Ti^{IV} Complexes with Novel, Chiral, Tridentate Amido-Amidinate or Monoanionic, Didentate Amidinate Ligands

Jian-Feng Li,[a] Shu-Ping Huang,*[a] Lin-Hong Weng,[b] and Dian-Sheng Liu*[a]

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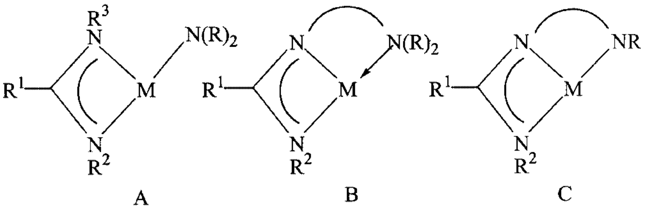
Reaction of LiL or a new type of dianionic ligand Li_2L (**2**) {H_2L = (1*R*,2*R*)-(–)-1-[N(H)C(Ph)N($SiMe_3$)]-2-[N(H)$SiMe_3$]-C_6H_{10}} with $TiCl_2(OiPr)_2$ yielded the novel complexes [TiCl(L)(O*i*Pr)$_2$] (**1**) and [Ti(L)(O*i*Pr)$_2$] (**3**), respectively. Treatment of Na_2L' {H_2L' = (1*R*,2*R*)-(–)-1,2-[N(H)C(Ph)N-($SiMe_3$)]$_2C_6H_{10}$]} with Ti(O*i*Pr)$_2Cl_2$ unexpectedly gave **3** via a unusual rearrangement/elimination reaction; The structure of complex **3** shows both an η^3-π bond and σ-bonds to the central metal. This is a new coordination model and is obtained for the first time for this type of amido-amidinate complex.

There has been an intense interest in organometallic complexes with amidinate ligands as these ligands have proven to be very versatile due to the ease of adapting their properties to the steric and electronic requirements of the metal centre simply by changing the substitution at the terminal nitrogen atoms.[1,2] For group 4 transition metals, amidinates have been used as ancillary ligands in olefin polymerization catalysis.[3,4] Recently, several groups have reported the introduction of an additional electron-donor amine or pyridine functionality thus forming six-electron-donor, three-coordinate ligands that are close analogues of Cp ligands.[5–9] This system may be sub-divided into models **A–C** (see Scheme 1): (**A**) a mixed ligand with the amine group and amidinate attached to the central metal via η^3-π and σ bonds {e.g. Ge[$C_6H_{11}NC(CMe_3)NC_6H_{11}$]$_2$};[10] (**B**) a linked amido-amidinate ligand with the tertiary amine functionality as a pendant group on the amidinate framework and the nitrogen of the amine bonding through a lone pair of electrons {e.g. [Al{N($SiMe_3$)C(Ph)N(CH_2)$_3NMe_2$}Cl_2];[9] (**C**) a linked amido-amidinate ligand but with η^3-π- and σ-bonds both to the central metal — a new type of ligand that we have developed.

Recently, we reported a fully characterized chiral amidinate ligand of type **B** (LiL) {HL = (1*R*,2*R*)-(−)-1-[N(H)C(Ph)N($SiMe_3$)]-2-[N(H)$SiMe_3$]C_6H_{10}} containing a pendant amine group.[11–13] To apply our preceding work in transition element chemistry and explore the ligand geometry and bonding modes, we report here the synthesis of



Scheme 1. Three ligand models

[TiCl(L)(O*i*Pr)$_2$] (**1**) from LiL, and, for the first time, a new, chiral, dianionic tridentate amido-amidinate ligand (Li_2L; **2**), similar to type **C** and its corresponding titanium compound [Ti(L)(O*i*Pr)$_2$] (**3**). The crystallographic studies and comparison of the complexes **1** and **3** show several noteworthy features.

Treatment of LiL with one equivalent of $TiCl_2(OiPr)_2$ gave the mixed-ligand monochloride complex [TiCl(L)(O-*i*Pr)$_2$] (**1**; Scheme 2). A second deprotonation of LiL with *n*BuLi gave white crystals of Li_2L (**2**) in high yield (80%). Reaction of **2** with $TiCl_2(OiPr)_2$ afforded yellow, crystalline [Ti(L)(O*i*Pr)$_2$] (**3**), in marked contrast to the didentate amidinate product **1**.

Interestingly, treatment of Na_2L' {H_2L' = [(1*R*,2*R*)-(−)-1,2-[N(H)C(Ph)N($SiMe_3$)]$_2C_6H_{10}$]} (derived from the lithium compound by reaction with *t*BuNa and synthesized in a manner analogous to that employed for the preparation of benzamidinates[6,9,11]) with $TiCl_2(OiPr)_2$ also gave compound **3**, probably via an unusual rearrangement/elimination reaction (Scheme 3)[14] that is actually the reverse reaction of the addition reaction. A similar reaction was reported by Richeson in which the treatment of two equivalents of Li[N($SiMe_3$)C(*t*Bu)N($SiMe_3$)] with $SnCl_2$ or $GeCl_2$ gave mixed amido-amidinate complexes of type **A** and loss

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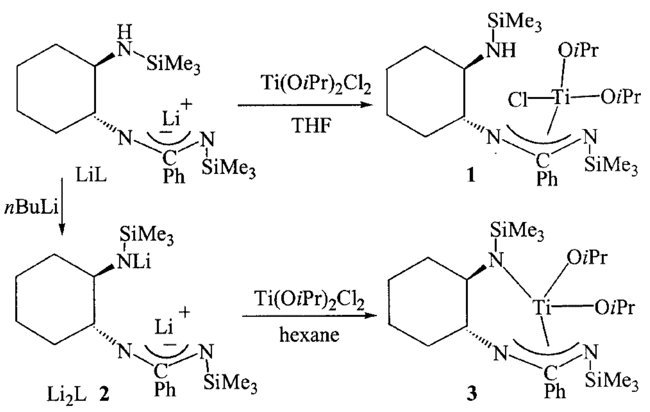
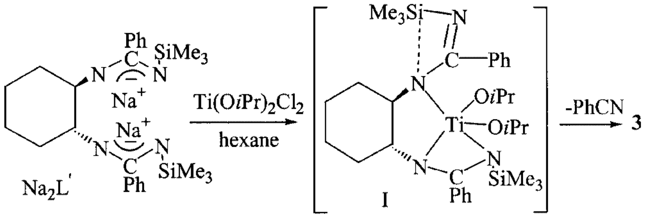
[a] School of Chemistry and Chemical Engineering, The Shanxi University,
Shanxi 030006, China
Fax: (internat.) +86-351/7018091
E-mail: dsliu@sxu.edu.cn
[b] Department of Chemistry, The Fudan University,
Shanghai, China



Scheme 2. Synthesis of complexes **1−3**

of tBuCN.[15] Their investigation showed that the lithium reagent rearranges to form the amido complex, with a 1,3 trimethylsilyl group migration and elimination of tBuCN, upon dissolution in Et_2O, prior to reaction with the metal chloride. In our case, from the ^1H and ^{13}C NMR spectroscopic data of [Na_2L'] there was no such rearrangement/elimination in hexane, and treatment of [Li_2L'] with $ZrCl_4$ gave a linked bis(amidinate) complex [$Zr(L')Cl_2(THF)$] without loss of PhCN (as confirmed by X-ray diffraction).[16] Thus, treatment of [Na_2L'] with $TiCl_2(OiPr)_2$ is likely to proceed via a transition state such as intermediate **I** in Scheme 3, and then lead directly to an amido-amidinate titanium complex of type **C** by an intramolecular rearrangement/elimination of $SiMe_3$/PhCN. The driving force for this reaction might be the steric effects of the isopropoxy groups attached to the Ti atom.



Scheme 3. Reaction of [Na_2L'] with $TiCl_2(OiPr)_2$

The structures of complexes **1−3** were determined by X-ray diffraction and elemental analysis; ^1H and ^{13}C NMR spectroscopy also gave satisfactory results. The molecular structure of **1** is shown in Figure 1. The ligand is doubly coordinated to the central metal atom with Ti−N bond lengths of 2.128(3) and 2.078(4) Å. The benzamidinate ligands form four-membered rings that are almost coplanar with the titanium atom [torsion angle N(5)−C(10)−N(6)−Ti(1) = 9.27°]. The dihedral angle between the benzyl moiety and N5−N6−Ti1 is almost vertical (95.4°), with the two isopropyl groups placed above/below the N5−N6−Ti1 plane.

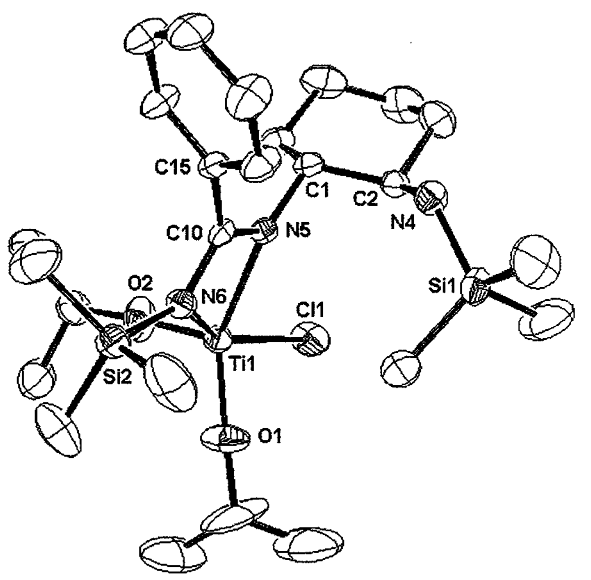


Figure 1. ORTEP view of **1** with thermal ellipsoids at 50% probability level (for one of the two independent molecules in the unit cell); all hydrogen omitted for clarity; selected bond lengths (Å) and angles (deg): N5−Ti1 2.128(3), N6−Ti1 2.078(4), C10−Ti1 2.521(4); N5−C10−N6 112.7(4), N5−Ti1−N6 63.51(13), N5−C1−C2 110.5(3), C1−C2−N4 111.8(4), C1−N5−Ti1 143.1(3)

The molecular structure of **2** is shown in Figure 2. Dimeric aggregation is observed and built around a nearly planar Li_4 ring. However, the coordination number of the Li atoms is different — two are four-coordinate and the other two are three- and two-coordinate — and the Li−Li distances range from 2.415(13) to 2.641(13) Å. Two of the five-membered Li−N−C−C−N rings adopt an envelope conformation.

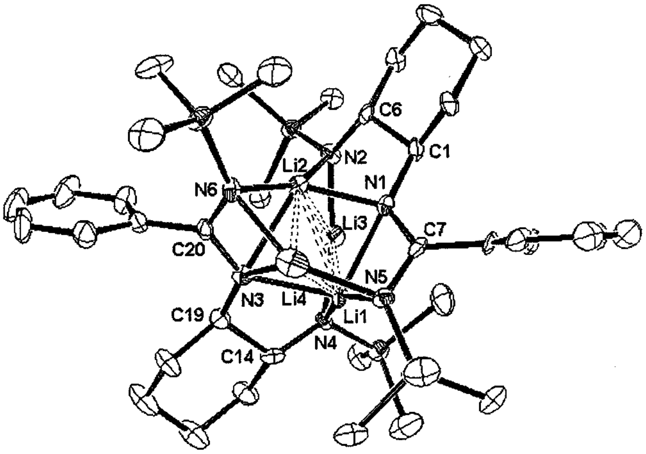


Figure 2. ORTEP view of **2** with thermal ellipsoids at 30% probability level; all hydrogen atoms omitted for clarity; selected bond lengths (Å) and angles (deg): Li1−N1 2.225(10), Li1−N4 1.982(10), Li1−N5 2.039(10), Li1−N3 2.133(9); N1−C7−N5 117.6(5), N6−C20−N3 116.0(5)

The crystal structure determination of **3** confirmed the tridentate nature and the chelating bonding mode of the linked amido-amidinate ligand (Figure 3). The ligand adopts an approximately meridional coordination mode with the amidinate attached to the metal in an η^3-fashion [two Ti−N bonds of 2.087(2) and 2.127(3) Å; Ti−C = 2.492(3) Å] and the amido group by a σ-bond [Ti−N = 1.972(2) Å], a distinct difference from complexes of type **B**, which have a coordinated lone pair of electrons and obvious differences in bond lengths.[8]

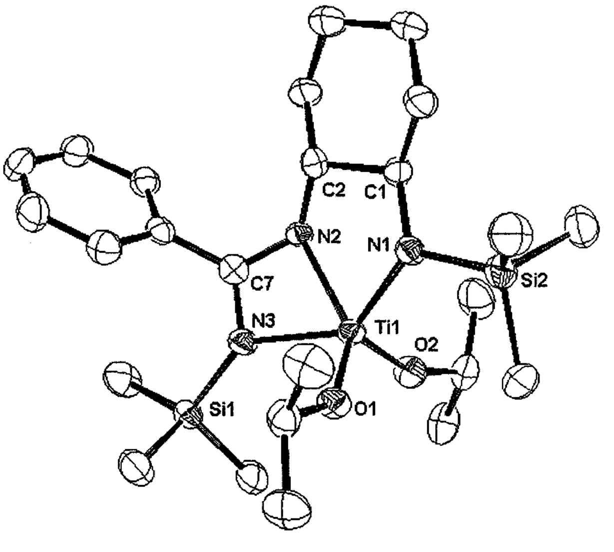


Figure 3. ORTEP view of **3** with thermal ellipsoids at 50% probability level; all hydrogen omitted for clarity; selected bond lengths (Å) and angles (deg): N1−Ti1 1.972(2), N2−Ti1 2.087(2), N3−Ti1 2.127(3), Ti1−C7 2.492(3); C2−C1−N1 108.9(2), C1−C2−N2 103.0(2), C2−N2−Ti1 116.79(18), N2−C7−N3 111.1(3), O1−Ti1−O2 108.82(10)

A comparison of the geometry in **3** with the parent complex **1** shows that the ligand responds to the tethering in the following way: The titanium atom in **3** links to N1 and N2 forming a five-membered ring and thus gives a rigid, bicyclic core with the cyclohexane. This behavior restricts the angles C2−C1−N1 [108.9(2)°] and C1−C2−N2 [103.0(2)°] [the same angles in **1** are 111.8(4) and 110.5(3)°]. As a result of this coordination sphere, the C2−N2−Ti1 angle [116.79(18)°] in **3** is dramatically smaller than the C1−N5−Ti1 angle in **1** [143.1(3)°]. The bond between Ti and the pendant amido group also greatly weakens the *trans* nature of the ligand, with the N1−C1−C2−N2 torsion angle in **3** being −42.68 (1)° [62.71(42)° in **1**].

Experimental Section

General: All manipulations were carried out under argon, using standard high-vacuum, Schlenk techniques. Deuterated solvents (C_6D_6, $CDCl_3$) were dried over Na/K alloy and vacuum transferred before use. Hexane, Et_2O and THF were distilled from over Na or Na/K alloy before use; chlorinated solvents were distilled from over activated molecular sieves (3 Å) or CaH_2. Benzonitrile was redistilled and dried over activated molecular sieves (4 Å) before use. ^{1}H (300 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker DRX-300 spectrometer at ambient temperature. Element analyses were performed by the Analysis Center of Shanxi University.

Preparation of [(1*R*,2*R*)-(−)-1-{NC(Ph)N(SiMe$_3$)}-2-{N(H)SiMe$_3$}-C$_6$H$_{10}$][TiCl(O*i*Pr)$_2$]: White solid TiCl$_2$(O*i*Pr)$_2$ (0.28 g, 1.12 mmol) was added at −78 °C to a solution of LiL (0.41 g, 1.12 mmol) in 20 mL of THF. The mixture was warmed to room temperature slowly and stirred for 12 h. Subsequently, the solvent was removed in vacuo and the residual yellow solid was extracted with hexane (15 mL). The extract was concentrated to ca. 5 mL and cooled to −10 °C for two days, yielding 0.49 g (79%) of pale-yellow, crystalline **1**. ^{1}H NMR (CDCl$_3$): δ = −0.12 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.06 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.72 (m, 1 H, C*H*), 0.92 (m, 1 H, C*H*), 1.33 (m, 12 H, 2 × OCHC$_2$*H*$_6$), 1.48 (m, 2H C*H*), 1.57 (m, 2 H, C*H*), 1.77 (m, 1 H, C*H*), 2.18 (m, 1 H, C*H*), 2.53 (m, 1 H, C*H*), 3.17 (m, 1 H, C*H*), 4.81 (m, 2 H, 2 × OC*H*C$_2$H$_6$), 7.19 (m, 2 H, Ph), 7.39 (m, 3 H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 2.4 [s, (*C*H$_3$)$_3$], 2.5 [s, (*C*H$_3$)$_3$], 26.4 (s, OCH*C*$_2$H$_6$), 26.5 (s, OCH*C*$_2$H$_6$), 33.9 (s, NCC*C*), 38.9 (s, NCC*C*), 54.8 (s, NC*C*), 66.8 (s, CN), 78.2 (s, CN), 83.4 (s, O*C*HC$_2$H$_6$), 83.6 (s, O*C*HC$_2$H$_6$), 129.2 (s, *C*$_5$H$_5$), 130.0 (s, *C*$_5$H$_5$), 136.0 (s, *C*C$_5$H$_5$), 181.2 (s, *C*Ph) ppm. $C_{25}H_{48}ClN_3O_2Si_2Ti$ (562.19): calcd. C 53.41, H 8.61, N 7.47; found C 53.45, H 8.68, N 7.28.

Preparation of Li$_2$L (2): *n*BuLi (2.98 mL, 2.22 M in hexane) was added carefully to a solution of LiL (2.436 g, 6.63 mmol) in hexane (50 mL) by syringe at 0 °C. The mixture was warmed to ambient temperature slowly and stirred overnight. The clear, pale-yellow solution was concentrated to ca. 15 mL, to give colorless, pillar-like, crystalline **2** (1.98 g, 80%). ^{1}H NMR ([D$_6$]benzene): δ = 0.06 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.59 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.85 (m, 1 H, C*H*),1.19 (m, 1 H, C*H*), 1.44 (m, 4 H, C*H*), 1.65 (m, 1 H, C*H*), 1.90 (m, 1 H, C*H*), 3.08 (m, 1 H, C*H*), 3.30 (m, 1 H, C*H*), 7.22 (m, 2 H, Ph), 7.43 (m, 3 H, Ph) ppm. ^{13}C NMR ([D$_6$]benzene): δ = 2.8 [s, (*C*H$_3$)$_3$], 5.3 [s, (*C*H$_3$)$_3$], 26.3 (s, NCC*C*), 27.1 (s, NCC*C*), 35.1 (s, NC*C*), 40.6 (s, NC*C*), 65.1 (s, CN), 67.5 (s, CN), 128.1−128.7 (m, *C*$_5$H$_5$), 141.5 (s, *C*C$_5$H$_5$), 180.4 (s, *C*Ph) ppm. $C_{19}H_{33}Li_2N_3Si_2$ (373.55): calcd. C 61.09, H 8.90, N 11.25; found C 61.23, H 9.11, N 11.01.

Preparation of [(1*R*,2*R*)-(−)-1-{NC(Ph)N(SiMe$_3$)}-2-(NSiMe$_3$)-C$_6$H$_{10}$][Ti(O*i*Pr)$_2$]: TiCl$_2$(O*i*Pr)$_2$ (0.28 g, 1.17 mmol) was added at 0 °C to a solution of Li$_2$L (**2**; 0.44 g, 1.17 mmol) in 25 mL of hexane. The mixture was warmed to room temperature and stirred overnight. Then, the yellow solution was filtered and reduced to ca.10 mL. Cooling to −20 °C for 5 days yielded 0.47 g (76%) of yellow crystalline **3**. ^{1}H NMR (CDCl$_3$): δ = −0.12 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.24 [s, 9 H, NSi(C*H*$_3$)$_3$], 0.98 (m, 2 H, C*H*), 1.33 (m, 12 H, 2×OCHC$_2$*H*$_6$), 1.57 (m, 4 H, C*H*), 1.80 (m, 1 H, C*H*), 1.96 (m, 1 H, C*H*), 2.81 (m, 1 H, C*H*), 3.57 (m, 1 H, C*H*), 4.66 (m, 2 H, 2 × OC*H*C$_2$H$_6$), 7.28 (m, 2 H, Ph), 7.40 (m, 3 H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 2.1 [s, (*C*H$_3$)$_3$], 4.3 [s, (*C*H$_3$)$_3$], 25.3 (s, NCC*C*), 26.2 (s, NCC*C*), 27.0 (s, OCH(*C*H$_3$)CH$_3$], 27.1 (s, OCH(CH$_3$)*C*H$_3$], 27.5 (s, OCH(*C*H$_3$)CH$_3$], 27.6 (s, OCH(*C*H$_3$)CH$_3$], 34.7 (s, NC*C*), 36.4 (s, NC*C*), 71.0 (s, CN), 71.3 (s, CN), 76.1 (s, O*C*HC$_2$H$_6$), 76.7 (s, O*C*HC$_2$H$_6$), 137.4 (s, *C*C$_5$H$_5$), 178.4 (s, *C*Ph) ppm. $C_{25}H_{47}N_3O_2Si_2Ti$ (525.74): calcd. C 57.12, H 9.01, N 7.99; found C 57.30, H 9.23, N 7.63.

Crystal Structure Analysis of 1−3: Bruker SMART APEX diffractometer/CCD area detector, Mo-K_α radiation (λ = 0.71073 Å). Crystal data for **1**: $C_{25}H_{48}ClN_3O_2Si_2Ti$, *M* = 562.19, orthorhombic, space group $P2_12_12_1$, *a* = 11.1529(15) Å, *b* = 13.5196(18) Å, *c* = 43.770(6) Å, α = 90.00°, *V* = 6599.7(15) Å^3, *Z* = 8, $D_{\mathrm{calcd.}}$ = 1.130 g/cm^3, *T* = 180(2) K, scan type ω, μ = 0.436 mm^{-1}, 27252 measured reflections, 11565 independent reflections (R_{int} =

0.0475), refinement on F^2, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0587, ωR_2 = 0.1294.

Crystal data for **2**: $C_{38}H_{66}Li_4N_6Si_4$, M = 747.09, orthorhombic, space group $P2_12_12_1$, a = 13.136(3) Å, b = 18.020(4) Å, c = 19.569(5) Å, α = 90.00°, V = 4632(2) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.071 g/cm^3, T = 180(2) K, scan type ω, μ = 0.159 mm^{-1}, 16612 measured reflections, 7566 independent reflections (R_{int} = 0.0945), refinement on F^2, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0688, ωR_2 = 0.0942.

Crystal data for **3**: $C_{25}H_{47}N_3O_2Si_2Ti$, M = 525.74, orthorhombic, space group $P2_12_12_1$, a = 10.566(2), b = 13.500(3), c = 21.385(4) Å, α = 90.00°, V = 3050.1(10) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.145 g/cm^3, T = 193(2) K, scan type ω, μ = 0.383 mm^{-1}, 12610 measured reflections, 5313 independent reflections (R_{int} = 0.0363), refinement on F^2, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0482, ωR_2 = 0.0888.

CCDC-183020 (**1**), -191953 (**2**) and -191954 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[14] $TiCl_2(OiPr)_2$ (0.19 g, 0.82 mmol) was added at 0 °C to a solution of Na_2L' (0.42 g, 0.82 mmol) in 20 mL of hexane. The mixture was warmed to room temperature and stirred for 48 h. Subsequently, the yellow solution was filtered and reduced to ca. 10 mL. Cooling to −20 °C for seven days yielded 0.32 g (74%) of yellow crystalline **3**.

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