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[1]Metallocenophanes (M = Fe, Ru) of Heavier Group 13 Elements (E = Al, Ga): Synthesis, Characterization, and Ring-Opening Polymerization

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Two new [1]ruthenocenophanes, Ru(η^5-C_5H_4)$_2$E(Me_2Ntsi) (Me_2Ntsi = C($SiMe_3$)$_2$$SiMe_2NMe_2$; E = Al, Ga), bridged by aluminum (**3a**) and gallium (**3b**), were synthesized by reaction of dilithioruthenocene with (Me_2Ntsi)ECl_2 in good to moderate yields (**3a**, 80%; **3b**, 36%). Both species were analyzed by standard techniques (multinuclear NMR spectroscopy, elemental analysis, UV−vis, MS), and their molecular structures were deduced from single-crystal X-ray analysis. Compared to the analogous [1]ferrocenophanes **2a,b**, compounds **3a,b** showed an increased ring tilt as indicated by the tilt angle α (**2a**, α = 14.33(14)°; **3a**, α = 20.31(19)°; **2b**, α = 15.83(19)°; **3b**, α = 20.91(19)°). Ring-opening polymerization (ROP) with previously published aluminum- and gallium-bridged [1]ferrocenophanes Fe(η^5-C_5H_4)$_2$E(Pytsi) (Pytsi = C($SiMe_3$)$_2$$SiMe_2$(2-$C_6H_4$N); E = Al (**1a**), Ga (**1b**)) and Fe(η^5-C_5H_4)$_2$E(Me_2Ntsi) (E = Al (**2a**), Ga (**2b**)) and the [1]ruthenocenophanes **3a,b** (this paper) has been shown to be very sluggish or unsuccessful. Only the ROP of **1b** with [Pd(dba)$_2$] (2 mol %, toluene, 25 °C, 48 h) resulted in polymeric material (GPC analysis: $M_w = 2.11 \times 10^4$, PDI = 3.0).

Introduction

Since the discovery by Manners et al. that strained, ring-tilted [1]ferrocenophanes ([1]FeCPs) yield well-defined organometallic polymers via ring-opening polymerization (ROP), most research in this area has focused on the ferrocene system.[1,2] Two reviews spanning both synthesis of strained metallacenophanes by Manners and properties of poly(ferrocenylsilane)s by Rehahn appeared very reccently.[3,4] Examples of other [1]metallacyclophanes had been restricted to the bis(benzene) complexes [1]vanadarenophanes and [1]chromarenophanes.[5,6] Recently, the field of strained [1]metallacyclophanes was expanded to heteroleptic sandwich complexes containing a five-membered cyclopentadienyl ring and a seven-membered cycloheptatrienyl ring. The first example, a silicon-bridged vanadium complex, was published by Elschenbroich et al.,[7] followed shortly by a report about a titanium complex published by Tamm et al.[8a] Since then, derivatives of [Cr(C_5H_5)(C_7H_7)] bridged by silicon,[9] [V(C_5H_5)(C_7H_7)] bridged by boron,[10] and [Ti(C_5H_5)(C_7H_7)] bridged by Ge[8b] have been described. Very recently, the first bridged species of a benzene−cyclopentadienyl complex containing manganese was published by Braunschweig et al.[11] All the above-mentioned strained compounds contain 3d metals. The only strained sandwich complexes containing a 4d metal are [1]ruthenocenophanes ([1]RuCPs) bridged by Zr- and Sn-containing moieties, respectively.[12] The propensity toward ROP is directly related to the inherent ring strain of a [1]metallacyclophane. The release of ring strain and relaxation back to the coplanar arrangement of the cyclic ligands had been shown to be the driving force for ROP. An indication of the extent of the strain present can be accomplished by a crystallographic measurement of the α angle, which is the angle between the two planes of the tilted cyclic ligands (Figure 1). For a given transition-metal sandwich compound, the amount of ring tilting mainly depends on the size of the bridging element, where a small bridging element results in a larger α angle. To this day, the largest ring tilt of α = 32.4(2)° was found for a boron-bridged [1]FeCP.[13] The incorporation of the group 13 elements Al and Ga into [1]FeCPs, like in **1a,b** and **2a,b** (Figure 1), resulted in a moderate ring tilt in the range of α

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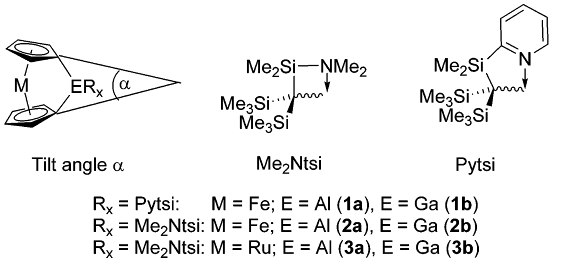


Figure 1. [1]Metallocenophanes stabilized with intramolecular coordinating ligands Me$_2$N(tsi) and Py(tsi).

= 14.33(14)−15.83(19)°,[14−16] values comparable to those exhibited by tin-bridged [1]FeCPs (Sn*t*Bu$_2$, α = 14.1(2)°;[17] SnMes$_2$, α = 15.2(2)° [18]). In contrast, the prototypical SiMe$_2$-bridged [1]FeCP shows a significant strain with α = 20.8(5)°.[19] Since the size of the bridging elements Al and Ga is invariant, we intended to increase the overall ring strain and therefore facilitate ROP by moving to a larger transition metal, namely, ruthenium.

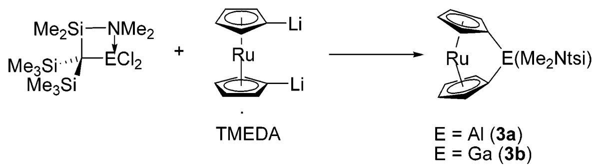
Within this paper, we describe the first aluminum- and gallium-bridged [1]ruthenocenophanes and our attempts to polymerize aluminum- and gallium-bridged [1]metallocenophanes.

Results and Discussion

Recently, we reported the improved synthesis of alumina- and galla[1]ferrocenophanes by employing the intramolecular coordinating ligand Me$_2$Ntsi (Me$_2$Ntsi = C(SiMe$_3$)$_2$SiMe$_2$NMe$_2$) instead of Pytsi (Pytsi = C(SiMe$_3$)$_2$SiMe$_2$(2-C$_6$H$_4$N)) (Figure 1).[16]

The ligand Me$_2$Ntsi, derived from the well-known trisyl ligand, −C(SiMe$_3$)$_3$, by a formal substitution of one methyl group with a Me$_2$N group, provides intramolecular coordination via the nitrogen donor and steric shielding through the trimethylsilyl groups. Element dichlorides (Me$_2$Ntsi)ECl$_2$ of aluminum and gallium are easily accessible in five steps from readily available starting materials.[20] The [1]FeCPs of aluminum (**2a**) and gallium (**2b**) had been obtained from reaction with 1,1′-dilithioferrocene in very good yields (**2a**, 96%; **2b**, 68%).[16] The stabilizing Me$_2$Ntsi ligand also allowed for the isolation of the first aluminum- and gallium-bridged bis(benzene) complexes of vanadium and chromium.[16]

Reaction of 1,1′-dilithioruthenocene with the respective dichloride of (Me$_2$Ntsi)ECl$_2$ in benzene yielded the new aluminum-bridged [1]RuCP **3a** and the gallium-bridged [1]RuCP **3b** in good to moderate yields (80% and 36%; eq 1).



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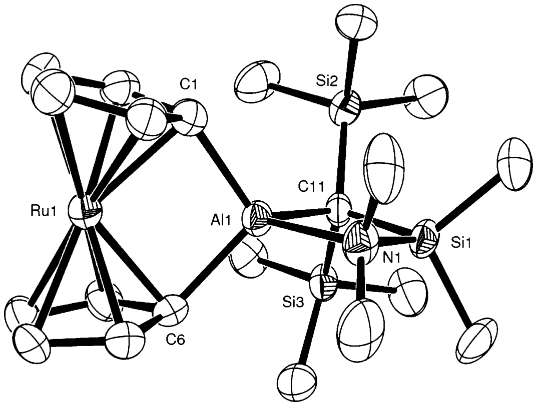

Figure 2. ORTEP plot of **3a** (thermal ellipsoids drawn at the 50% probability level). H atoms and half a molecule of n-hexane are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−C1, 2.018(5); Al1−C6, 2.007(6); Al1−C11, 2.034(5); Al1−N1, 2.015(4); Al1−Ru1, 2.7534(16); C1−Al1−C6, 101.3(2); N1−Al1−C11, 86.4(2); α = 20.31(19).

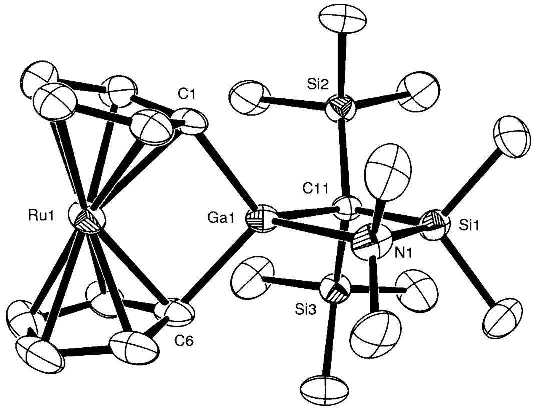

Figure 3. ORTEP plot of **3b** (thermal ellipsoids drawn at the 50% probability level). H atoms and half a molecule of benzene are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1−C1, 2.047(3); Ga1−C6, 2.037(3); Ga1−C11, 2.054(3); Ga1−N1, 2.107(3); Ga1−Ru1, 2.8230(5); C1−Ga1−C6, 98.42(13); N1−Ga1−C11, 84.62(12); α = 20.91(19).

Both complexes can be crystallized from n-hexane or benzene, resulting in half of a solvent molecule in the asymmetric unit, as revealed by single-crystal X-ray crystallography (Table 2, Figures 2 and 3).

The bridging group 13 element in **3a** and **3b** is 4-fold coordinated with bond lengths and angles similar to those found for the respective [1]FeCPs.[16] Expectedly, the main difference between the new [1]RuCPs and the known [1]FeCPs is revealed by the tilt angle α. The gallium compound **3b** with α = 20.91(19)° seems to be slightly more strained than **3a** with α = 20.31(20)°. Compared to the previously published [1]FeCPs [α = 14.33(14)° (**2a**) and 15.83(19)° (**2b**)],[16] this means an increase of the tilt angle of 42% (5.98°) for **3a** and 32% (5.08°) for **3b**. The tilt angles α for **3a,b** are comparable to those of the prototypical Me$_2$Si-bridged [1]FeCPs **4** (α = 20.8(5)°).[19] The extents of the tilt in **2a,b** and **3a,b** are also reflected by a typical red shift and increase in absorption coefficient of the lowest absorption band in the visible spectrum (Table 1).[18,21]

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Table 1. UV−Vis Data of 2a,b and 3a,b[a]

Fe	λ_{max}	ϵ	α	Ru	λ_{max}	ϵ	α
Cp_2Fe	440	99		Cp_2Ru	322	160	
2a	477	140	14.3	**3a**	357	560	20.3
2b	479	155	15.8	**3b**	358	365	20.9
Me_2Si[b]	482	375	20.8	Mes_2Sn[c]	363	436	20.6

[a] Units: λ_{max}, nm; ϵ, L/(mol·cm); α, deg. [b] Data taken from ref 22. [c] Data taken from ref 12.

Table 2. Crystal and Structural Refinement Data for 3a,b

	$\mathbf{3a}\cdot{}^1/_2C_6H_{14}$	$\mathbf{3b}\cdot{}^1/_2C_6H_6$
empirical formula	$C_{24}H_{45}AlNRuSi_3$	$C_{24}H_{41}GaNRuSi_3$
fw	559.93	598.64
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a, Å	9.0629(6)	9.0977(3)
b, Å	12.8123(9)	9.1156(3)
c, Å	13.6050(7)	19.1531(7)
α, deg	110.401(4)	79.084(2)
β, deg	90.731(4)	84.375(2)
γ, deg	98.070(4)	62.2079(17)
vol, $Å^3$	1462.87(17)	1379.65(8)
d(calcd), mg/m^3	1.271	1.441
temp, K	173(2)	173(2)
abs coeff, mm^{-1}	0.700	1.666
θ range, deg	2.63−26.00	2.53−27.41
no. of reflns collected	17766	22122
no. of independent reflns	5714 [*R*(int) = 0.0931]	6195 [*R*(int) = 0.0549]
abs correction	*ψ* scan	*ψ* scan
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/ restraints/ params	5714/168/339	6195/0/282
GOF on F^2	1.028	1.044
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0574, wR2 = 0.1219	R1 = 0.0386, wR2 = 0.0813
R indices (all data)	R1 = 0.0920, wR2 = 0.1385	R1 = 0.0552, wR2 = 0.0894
largest diff peak and hole, e·$Å^{-3}$	1.310 and −0.652	0.955 and −1.043

Table 3. Comparison of DSC Data

	1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4**[c]
mp (°C)	*a*	*a*	177	183	*a*	*a*	78
onset (°C)	180	173	212	220	216	*b*	120
Δ*H* (kJ/mol)	−30	−55	−59	−43	−55	*b*	−80

[a] No melting point detected. [b] No exotherm detected. [c] $Fe(\eta^5\text{-}C_5H_4)_2SiMe_2$ (**4**), data taken from ref 19.

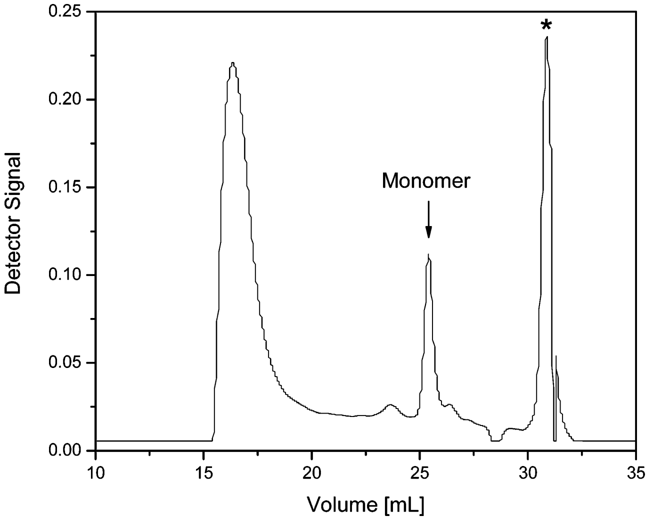

Figure 4. GPC trace obtained from polymerization of **1b** with [Pd(dba)$_2$] (2 mol %, toluene, 25 °C, 48 h). The asterisk indicates the internal standard toluene.

Ring-Opening Polymerization. We started to explore the application of compounds **1**−**3** as monomers in ROPs. Thermal, anionic, transition-metal-catalyzed, and photocontrolled ROPs are the four major pathways to synthesize high-molecular-weight polyferrocenes.[1−4] To test the ability of ring opening of a new monomer, usually a differential scanning calorimetry (DSC) experiment is performed. This experiment can provide a melting point (endothermic peak), the onset temperature for thermal ROP, and the enthalpy of ring strain release.

Compounds **1a**−**3a** all showed exothermic peaks, which we interpret as the result of ring opening (Table 3). Compounds **2a,b** also showed a sharp melting point without decomposition. Interestingly, **3b** showed a featureless spectrum in repeated DSC experiments up to 300 °C, indicating that neither melting nor ring opening occurred (see the Supporting Information). To date, we cannot explain this unusual behavior of **3b**. Even though the DSC results looked promising with respect to preparing new polymers via thermal ROP, all preparative attempts to obtain new polymers failed. In addition, we tested our monomers of types **1**−**3** with respect to anionic, transition-metal-catalyzed, and photocontrolled ROP; however, preliminary results showed that only the transition-metal-catalyzed ROP resulted in polymeric material (see below). All other attempts proved to be either sluggish or unsuccessful, and full experimental details are given in the Supporting Information.

The most promising results were obtained with transition-metal(0) complexes as catalysts. For **1b** we did a series of experiments using 2 mol % [Pd(dba)$_2$] (dba = dibenzylideneacetone) in toluene or THF at ambient temperature or 40 °C for 48 h and analyzed the samples via GPC (Figure 4). In all cases, polymeric material was found independent of the solvent or temperature.

The solvent was removed from the reaction mixture on a rotaevaporator and directly injected into the GPC instrument. The polymer fraction was eluted between 15 and 20 mL, giving a calculated polymer weight M_w of 2.11 × 10^4 with a PDI of 3.0. Interestingly, under these conditions, unreacted monomer could be detected by GPC (V = 26 mL). We are currently working on optimizing the reaction conditions, including a workup procedure to purify the polymer from lower molecular weight oligomers and unreacted monomer. We also started to employ light scattering methods to unambiguously analyze polymer weights.

Summary and Conclusions

Within this paper we presented the synthesis of the first strained [1]RuCPs bridged by the group 13 elements aluminum (**3a**) and gallium (**3b**). Both compounds are very similar to their 3d metal counterparts **2a,b**,[16] with the main difference being the expected larger ring tilt in [1]RuCPs. Preliminary results on the ring-opening polymerization of aluminum- and gallium-bridged [1]metallocenophanes **1a,b**, **2a,b,** and **3a,b** were discussed. All strained complexes except for **3b** showed an exothermic ring opening at elevated temperatures as measured by DSC. However, out of attempted thermal, anionic, photocontrolled, and transition-metal-catalyzed ROP, only the latter method using [Pd(dba)$_2$] and monomer **1b** gave the first evidence of the formation of polymeric material. In conclusion, there might be three contributing factors to the little success of ROP so far. First, it seems that the intramolecular coordinating ligand Me_2Ntsi is too bulky and protects the C_5H_4 bridging element bonds from nucleophilic attack or oxidative insertion of an ROP initiator. Second, it is known that side group interactions between sterically demanding substituents cause a substantial destabilization of the targeted polymer, resulting in a significant decrease of polymerization enthalpy.[23] Third, although the monomers seem to thermally ring open, the Al−C or Ga−C bond formation in the propagation step might be hampered. It should be mentioned that attempts to polymerize the only other example of a group 13 bridged [1]metallocenophane, a boron-bridged [1]FeCP, by thermal ROP and transition-metal-catalyzed ROP were also sluggish or unsuccessful.[23] To date, the only reported, well-characterized polyferrocene containing a group 13 element was obtained by polycondensation of an unstrained ferrocenylborane followed by derivatization to make the material soluble and less air sensitive.[24] The material was then analyzed by GPC and MALDI TOF−TOF and showed a polymerization degree of 21 repeating units.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques, if not noted differently. For synthesis the solvents were dried using a Braun solvent purification system and stored under nitrogen over 4 Å molecular sieves. C_6D_6 and C_7D_8 were degassed prior to use and stored under nitrogen over 4 Å molecular sieves. $AlCl_3$ and $GaCl_3$ were purchased from VWR, and $AlCl_3$ was sublimed prior to use. $RuCl_3{\cdot}xH_2O$ (∼41% Ru) was purchased from Alfa Aesar and used as received. $[Pd(dba)_2]$ was purchased from Acros Chemicals (16−21% Pd). ^1H, ^{13}C, and ^{27}Al NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. ^1H and ^{13}C chemical shifts were referenced to peaks of the deuterated solvent (C_6D_6, ^1H δ 7.15, ^{13}C δ 128.0; C_7D_8, $-CD_3$ ^1H δ 2.10, ^{13}C δ 20.4). ^{27}Al chemical shifts were referenced to the peaks of $[Al(acac)_3]$ in C_6D_6 (^{27}Al δ 0.0). All NMR spectra were obtained in C_6D_6 at 25 °C, unless noted differently. Mass spectra were measured on a VG 70SE and were reported in the form *M* (*I*) [F], where *M* is the mass observed, *I* (%) is the intensity of the peak relative to the most intense peak in the spectrum, and F is the molecular ion or fragment. Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer; samples were prepared in a glovebox, and V_2O_5 was added to promote combustion.

For polymerization and light scattering experiments the solvents were vacuum transferred from solutions containing the deep red 1,1-diphenylhexyllithium as an indicator. These so-prepared solvents were moved into a glovebox. All manipulations were carried out in a glovebox; glassware and NMR tubes for flame-sealing experiments were stored in an oven at 200 °C for at least 1 h and moved directly into the antechamber of a glovebox. THF solutions for DLS (∼5 mg/mL) were prepared in a glovebox, filtered a minimum of two times through a Millex-FG13 PTFE syringe filter with a 0.2 μm pore size directly into a 12 μL quartz cuvette capped with a plastic lid, and sealed with Parafilm. DLS measurements were performed on a DynamPro-MS800.

Ruthenocene[25] and 1,1′-dilithioruthenocene·TMEDA[26] were synthesized according to the literature.

Synthesis of 3a. A solution of $(Me_2Ntsi)AlCl_2$ (0.465 g, 1.27 mmol) in benzene (10 mL) was added dropwise via tubing to a suspension of dilithioruthenocene·TMEDA (0.457 g, 1.27 mmol) in benzene (10 mL). After the solution was stirred for 16 h, its color had changed to gold-brown. After filtration, the reaction mixture was concentrated, upon which crystallization of pure **3a** occurred at 8 °C (0.53 g, 80%). These crystals contain half a molecule of benzene in the asymmetric unit. X-ray-quality crystals were obtained through recrystallization from n-hexane. ^1H NMR (500 MHz): δ 0.16 (s, 6H, $SiMe_2$), 0.43 (s, 18H, $SiMe_3$), 2.00 (s, 6H, NMe_2), 3.98, 4.48 (pst, 4H, C_5H_4), 5.21 (pst, 4H, C_5H_4). ^{13}C NMR (125.8 MHz): δ 2.7 ($SiMe_2$), 7.7 ($SiMe_3$), 40.7 (NMe_2), 50.3 (*ipso*-C, C_5H_4, −40 °C, C_7D_8), 75.6, 76.2, 77.9, 78.2 (C_5H_4), one C is obscured. ^{27}Al NMR (130.3 MHz): δ 149 ($h_{1/2} = 2800$ Hz). MS (70 eV, EI+): *m/z* (rel intens) 517 (49) $[M^+]$, 502 (46) $[M^+ - Me]$, 459 (47) $[M^+ - SiMe_2]$, 401 (30) $[MH^+ - Me_2NSiMe_2]$, 232 (31) $[RuCp_2^+]$, 73 (100) $[SiMe_3^+]$. UV (THF): λ_{max} [nm (ϵ)] 357 (560). Anal. Calcd for $C_{21}H_{38}AlRuNSi_3{\cdot}0.5C_6H_6$ (555.89): C, 51.85; H, 7.43; N, 2.52. Found: C, 50.36; N, 7.40; H, 2.71.

Synthesis of 3b. A solution of $(Me_2Ntsi)GaCl_2$ (0.564 g, 1.39 mmol) in benzene (10 mL) was added dropwise via tubing to a suspension of dilithioruthenocene·TMEDA (0.500 g, 1.39 mmol) in benzene (10 mL). After the solution was stirred for 16 h, its color had changed to gold-brown. After filtration, the reaction mixture was concentrated, upon which crystallization of pure **3b** occurred at 8 °C (0.30 g, 36%). These crystals contain half a molecule of benzene in the unit cell. ^1H NMR (500 MHz): δ 0.16 (s, 6H, $SiMe_2$), 0.40 (s, 18H, $SiMe_3$), 2.03 (s, 6H, NMe_2), 3.99, 4.38 (pst, 4H, C_5H_4), 5.22 (pst, 4H, C_5H_4). ^{13}C NMR (125.8 MHz): δ 2.7 ($SiMe_2$), 6.9 ($SiMe_3$), 40.8 (*ipso*-C, C_5H_4, −40 °C, C_7D_8), 41.8 (NMe_2), 75.0, 75.6, 78.1 (C_5H_4), one C is obscured. MS (70 eV, EI+): *m/z* (rel intens) 559 (1.7) $[M^+]$, 246 (67) $[Me_2N(tsi)H^+ - Me]$, 232 (22) $[RuCp_2^+]$, 102 (27) $[SiMe_2NMe_2^+]$, 78 (100) $[C_6H_6^+]$, 73 (48) $[SiMe_3^+]$. UV (THF): λ_{max} [nm (ϵ)] 358 (365). Anal. Calcd for $C_{21}H_{38}GaNRuSi_3{\cdot}0.5C_6H_6$ (598.64): C, 48.15; H, 6.90; N, 2.34. Found: C, 49.32; H, 8.36; N, 3.67.

Crystal structure determination. The crystal data of **3a,b** was collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[27] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[28] SIR97[29] was used to solve the structure and SHELXL-97[30] was used to refine the structure. ORTEP-3 for Windows[31] was used for molecular graphics and PLATON[32] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom for aromatic protons. U_{iso} is constrained to be 1.5 times U_{eq} for methyl protons. For compound **3a**, a solvent n-hexane molecule was found disordered around a center of symmetry. It was modelled in two different positions. The atoms were highly constrained to acceptable n-hexane geometries. After the n-hexane molecule had settled in positions, the positions and anisotropic displacement factors were frozen to complete the refinement.

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Supporting Information Available: Crystallographic data for **3a,b** in CIF file format, details on the analysis of the polymers (GPC, DLS, MALDI-TOF), and experimental details on attempts with thermal, anionic, and photocontrolled ROP. This material is available free of charge via the Internet at http://pubs.acs.org.

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