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Synthesis and Characterization of Heavier Group 13 Element Ferrocenophanes: The First Gallium-Bridged [1]Ferrocenophane and an Unusual Indium Species

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On the basis of our previous results with aluminum, we herein report the synthesis of the first gallium-bridged [1]ferrocenophane. The attempt to synthesize the respective indium compound resulted in an unusual ferrocenophane containing an In−(μ-Cl)$_2$−In group in the bridging position. All compounds have been characterized by NMR spectroscopy and single-crystal X-ray structural determination.

Introduction

Since their discovery in 1975 by Osborne and Whiteley,[1] strained [1]ferrocenophanes (Figure 1) have sparked much interest throughout the scientific community. Manners et al. showed that strained [1]ferrocenophanes can serve as monomers for polymetallocenes via ring-opening polymerization (ROP).[2] Until recently, strained [1]ferrocenophanes containing a bridging group 13 element were only known for boron (ER$_x$ = BN(SiMe$_3$)$_2$, BN(SiMe$_3$)*t*Bu, BN*i*Pr$_2$).[3] Very recently, we successfully synthesized the first [1]ferrocenophane containing the heavier group 13 element aluminum. The [1]aluminaferrocenophane ([1]Al−FCP), equipped with the stabilizing "pytrisyl" ligand [ER$_x$ = Al(Pytsi) with Pytsi = C(SiMe$_3$)$_2$SiMe$_2$(2-C$_5$H$_4$N)], was characterized by a single-crystal X-ray analysis.[4] The pytrisyl ligand, derived from the parent trisyl ligand C(SiMe$_3$)$_3$ by a formal substitution of one methyl group with a pyridyl ring, provides intramolecular coordination via the N atom of the pyridine ring and steric shielding through the trimethylsilyl groups. The pytrisyl ligand was introduced in 2000[5] and has mainly been used for transition metal chemistry.[6]

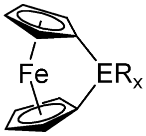

Figure 1. ER$_x$-bridged [1]ferrocenophane.

Unstrained [1.1]ferrocenophanes, formal dimers of [1]ferrocenophanes, where two ferrocene moieties are bridged by two metals, are investigated for their redox properties as model compounds for electronic interactions of iron centers.[7] So far, [1.1]ferrocenophanes containing group 13 elements have been known for boron[7] and gallium.[8] Very recently, we characterized the first aluminum-containing [1.1]ferrocenophane by single-crystal X-ray analysis.[9] Within this publication we report on our results to synthesize gallium- and indium-bridged [1]ferrocenophanes.

Results and Discussion

The successful synthesis of the first [1]Al−FCP was achieved by reaction of dilithioferrocene with (Pytsi)AlCl$_2$.[4] To apply the same method to gallium and indium, the respective starting compounds (Pytsi)ECl$_2$ [E = Ga (**1**), In (**3**)] were needed. The aluminum compound (Pytsi)AlCl$_2$ was described in 2005,[10] and the same publication described the attempted synthesis of the dihalides (Pytsi)GaBr$_2$ and (Pytsi)InCl$_2$ (**3**). However, only partly hydrolyzed compounds of the type (Pytsi)EX$_x$(OH)$_y$ could be isolated, and the authors speculated that this was due to partly hydrolyzed

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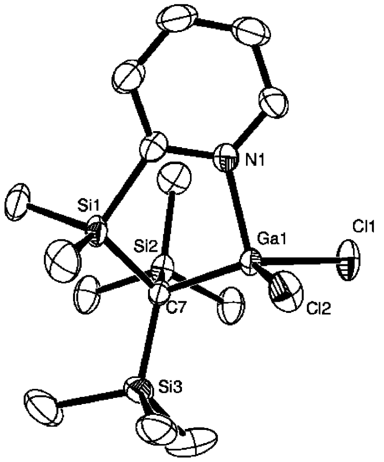
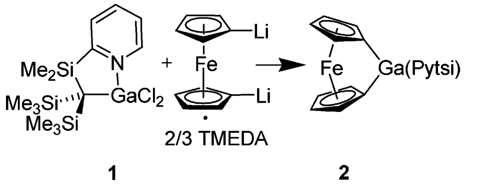


Figure 2. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1−N1 = 2.004(2), Ga1−C7 = 1.988(2), Ga1−Cl1 = 2.1816(7), Ga1−Cl2 = 2.2016(7), N1−Ga1−C7 = 98.03(9), N1−Ga1−Cl1 = 104.91(7), N1−Ga1−Cl2 = 98.95(7), Cl1−Ga1−Cl2 = 103.73(3), Cl2−Ga1−C7 = 121.49(8), C7−Ga1−Cl1 = 124.77(8).

starting materials.[10] We encountered no problems in isolating analytically pure **1** and **3** in good yields by using readily available $GaCl_3$ and $InCl_3$ (see Experimental Section for details).

As expected, the starting gallane **1** is a monomeric species in the solid state (Figure 2, Table 1). The Ga−N bond length of 2.004(2) Å is slightly shorter than that of 2.047(5) Å found in the (Pytsi)GaBr(OH),[10] with a similar difference found for the Ga−C bond lengths [1.988(2) Å for **1** and 2.008(5) Å for (Pytsi)GaBr(OH)]. As expected, the M−N bond of the respective dichloro alane (Pytsi)$AlCl_2$ is, at 1.9383(16) Å, significantly shorter,[10] exemplifying the well-known fact that a $GaCl_2$ moiety is the weaker Lewis acceptor for a hard Lewis donor compared to an $AlCl_2$ group.



(eq. 1)

1 **2**

A slurry of dilithioferrocene·2/3TMEDA in toluene was slowly added to a cooled solution of **1** in toluene to give the gallium-bridged [1]ferrocenophane **2** (eq 1). Compound **2** was isolated as deep red crystal from hexane in a yield of 59%. Compound **2** is a gallium-bridged [1]ferrocenophane, which is clearly revealed by its NMR data. It shows signal pattern and shifts in the ^{1}H and ^{13}C NMR spectra similar to those of the [1]Al−FCP;[4] both ferrocenophanes are time-averaged C_s symmetrical species in solution.

So far, several attempts to solve the structure of **2** by single-crystal X-ray analysis ended in partially solved structures (Figure 3; see Experimental Section for details). The best solution shows four molecules in the asymmetric unit ($P2_1$) with an R value of 14.3%. The crystals of **2** diffracted very poorly, and the data do not give a complete crystal structure of **2** with accurate bond lengths and bond angles, but show with certainty the presence of the targeted [1]Ga−FCP (Figure 3). A set of tilt angles is commonly used to describe strained [1]ferrocenophanes (Figure 4).[11] The asymmetric unit of compound **2** exhibits four molecules with tilt angles α of 13.6(2.1)°, 15.0(1.6)°, 15.4(1.9)°, and 18.8(1.8)°, resulting in an average of 15.7°. This is a very reasonable value if compared with $\alpha = 14.9(3)°$ found for the [1]Al−FCP.[4]

It is common practice to deduce the amount of ring strain present in [1]ferrocenophanes from two NMR parameters: the difference in the splitting of the Cp protons (denoted as $\Delta\delta$) and the upfield shift of the two *ipso*-C atoms of each Cp ring in the ^{13}C NMR spectra. The ^{1}H NMR spectra of **2** show four pseudotriplets at δ = 4.08, 4.45, 4.61, and 4.65, corresponding to a $\Delta\delta$ = 0.57, and the resonance of the *ipso*-C is found at δ = 47.24. The respective values for the [1]Al−FCP are 0.77 ($\Delta\delta$) and 52.92 (*ipso*-C). For comparison, the highly strained sulfur-bridged [1]ferrocenophane (ER_x = S), with the large tilt angle of $\alpha = 31.05(10)°$, shows a splitting of the two pseudotriplets of $\Delta\delta$ = 0.65 and the *ipso*-C resonates at δ = 14.6.[12] From first glance, the comparable large $\Delta\delta$ of the less strained compound **2** and [1]Al−FCP, respectively, might indicate highly strained molecules. However, most of the [1]ferrocenophanes are C_{2v} symmetrical species resulting in two pseudotriplets. Consequently, the $\Delta\delta$ value expresses the splitting between the two Cp protons adjacent to the bridge and the two Cp protons away from the bridge. To obtain a more realistic splitting value $\Delta\delta$, we assigned all four pseudotriplets to Cp protons in compound **2** using NOE experiments (Figure 5). The difference between average chemical shifts of Cp protons adjacent to gallium (H_a and $H_{a'}$) and away from gallium (H_b and $H_{b'}$) amounts to $\Delta\delta$ = 0.37; a similar procedure gives a $\Delta\delta$ of 0.49 ppm for the [1]Al−FCP.[4] Still, compared with other [1]ferrocenophanes such as [1]Si−FCP ($ER_x = SiMe_2$; $\alpha = 20.8(5)°$; $\Delta\delta$ = 0.40),[13] [1]Ge−FCP ($ER_x = GeMe_2$; $\alpha = 19.0(9)°$; $\Delta\delta$ = 0.26),[13] [1]Sn−FCP ($ER_x = SntBu_2$; $\alpha = 14.1(2)°$; $\Delta\delta$ = 0.22; $ER_x = SnMes_2$; $\alpha = 15.2(2)°$; $\Delta\delta$ = 0.13),[13] and [1]B−FCP ($ER_x = BN(SiMe_3)_2$; $\alpha = 32.4(2)°$; $\Delta\delta$ = 0.50; $ER_x = BNiPr_2$; $\alpha = 31.0(2)°$ and 31.4(2)°; $\Delta\delta$ = 0.39)[3] the splitting in **2** and [1]Al−FCP, respectively, are large and do not correlate nicely with the small ring tilt.

As an indication for ring strain, the *ipso*-C shift seems more reliable, because it is not dependent on the overall symmetry of the [1]ferrocenophane. The values for the *ipso*-C atoms in **2** (δ = 47.24) and [1]Al−FCP (δ = 52.92) are significantly upfield shifted with respect to parent ferrocene (δ = 68). However, they are only slightly downfield from the value of the known [1]B−FCP (δ = 44−45), which does not correlate with the tremendous difference in the ring tilt.[3b] The boron-bridged compounds exhibit the largest known ring tilt in ferrocenophanes, but their *ipso*-C resonances are compared with the similar strained [1]S−FCP (δ = 14.6) appearing

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Table 1. Crystal and Structural Refinement Data for Compounds 1, 3, and 4

	1	3	4·2.5toluene
empirical formula	$C_{14}H_{28}Cl_2GaNSi_3$	$C_{28}H_{56}Cl_4In_2N_2Si_6$	$C_{55.50}H_{84}Cl_2FeIn_2N_2Si_6$
fw	435.26	960.7318	1304.18
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic
space group (No.)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P\bar{1}$ (2)
Z	2	2	2
a, Å	9.0460(2)	9.2181(2)	14.1309(9)
b, Å	10.0441(2)	24.3893(5)	14.7231(11)
c, Å	11.8243(3)	12.5633(3)	16.135(2)
α, deg	84.7182(10)	90	72.624(4)
β, deg	89.2236(10)	131.6290(10)	77.960(6)
γ, deg	87.5315(10)	90	87.868(4)
vol, $Å^3$	1068.74(4)	2111.22(9)	3132.1(5)
d (calc), mg/m^3	1.353	1.511	1.383
temp, K	173(2)	173(2)	173(2)
abs coeff, mm^{-1}	1.700	1.537	1.194
θ range, deg	2.04 to 27.65	2.32–27.47	2.90–25.03
no. of reflns collected	9350	8767	40 880
no. of indep reflns	4911	4810	11 048
abs correction	none	semiempirical from equivalents	
ref method	full-matrix least-squares on F^2		
no. of data/restr/params	4911/0/198	4810/0/198	11 048/242/638
goodness-of-fit on F^2	1.030	1.061	1.102
final R indices [$I > 2\sigma(I)$]	R1 = 0.0373, wR2 = 0.0793	R1 = 0.0334, wR2 = 0.0653	R1 = 0.0595, wR2 = 0.1030
R indices (all data)	R1 = 0.0587, wR2 = 0.0888	R1 = 0.0481, wR2 = 0.0709	R1 = 0.0882, wR2 = 0.1114
largest diff peak and hole, e $Å^{-3}$	0.382 and −0.467	0.493 and −0.688	0.988 and −0.793

at unexpected low field.[3b] Braunschweig and Manners suggested that this is a result of the electropositive nature of the bridging boron atom.[3b] However, silicon is more electropositive than boron, but the *ipso*-C atoms of less-strained [1]Si−FCP are found at higher field (ER_x = $SiMe_2$; $\delta = 33.1$).[13] In summary, one can say that an upfield shift of the *ipso*-C atom resonances compared to the parent ferrocene indicates tilted Cp rings, but a simple correlation for all known [1]ferrocenophanes seems not to exist.

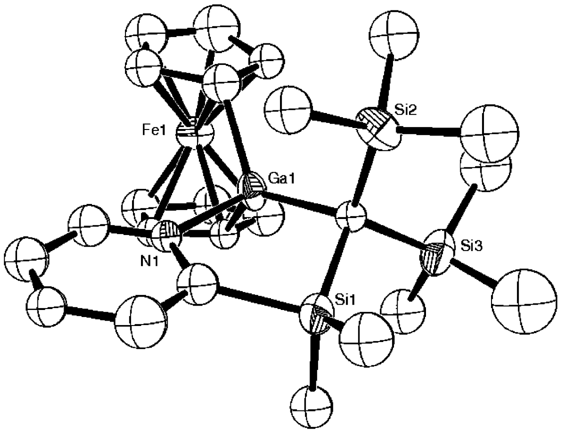


Figure 3. Molecular framework structure of **2**. One of four independent molecules is shown (see Experimental Section for details).

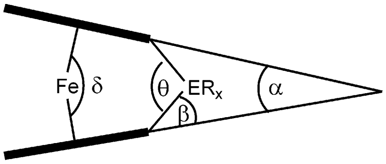


Figure 4. Common set of tilt angles to describe [1]ferrocenophanes.

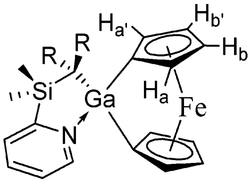


Figure 5. Assignment of the Cp protons via NOE experiment (R = $SiMe_3$): $\delta = 4.08$ (H_a), 4.45 ($H_{a'}$), 4.61 (H_b), 4.65 ($H_{b'}$).

In a manner similar to that described for the gallane **2**, we attempted to synthesize an indium-bridged [1]ferrocenophane. We synthesized the required starting complex (Pytsi)$InCl_2$ (**3**) from $InCl_3$ and Li(thf)(Pytsi)[5]. As revealed by a single-crystal X-ray analysis, compound **3** forms dimers in the solid state (Figure 6; Table 1). This is not surprising, because indium prefers higher coordination numbers than 4.

Each indium atom is 5-fold coordinated, with two chlorine atoms bridging the two metal centers and two terminal chlorine ligands, which are *trans* to each other (Figure 6). Both indium atoms are in a center of a distorted trigonal bipyramid with both polyhedra sharing the Cl2−Cl2′ edge to form a centrosymmetric dimer. For example, In1 is coordinated by Cl1, Cl2, and C7 in the equatorial position (angle sum = 359.9°) and by N1 and Cl2′ in the axial position (N1−In1−Cl2′ = 162.50(6)°) (Figure 6). Both chlorine bridges are asymmetric, e.g., with a long In1−Cl2′ bond of 2.7706(7) Å and a short In1−Cl2 bond of 2.4812(7) Å.

The dimer **3** (C_i point group symmetry) is very flexible in solution. The ^1H and ^{13}C NMR spectra show only one type of pytrisyl ligand, which is C_s symmetrical in solution, e.g., only one singlet for $SiMe_2$ and one singlet for the $SiMe_3$ groups. These NMR data could be interpreted in several ways, and one can speculate that a fast monomer−dimer equilibrium occurs in solution.

Similar to the synthesis of compound **2** (eq 1), a synthesis of an [1]In−FCP was attempted. The only isolatable product from this batch was the unexpected ferrocenophane **4**, and consequently, we changed the In

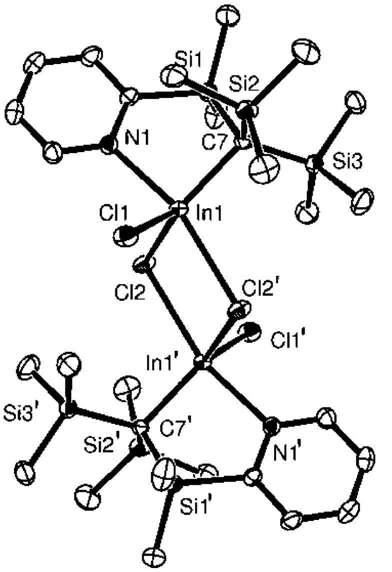
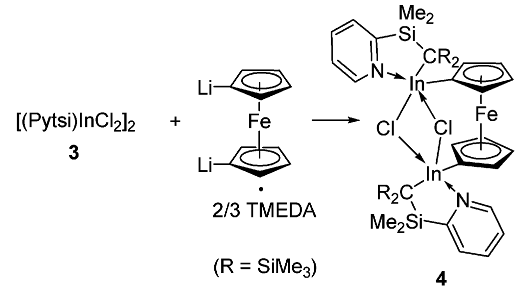


Figure 6. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity. Primed atoms are generated by $-x$, $-y$, $-z$ operation. Selected bond lengths (Å) and angles (deg): In1−Cl1 = 2.3845(7), In1−Cl2 = 2.4812(7), In1−Cl2′ = 2.7706(7), In1−C7 = 2.195(3), In1−N1 = 2.307(2), Cl1−In1−C7 = 124.01(8), Cl2−In1−C7 = 126.80(8), Cl1−In1−Cl2 = 109.10(3), N1−In1−Cl2′ = 162.50(6), N1−In1−C7 = 90.07(9), N1−In1−Cl1 = 90.25(6), N1−In1−Cl2 = 86.53(6), Cl2′−In1−C7 = 105.89(7), Cl2′−In1−Cl1 = 86.73(3), Cl2′−In1−Cl2 = 78.21(2).

to Fe ratio to 2:1 to optimize the synthesis of the novel compound **4** (eq 2).



(eq. 2)

Dropwise addition of the poorly soluble complex **3** in toluene to a cooled slurry of dilithioferrocene·2/3TMEDA[16] in toluene and subsequent filtration yielded an orange solution, which was concentrated, resulting in a crystallization of **4** at −10 °C. Suitable crystals for X-ray diffraction were taken directly out of the toluene solution (Figure 7; Table 1).

The isolated ferrocene derivative **4** contains a similar In−(μ-Cl)$_2$−In unit as the starting indane **3**, but in contrast to compound **3**, there is no 2-fold symmetry element that renders the two molecular halves of **4** identical. However, the molecular geometry of compound **4** is very close to C_2 point group symmetry. Each indium atom is trigonal bipyramidally surrounded. In each case, a set of two C atoms and one Cl atom define the equatorial plane (angle sum = 359.9° for In1 and In2, respectively); N and Cl atoms are coordinated at the axial positions (N1−In1−Cl1 = 162.37(11)° and N21−In2−Cl2 = 161.86(12)°; Figure 7). As for **3**, the In−(μ-Cl)$_2$−In moiety shows a short [In1−Cl2 = 2.5087(14) Å and In2−Cl1 = 2.5072(15) Å] and a long [In1−Cl1 = 2.8322(15) Å and In2−Cl2 = 2.8655(15) Å] indium chlorine bond. These distances are slightly longer than those found in **3** [In1−Cl2 = 2.4812(7) Å, and In1−Cl2′ = 2.7706(7) Å; Figure 6], which might reflect the weaker Lewis-acidity of indium in **4**, caused by fewer chloride substituents. Compound **4** is unstrained, as revealed by a tilt angle α = 2.10(45)°; the Cp rings are staggered at an average angle of 29.12(38)° to each other. It seems that the rotational flexibility of the Cp ligands in ferrocene allows for an ideal adjustment to fit in an In−(μ-Cl)$_2$−In unit.

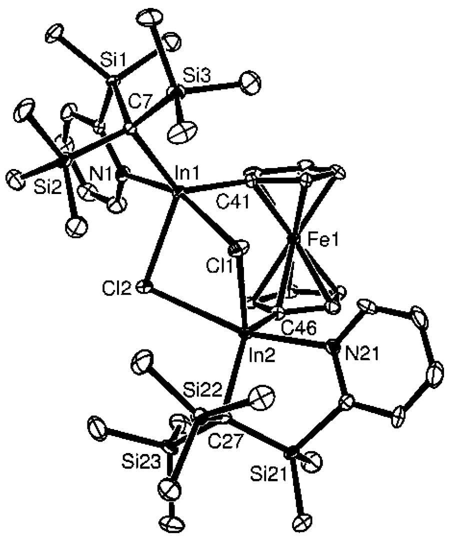


Figure 7. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): In1−Cl1 = 2.8322(15), In2−Cl2 = 2.8655(15), In1−Cl2 = 2.5087(14), In2−Cl1 = 2.5072(15), In1−C7 = 2.236(5), In2−C27 = 2.227(5), In1−N1 = 2.364(5), In2−N21 = 2.358(4), In1−C41 = 2.155(6), In2−C46 = 2.136(6), Cl2−In1−C7 = 120.58(14), Cl1−In2−C27 = 120.61(15), C7−In1−C41 = 128.1(2), C27−In2−C46 = 128.2(2), C41−In1−Cl2 = 111.30(15), C46−In2−Cl1 = 111.12(15), N1−In1−Cl1 = 162.37(11), N21−In2−Cl2 = 161.86(12), N1−In1−C7 = 87.29(18), N21−In2−C27 = 86.72(18), N1−In1−Cl2 = 84.69(12), N21−In2−Cl1 = 84.83(12), N1−In1−C41 = 95.17(19), N21−In2−C46 = 95.22(19), Cl1−In1−C7 = 102.66(14), Cl2−In2−C27 = 103.95(14), Cl1−In1−Cl2 = 77.73(5), Cl1−In2−Cl2 = 77.12(5), Cl1−In1−C41 = 90.09(15), Cl2−In2−C46 = 89.66(15).

The NMR spectra of **4** can be interpreted as being caused by C_2 symmetrical molecules with a chlorine-bridged structure similar to that revealed in the crystal lattice: one set of signals for asymmetric pytrisyl ligands and one set of signals for asymmetric Cp groups. These C_2 symmetrical species must be a racemic mixture of molecules with the same relative configuration at each In atom, the *rac* isomers. There are no signs of the presence of diastereomers with opposite configurations at each In atom, the *meso* isomers. The molecular structure of **4** in the crystal lattice gives the impression that a respective *meso* isomer *with* an In−(μ-Cl)$_2$−In

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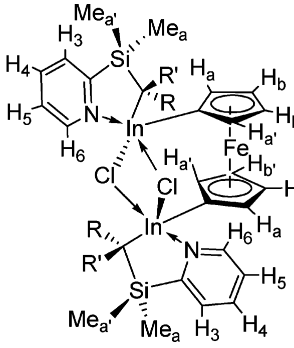

Figure 8. Assignment of the ^{1}H NMR peaks for **4** (R and R′ = $SiMe_3$; nonprimed groups R and Me_a are on the same side of the ferrocene moiety; primed groups R′ and $Me_{a'}$ are on the opposite side of the ferrocene moiety (see Experimental Section for details).

moiety is impossible for steric reasons. If the two molecular halves are *not* linked through Cl bridges, a mixture of *rac* and *meso* isomers should be present. The fact that this is not the case supports the interpretation of the NMR data as being caused by compound **4** with a structure similar to that in the crystal lattice. Interestingly the four pseudotriplets of the Cp groups resonate at δ 3.44, 4.18, 4.43, and 5.18, resulting in a very large splitting of $\Delta\delta = 1.74$ ppm. However, the ^{13}C NMR spectrum displays the *ipso*-C at δ 67.71, clearly indicating an unstrained ferrocenophane. In the course of assigning ^{1}H NMR peaks to protons in **4** by NOESY experiments we found that compound **4** fluctuates in solution (Figure 8). If one methyl of the $SiMe_2$ group, the methyl groups of a $SiMe_3$ moiety, or one CH proton is irradiated, one can observe, in addition to nuclear Overhauser effects, magnetization transfer to respective diastereotopic protons (Figure 8; Me_a to Me_a′, R to R′, H_a to H_a′, H_b to H_b′ and vice versa). This clearly indicates that the two enantiomers of the *rac* isomer form an equilibrium.

The equilibration between the *R*/*R* isomer and the *S*/*S* isomer is slow at ambient temperatures, and signals do not coalesce in a ^{1}H NMR spectrum (500 MHz). In the temperature range of 25 to 80 °C coalescence between the primed and nonprimed atoms and groups, respectively, is observed, indicating a time-averaged C_{2v} symmetrical molecule. Besides exhibiting dynamic behavior, compound **4** is temperature sensitive. After one series of variable-temperature experiments, new signals appeared in the ^{1}H NMR spectrum remeasured at ambient temperature, indicating unidentified thermolysis products. We have no experimental evidence on how the equilibration takes place. It is known for 4- and 5-fold-coordinated indium species that the donor bond between In atoms and the dimethylamino group from the chelating “one-arm” phenyl ligand 2-$Me_2NCH(Z)C_6H_4$ (Z = H, Me)[14] breaks and re-forms in solution. We assume that a similar process takes place with the pyridine donor groups in compound **4**, and it is feasible that both pyridine ligands are lifted off the In atoms, followed by rotations of the pytrisyl ligand around the In−C bonds, and are reattached, which results in inversions of both metal centers. A process like this could explain the observed equilibration.

Conclusion

As in the case of the aluminum-bridged [1]ferrocenophane, the pytrisyl ligand provides the right combination of steric bulkiness and intramolecular coordination to allow the synthesis of the first example of a gallium-bridged [1]ferrocenophane (**2**). For the heavier homologue indium, we isolated the first example of a ferrocene molecule bridged by an indium-containing moiety (**4**). Interestingly, the synthesis is diastereoselective and the resulting product fluctuates in solution. It is evident from solution NMR experiments that the two Cp ligands in compound **4** are bridged by a In−(μ-Cl)$_2$−In unit; the molecular structure of **4** in solution is similar to that found in the solid state. IUPAC defines ferrocenophanes as “compounds in which the two ring components of ferrocene are linked by one or more bridging chains”.[15] Because of the linkage between the Cp ligands, compound **4** is clearly a ferrocenophane. However, the bridging In−(μ-Cl)$_2$−In unit is not a simple chain, and therefore, an IUPAC name for species **4** as a ferrocenophane is not defined.

The bridging In−(μ-Cl)$_2$−In unit of the starting indane **3** is preserved in the product **4**, which suggests that a monomerization of the starting indium dihalide might open the door to the targeted [1]In−FCP. We are currently increasing the bulkiness of the pytrisyl ligand by introducing sterically demanding groups in position 6 of the pyridine ring. This might prevent dimerization and, therefore, change the course of the reaction with dilithioferrocene. We hope to report on the outcome shortly.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques, if not noted differently. Solvents were dried using a Braun solvent purification system and stored under Argon over a 4 Å molecular sieve. C_6D_6 and C_7D_8 were degassed prior to use and stored under argon over a 4 Å molecular sieve. $GaCl_3$ (99.99%, Aldrich) and $InCl_3$ (99.99%, Alpha Aesar) were purchased and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer; chemical shifts were referenced to the residual protons of the deuterated solvent. All NMR spectra were recorded 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. Only ions with intensities higher than 10% are listed. 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.

Synthesis of 1. Li(thf)(Pytsi) (1.939 g, 5.19 mmol)[5] dissolved in Et_2O (30 mL) was cooled to −80 °C and added to a stirring solution of $GaCl_3$ (0.920 g, 5.22 mmol) in Et_2O (40 mL; −80 °C). The reaction mixture was stirred at −80 °C for 20 min before being warmed to ambient temperature, with stirring continued for 16 h to give a yellow solution. Subsequently, the solvent was removed from the filtered solution. The remaining white solid was then sublimed at 130 °C at high vacuum to yield **1** as a white crystalline solid (1.672 g, 74%). ^{1}H NMR (500 MHz): δ 0.29 (s, 18H, $SiMe_3$), 0.36 (s, 6H, $SiMe_2$), 6.37 (pst, 1H, 5-H), 6.82−6.84 (m, 2H, 3-H, 4-H), 8.42 (d, 1H, 6-H). ^{13}C NMR (125.8 MHz): δ 3.25 ($SiMe_2$), 5.84 ($SiMe_3$), 125.64 (5-C), 129.37 (3-C), 139.93 (4-C), 146.29 (6-C), 169.27 (*ipso*-C, C_5H_4N). Carbon attached to gallium was obscured in the baseline. MS (70 eV, EI+): *m/z* (%) 420 (27) [$M^+ - Me$], 264 (100) [$Pytsi^+ - 2$ Me]. Anal. Calcd for $C_{14}H_{28}Cl_2GaNSi_3$ (435.264): C, 38.63; H, 6.48; N, 3.22. Found: C, 38.74; H, 6.49; N, 3.07.

Synthesis of 2. (Pytsi)$GaCl_2$ (**1**) (0.621 g, 1.42 mmol) was dissolved in toluene (15 mL) and chilled to −10 °C. A suspension of dilithioferrocene·2/3TMEDA (0.506 g, 1.83 mmol)[16] in toluene (15 mL) was added dropwise via tubing. After stirring for 16 h, the color of the solution changed to red. After filtration, the solvent was removed at high vacuum (25 °C/0.01 mbar) to yield a red, viscous oil. The residue was extracted with hexane (2 × 10 mL). After concentration, product **2** (0.460 g, 59%) was obtained as red crystals at ambient temperature. ^1H NMR (500 MHz): δ 0.38 (s, 18H, $SiMe_3$), 0.43 (s, 6H, $SiMe_2$), 4.08 (H_a), 4.45 ($H_{a'}$), 4.61 (H_b), 4.65 ($H_{b'}$) (pst, 8H, Cp, see Figure 5), 6.46 (pst, 1H, 4-H or 5-H), 6.85 (pst, 1H, 4-H or 5-H), 6.96 (d, 1H, 3-H), 8.73 (d, 1H, 6-H). ^{13}C NMR (125.8 MHz): δ 1.27 (Si-*C*($SiMe_3$)$_2$-Ga), 3.22 ($SiMe_2$), 5.94 ($SiMe_3$), 47.24 (*ipso*-C, Cp), 75.39, 75.53, 76.71, 77.19 (Cp), 124.22 (5-C), 129.40 (3-C), 138.21 (4-C), 147.87 (6-C), 172.74 (*ipso*-C, C_5H_4N). MS (70 eV, EI+): *m/z* (%) 547 (100) [M^+], 532 (69) [$M^+ -$ Me], 293 (91) [$Pytsi^+ -$ H], 278 (69) [$Pytsi^+ -$ H − Me], 264 (42) [$Pytsi^+ - 2$ Me], 73 (10) [$SiMe_3^+$]. Anal. Calcd for $C_{24}H_{36}GaFeNSi_3$ (548.379): C 52.57, H 6.62, N 2.55. Found: 53.22, 6.80, 2.31.

Synthesis of 3. Li(thf)(Pytsi) (1.901 g, 5.09 mmol) was dissolved in THF (20 mL, −80 °C) and added to a solution of $InCl_3$ (1.125 g, 5.09 mmol) in THF (40 mL; −80 °C). The reaction mixture was stirred at −80 °C for 20 min before slowly being warmed to ambient temperature, with stirring continued for 16 h to give a green solution initially, and finally a yellow solution. Subsequently, the solvent was removed, and the residue washed with hexane (2 × 30 mL) and filtered. Upon removal of all volatiles at ambient temperature, a white solid remained, which was then sublimed at 135 °C at high vacuum (0.01 mbar) to yield **3** as a white crystalline solid (1.634 g, 67%). ^1H NMR (500 MHz): δ 0.20 (s, 18H, $SiMe_3$), 0.32 (s, 6H, $SiMe_2$), 6.30 (pst, 1H, 5-H), 6.74 (pst, 1H, 4-H), 6.81 (d, 1H, 3-H), 8.30 (d, 1H, 6-H). ^{13}C NMR (125.8 MHz): δ 3.13 ($SiMe_2$), 6.31 ($SiMe_3$), 125.46 (5-C), 129.54 (3-C), 139.16 (4-C), 148.40 (6-C), 170.14 (*ipso*-C, C_5H_4N). Carbon attached to indium was obscured in baseline. MS (70 eV, EI+): *m/z* (%) 464 (15) [$M^+ -$ Me], 444 (16) [$M^+ -$ Cl], 264 (100) [$Pytsi^+ - 2$ Me]. Anal. Calcd for $C_{14}H_{28}Cl_2InNSi_3$ (480.364): C, 35.01; H, 5.88; N, 2.92 Found: C, 35.62; H, 5.97; N, 2.31.

Synthesis of 4. A suspension of **3** (1.562 g, 1.62 mmol) in toluene (50 mL) was added dropwise via tubing to a suspension of dilithioferrocene·2/3TMEDA (0.448 g, 1.62 mmol)[16] in toluene (20 mL) that was chilled to −10 °C. After stirring for 16 h, the color of the solution had changed to orange. After filtration and concentration at high vacuum (25 °C/0.01 mbar), crystallization occurred at −10 °C (0.990 g, 57.0%). Single-crystal X-ray analysis was performed on a toluene wet crystal. ^1H NMR (500 MHz; see Figure 8 for assignments): δ 0.22 (s, 3H, Me_a of $SiMe_2$), 0.34 (s, 9H, R′ = $SiMe_3$), 0.48 (s, 3H, Me_a' of $SiMe_2$), 0.59 (s, 9H, R = $SiMe_3$), 3.44 (H_a), 4.18 (H_b), 4.43 (H_b'), 5.18 (H_a') (pst, 4H, Cp), 6.62 (pst, 1H, 5-H), 6.92 (pst, 1H, 4-H), 7.03 (d, 1H, 3-H), 9.25 (d, 1H, 6-H). ^{13}C NMR (125 MHz): δ 0.57, 3.01 ($SiMe_2$), 4.60, 4.96 ($SiMe_3$), 5.32 (Si-*C*($SiMe_3$)$_2$-In, −40 °C, C_7D_8), 67.71 (*ipso*-C, Cp), 69.61, 70.21, 74.26, 75.76 (Cp), 122.73, 127.84, 136.09, 147.47, 169.48 (aromatic, C_5H_4N). MS (70 eV, EI+): *m/z* (%) 629 (22) [MH^+ − (Pytsi)In(Cl)], 444 (32) [(Pytsi)$InCl^+$], 264 (100) [$Pytsi^+ - 2$ Me], 115 (11) [In^+]. Anal. Calcd for $C_{38}H_{64}Cl_2FeIn_2N_2Si_6$ (1073.843): C, 42.50; H, 6.01; N, 2.61. Found: C, 43.61; H, 6.12; N, 2.59.

X-ray Structural Analysis for 1, 2, 3, and 4. Data were collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[17] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[18] The program SIR97[19] was used to solve the structure, and SHELXL97[20] was used to refine the structure. All H atoms were placed in calculated positions, with C−H distances in the range 0.95−0.99 Å, and included in a riding model approximation. For compound **1**, U_{iso}(H) was constrained to be 1.2U_{eq}(C) for all protons. For **3** and **4**, U_{iso}(H) was constrained to be 1.2U_{eq}(C) for all aromatic protons and 1.5U_{eq}(C) for all methyl protons.

The crystals of **2** diffracted very poorly, and data could be obtained only to a maximum diffraction angle of 22° using Mo radiation. The unit cell had three angles near 90° with cell edges of 14.342, 18.200, and 20.442 Å. Systematic absences suggested $P2_12_12_1$ or $P2_12_12$, but neither SIR97[19] nor SHELXS97[20] could find a solution in either of these space groups. The data were processed as triclinic and solved with SIR97[19] to give an eight-molecule solution and refined using SHELXL97[20] using rigid models of the Al analogue of **2**[4] to complete the molecules. The eight molecules were examined using PLATON,[21] and conversion to $P2_1$ was suggested. In $P2_1$ the asymmetric unit had four molecules. All atoms were refined isotropically with no constraints, and the structures of the four molecules were maintained. The Ga, Fe, and Si atoms were then refined anisotropically. The number of data did not allow all atoms to be refined anisotropically, but 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 and 1.5 times U_{eq} of the carrier atoms for methyl hydrogen atoms. The *R* value refined to 0.143. All four molecules maintained their geometry. No further symmetry elements could be identified. The angles between the cyclopentadienyl rings for the four molecules are 13.6(2.1)°, 15.0(1.6)°, 15.4(1.9)°, and 18.8(1.8)° for an average of 15.7°. An ORTEP diagram of one of the molecules is shown in Figure 3. The data do not give a complete crystal structure of **2** with accurate bond lengths and bond angles, but they do determine the arrangement of the atoms of **2**.

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Supporting Information Available: Crystallographic data for **1**, **3**, and **4** in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.

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