization with homoleptic **5b−d** and **5f**.

Homoleptic **5c** and **5f** likewise showed very low polymerization activity from a small number of catalyst centers in the absence of benzyl alcohol (Table 4), but became moderately active in its presence (Table 4, Figure 5). Both catalysts show unexpectedly low polymer molecular weight in the presence of benzyl alcohol, and **5f** was the first Cu catalyst presented here which gave polydispersities above 1.1. Comparison of the conversion/time data in Figure 5 reveals that the structurally similar *N*-benzyl complexes **5d** and **5f** also have very similar activities. Apart from the loss of polymer molecular weight control, there seems thus to be no noticeable impact of the succinimido substituent on polymerization. Complexes **5b** and **5c** with mono-ortho-substituted *N*-aryl substituents also show very similar activity, about half as high as the *N*-alkyl derivatives. Contrary to **5d** and **5f**, they show the presence of an induction period. Both, delayed initiation as well as lower activity, would be expected in **5b** and **5c** because of the higher acidity of *N*-aryl diketimines compared to *N*-alkyl diketimines. All polymers obtained with **5b−d**, and **5f** were essentially atactic with a slight heterotactic bias (P_r = 0.52−0.60). The P_r-value obtained for **5d**/BnOH (P_r = 0.59−0.60) is 3% higher than for **4d**, although the active species should be identical in both polymerizations. This might simply be due to experimental error. However, we have noted a similar behavior in diketiminate magnesium complexes, which showed a slightly decreased P_r value (change <5%) in the presence of excess alcohol.[24]

CONCLUSIONS

The chemistry of Cu(II) diketiminate alkoxide complexes is governed by their strong tendency to achieve four-coordination in square-planar geometry on one hand and the steric constraints of the diketiminate ligand on the other. In the case of sterically undemanding *N*-alkyl diketimines, the monomeric intermediate *nacnac*CuO*i*Pr, obtained upon re-

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action of Cu(O*i*Pr)$_2$ with diketimine, stabilizes via simple dimerization. Sterically more demanding mono-ortho-substituted *N*-aryl substituents, such as 9-naphthyl nor 2-isopropylphenyl, do not yield a dimeric heteroleptic complex. Instead, homoleptic Cu(*nacnac*)$_2$ is obtained, which seems to be the thermodynamic rather than the kinetic product. Further increase in steric bulk, that is, the use of 2,6-disubstituted *N*-aryl substituents such as the ubiquitous 2,6-diisopropylphenyl, prevents the formation of the homoleptic complex for steric reasons. In the absence of β-hydrogen atoms on the alkoxide ligand, the three-coordinated intermediate can then be isolated as the reaction product. If β-hydrogen atoms are present, decomposition, presumably via β-H-elimination, will yield the respective ketone or aldehyde and unknown Cu-containing products.

Heteroleptic (X*nacnac*^{Bn}CuO*i*Pr)$_2$ showed activities in lactide polymerization comparable to the best catalysts reported. The catalysts show high molecular weight control with polydispersities typically below 1.1 even under immortal polymerization conditions and do not suffer from side reactions such as transesterification, epimerization, or (undesired) chain transfer. Combined with their high activity, they are promising candidates for the production of block-copolymers, and we are currently investigating the scope of these catalysts with regards to different monomers.

Homoleptic Cu(*nacnac*)$_2$ can be activated by alcohol as a cocatalyst to yield moderately active polymerization catalysts (1 h to completion at room temperature) which retain the high polymer molecular weight control of the heteroleptic complexes. The easy accessibility of Cu bisdiketiminate complexes drastically simplifies synthetic requirements. Since only a small part of the homoleptic complex is activated for polymerization, polymer molecular weight is determined from the monomer:alcohol ratio, and small amounts of catalyst decomposition by impurities should be tolerated without impact on the obtained polymer molecular weight. These catalysts do not contain an initiating group and are thus suitable catalysts for the polymerization of macroinitiators.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out using Schlenk or glovebox techniques under nitrogen atmosphere. Cu(O*i*Pr)$_2$,[25] *nacnac*^{dipp}H (**3a**),[26] *nacnac*^{ipp}H (**3b**),[27] *nacnac*^{Naph}H (**3c**),[28] and *nacnac*^{Bn}H (**3d**)[29] were prepared according to literature. Solvents were dried by passage through activated aluminum oxide (MBraun SPS), deoxygenated by repeated extraction with nitrogen, and stored over molecular sieves. C_6D_6 was dried over sodium and degassed by three freeze−pump−thaw cycles. $CDCl_3$ and CD_2Cl_2 were dried over 3 Å molecular sieves. *rac*-Lactide (98%) was purchased from Sigma−Aldrich, purified by 3× recrystallization from dry ethyl acetate and kept at −30 °C. All other chemicals were purchased from common commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AVX 400 spectrometer. The chemical shifts were referenced to the residual signals of the deuterated solvents (C_6D_6: ^{1}H: δ 7.16 ppm, ^{13}C: δ 128.38 ppm, $CDCl_3$: ^{1}H: δ 7.26 ppm, CD_2Cl_2: ^{1}H: δ 5.32 ppm, CD_3CN: ^{1}H: δ 1.94 ppm, ^{13}C: δ 1.32 ppm). Elemental analyses were performed by the Laboratoire d'analyze élémentaire (Université de Montréal). Molecular weight analyses were performed on a Waters 1525 gel permeation chromatograph equipped with three Phenomenex columns and a refractive index detector at 35 °C. THF was used as the eluent at a flow rate of 1.0 mL·min^{-1} and polystyrene standards (Sigma−Aldrich, 1.5 mg·mL^{-1}, prepared and filtered (0.2 mm) directly prior to injection) were used for calibration. Obtained molecular weights were corrected by a Mark−Houwink factor of 0.58.[30]

***N,N′*-dibenzyl-2-amino-3-chloro-4-imino-2-pentene, Cl*nacnac*^{Bn}H, 3e.** To a solution of **3d** (5.48 g, 19.7 mmol) in dry THF (150 mL) was added *N*-chlorosuccinimide (3.00 g, 22.4 mmol). After stirring at room temperature for 45 min, a white precipitate formed which was removed by filtration. H_2O (500 mL) was then added. The product was extracted using hexanes (2 × 600 mL). After drying over Na_2SO_4 the solvent was evaporated. The obtained yellow oil was crystallized from dry ethanol at −80 °C, washed with cold dry ethanol and recrystallized from refluxing ethanol. The eluate yielded a second fraction at −80 °C (colorless crystals, 3.41 g, 55%).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 12.22 (bs, 1H, NH), 7.25−7.19 (m, 10H, Ph), 4.49 (s, 4H, NCH_2), 2.18 (s, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ 160.3 (*C*═N), 140.5 (*ipso* Ph), 128.6 (*ortho* or *meta* Ph), 127.3 (*ortho* or *meta* Ph), 126.8 (*para* Ph), 127.7 (ClC), 51.5 (NCH_2), 17.3 (Me). Anal. Calcd. for $C_{19}H_{21}ClN_2$: C, 72.95; H, 6.77; N, 8.95. Found: C, 72.89; H, 6.66; N, 9.17.

***N,N′*-dibenzyl-2-amino-3-succinimido-4-imino-2-pentene, 3-succinimido-*nacnac*^{Bn}H, 3f.** N-Bromosuccinimide (224 mg, 1.26 mmol) and *nacnac*^{Bn}Li(THF) (440 mg, 1.24 mmol) were suspended in THF (30 mL) and heated at 60 °C for 24 h to afford a brown solution. 1,4-Dioxane (1 mL) was added to precipitate LiCl. After additional stirring for 15 min at room temperature, the mixture was filtered and the filtrate evaporated. The resulting brown residue was dissolved in dichloromethane (3 mL). Hexane (12 mL) was added, the mixture filtered, and the filtrate allowed to slowly evaporate, yielding dark-yellow crystals (250 mg, 54%). ^{1}H NMR (CD_3CN), 400 MHz, 298 K): δ 12.57 (bs, 1H, NH), 7.28−7.19 (m, 10H, Ph), 4.47 (s, 4H, CH_2), 2.76 (s, 4H, NCH_2), 1.76 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, 101 MHz, 298 K): δ 179.3 (*C*═O), 161.6 (*C*═N), 141.5 (*ipso* Ph), 129.5 (*ortho* or *meta* Ph), 128.4 (*ortho* or *meta* Ph), 127.7 (*para* Ph), 98.9 (NC), 51.5 (NCH_2), 28.8 (CH_2), 14.8 (Me). Anal. Calcd. for $C_{23}H_{25}N_3O_2$: C, 73.57; H, 6.71; N, 11.19. Found: C, 73.28; H, 6.69; N 10.84.

[*nacnac*^{Bn}Cu(*μ*-O)*i*Pr]$_2$, 4d.[16] Cu(O*i*Pr)$_2$ (500 mg, 2.75 mmol) was suspended in toluene (20 mL). **3d** (610 mg, 2.20 mmol) was added slowly to the mixture and allowed to react at room temperature for 18 h. The reaction mixture changed color from deep green to deep blue. Solvent and isopropanol were removed under reduced pressure. The blue solid was taken up in toluene (15 mL) and filtered through a fine frit. The filtrate was placed at −25 °C yielding purple-red crystals (550 mg, 63%). Anal. Calcd. for $C_{22}H_{28}CuN_2O$: C, 66.06; H, 7.05; N, 7.00. Found: C, 66.33; H, 7.22; N 6.82. UV/vis (toluene): λ/nm (ε·M·cm) 357 (10000), 431 (570), 523 (560), 720 (sh, 100). UV/vis (THF): λ/nm (ε·M·cm) 421 (sh 470), 533 (400).

[*nacnac*^{Bn}Cu(*μ*-O)*i*Pr]$_2$, 4e. Using the same procedure as for **4d**. Cu(O*i*Pr)$_2$ (500 mg, 2.75 mmol), hexanes or toluene (20 mL), **3e** (690 mg, 220 mmol) yielded 350 mg (0.80 mmol, 36%) of purple-red crystals.

Anal. Calcd. for $C_{22}H_{27}ClCuN_2O$: C, 60.82; H, 6.26; N, 6.45. Found: C 60.76, H 6.17, N 6.34.

Cu(*nacnac*^{ipp})$_2$, 5b. Diketimine **3b** (2.00 g, 5.98 mmol) was added to a heterogeneous solution of Cu(O*i*Pr)$_2$ (0.54g, 2.98 mmol) in toluene (20 mL) and allowed to stir overnight. The solvent was then removed in vacuo from the dark green solution, giving a dark green waxy solid. The mixture was dissolved in a minimum of hexanes and filtered over Celite. Pure product was isolated by crystallization at −35 °C to yield purple crystals (0.68 g, 0.93 mmol, 63%). Mp: 154 °C. Anal. Calcd. for $C_{46}H_{58}CuN_4$: C, 75.63; H, 8.00; N, 7.67. Found: C, 75.47; H, 8.02; N, 7.47. UV/vis (toluene): λ/nm (ε·M·cm): 440 (sh, 1400), 460 (1300).

Cu(*nacnac*^{Naph})$_2$, 5c. Following the same procedure as for **5b**, **3c** (0.82 g, 1.1 mmol), Cu(O*i*Pr)$_2$ (0.10 g, 0.54 mmol), toluene (10 mL) gave a dark green waxy solid. The mixture was dissolved in a minimum of dichloromethane and filtered over Celite. Crystallization by slow evaporation yielded green crystals (0.21 g, 0.28 mmol, 51%). Mp: 149 °C. Anal. Calcd. for $C_{50}H_{42}CuN_4$: C, 78.76; H, 5.55; N, 7.35. Found: C, 78.79; H, 5.63; N, 7.33. UV/vis (toluene): λ/nm (ε·M·cm) 537 (1000), 670 (1200).

Cu(*nacnac*^{Bn})$_2$, 5d. Following the same procedure as for **5b**, **3d** (0.70 g, 2.5 mmol), Cu(O*i*Pr)$_2$ (0.25 g, 1.2 mmol), toluene (20 mL)

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gave a purple wax-like solid. The mixture was dissolved in a minimum of hexanes and filtered over Celite. **5d** was isolated by crystallization at −35 °C as purple crystals (0.98 g, 0.158 mmol, 64%). Mp: 62 °C. Anal. Calcd. for $C_{38}H_{42}CuN_4$: C, 73.81; H, 6.85; N, 9.06. Found: C, 73.74; H, 6.81; N, 9.02. UV/vis (toluene): λ/nm (ε·M·cm) 446 (550), 546 (1500).

Cu(3-succinimido-*nacnac*^{Bn})$_2$, 5f. Following the same procedure as for **5b**, **3f** (0.32 g, 0.74 mmol), Cu(O*i*Pr)$_2$ (65 mg, 0.36 mmol), toluene (10 mL) gave a dark-purple waxy solid. The solid was dissolved in a minimum of dichloromethane and filtered over Celite. Crystallization by slow evaporation yielded 0.30 g (0.74 mmol, 87%) of purple crystals. Mp: 174 °C. Anal. Calcd. for $C_{46}H_{48}CuN_6O_4 \cdot CH_2Cl_2$: C, 62.90; H, 5.62; N, 9.36. Found: C, 62.06; H, 5.71; N, 8.96. (One equivalent of dichloromethane was found in the X-ray structure.) UV/vis (toluene): λ/nm (ε·M·cm) 432 (620), 531 (1300), 726 (sh, 400).

***rac*-Lactide Polymerization.** In the glovebox a stock solution of the catalyst (100 μL, 5.0×10^{-2} M in CH_2Cl_2, 5.0 μmol) was added to lactide (220 mg, 1.5 mmol) in dichloromethane (2.5 mL). If desired, benzyl alcohol (5.0×10^{-2} M in CH_2Cl_2) was added to the reaction mixture. Samples for kinetic investigations were taken at the desired intervals and added to vials already containing a dichloromethane solution of acetic acid (5 mM). Reaction mixtures were quenched at the desired polymerization time by addition of a dichloromethane solution of acetic acid (5 mM). For samples as well as the bulk reaction, volatiles were immediately evaporated. Solid polymer samples were stored at −80 °C. Conversion was determined from ^{1}H NMR in $CDCl_3$ by comparison to remaining lactide. P_r values were determined from homodecoupled ^{1}H NMR spectra.

X-ray Diffraction. Single crystals were obtained directly from isolation of the products as described above. Diffraction data were collected with Cu Kα radiation on Bruker Microstar/Proteum, equipped with Helios mirror optics and rotating anode source or on a Bruker APEXII with a Cu microsource/Quazar MX optics using the APEX2 software package.[31] Data reduction was performed with SAINT,[32] absorption corrections with SADABS.[33] Structures were solved with direct methods (SHELXS97). All non-hydrogen atoms were refined anisotropic using full-matrix least-squares on F^2 and hydrogen atoms refined with fixed isotropic U using a riding model (SHELXL97).[34] In **5f**, cocrystallized dichloromethane was found to be disordered and refined with appropriate restraints (0.7:0.3 occupancy). In **5c**, one diketiminate ligand was found disordered with N-naphtyl orientations inverted by 180 °C. The disorder was resolved using appropriate restraints (SIMU/SADI) and refined to 0.7:0.3 occupation. Additional fluxionality exists and electron density indicates even further *N*-napthyl rotamers, which were not resolved. Further experimental details can be found in Table 4 and in the Supporting Information (CIF).

■ ASSOCIATED CONTENT

Supporting Information

Figures S1−S4. Details of the crystal structure determinations (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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