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Isolation and Structural Characterization of *cis*- and *trans*-Forms of $[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$

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Deprotonation of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene with 2 equiv of *n*-BuLi in THF provides the silicon-bridged dianion $Li_2[\mu\text{-}(C_5H_3)_2(SiMe_2)_2]$, which was reacted with $\eta^5\text{-}(C_5Me_5)TiCl_3$ to provide the bimetallic complexes *trans*- and *cis*-$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**1**, **2**), respectively, in approximately a 1:1 ratio. The *trans*-form, **1**, precipitates from the reaction medium and thus could be separated from the *cis*-isomer, **2**. Reaction of the dianion with $\eta^5\text{-}(C_5H_5)TiCl_3$ produced only *trans*-$[(\eta^5\text{-}C_5H_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**3**). Reaction of **1**−**3** with 4 equiv of MeLi provided the corresponding tetramethyl derivatives. The solid state structures of **1** and **2** were determined by single-crystal X-ray analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.967(2)$ Å, $b = 13.772(2)$ Å, $c = 8.983(2)$ Å, $\beta = 105.92°$, and $Z = 2$. Compound **2** crystallizes in the tetragonal space group $P4_32_12$ with $a = b = 10.648(2)$Å, $c = 32.030(8)$ Å, and $Z = 4$. The central ring of the disilaindacenyl ligand is planar in **1** with the two metal units bound to the outer Cp units but on opposite sides of the ligand faces. The central ring in **2** exhibits a boat conformation with both metal units bound to the convex face of the ligand. The Ti⋅⋅⋅Ti distance in *trans*-**1** is 6.94 Å, shorter than the 7.33 Å observed in *cis*-**2**. A summary and comparison of the four structural types observed for bimetallic complexes of the type $[ML_n]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ is presented.

Introduction

Binuclear complexes could potentially exhibit cooperative electronic and chemical effects which would be useful in catalysis. In principle, ligands could be designed that control the distance between the two metal centers. The role of metallocenes as catalyst precursors for the polymerization of olefins is well-known,[1] and more recently these complexes have been used for the dehydrocoupling of primary silanes to polysilanes.[2] If two cyclopentadienyl ligands are bridged by a single unit as in $[\mu\text{-}SiMe_2(C_5H_4)_2]^{2-}$ the relative orientation between the two metals may vary in an uncontrolled manner due to rotation about the Si−Cp bond. With two $SiMe_2$ bridges between the Cp units as in $[\mu\text{-}(SiMe_2)_2(C_5H_3)_2)]^{2-}$ a less flexible system would result in which the metals could bind to the same (*cis*) or opposite (*trans*) faces of the ligand. The Me_2Si-bridged cyclopentadiene precursor 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene, H_2L, is readily prepared from $(C_5H_5)SiMe_2Cl$ either by the method introduced by Jones[3a] or more recently from a modification for production of large quantities reported by Köhler.[3b] The disilaindacene is produced as a mixture of isomers ($H_2L_a/H_2L_b = 2.4/1$)[3b,4] and can be deprotonated with 1 equiv of *n*-BuLi to give LiLH as a mixture of two enantiomers and with 2 equiv to give Li_2L[5] as summarized in Scheme 1, where the Me groups or silicon is omitted for clarity. Both H_2L and HL^- have been shown to be fluxional in solution.[3b]

A degree of flexibility is available in sequences that lead to incorporation of metal centers since H_2L, LH^-, and L^{2-} all react directly with suitable metal substrates. From metal precursors of the type M(0), MX_x, and "Cp′MCl" are formed monometallic complexes such as Cp′MLH[6−8] and HLMLH[6] and bimetallic complexes such as Cp′MLMCp′,[9−13] Cp′MLM′Cp′,[12] or $Cl_{x-1}MLMCl_{x-1}$.[12−14] Combinations of reactions have also led to trimetallic complexes MLM′LM, with $M = M'$[8] or $M \neq M'$,[6,8] in addition to higher oligomers.[10] Isomeric versions of monometallic through trimetallic complexes have been generated.

Prior reports have focused on the formation of complexes of electron-rich metals although one study describes the

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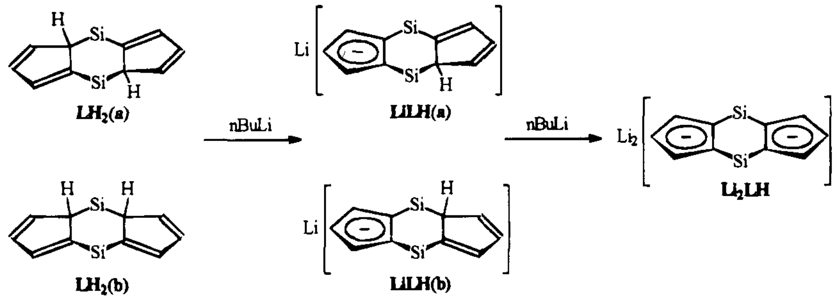
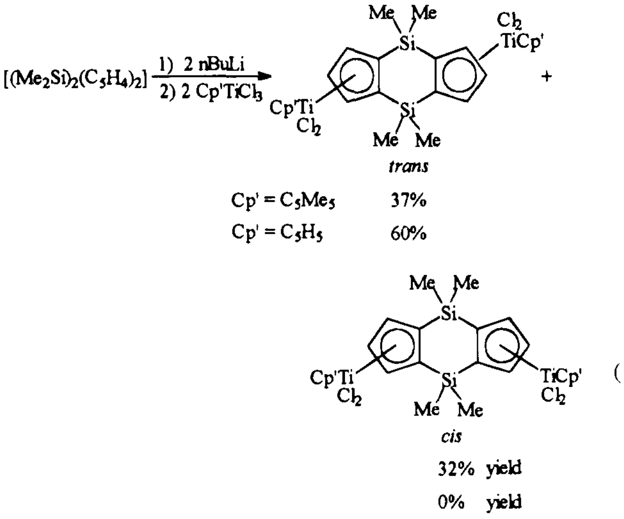
Scheme 1



formation of *trans*-$Cl_3TiLTiCl_3$ from Tl_2L and $TiCl_4$.[14] In this report we describe the reaction of $Cp'TiCl_3$ with Li_2L to give the first bent-metallocene derivatives of L^{2-}, $Cl_2Cp'TiLTiCp'Cl_2$. A mixture of *cis*- and *trans*-isomers was formed which have been separated and each crystallographically characterized.

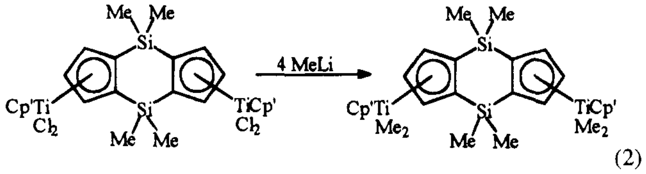
Results

The reaction of $Li_2[\mu\text{-}(Me_2Si)_2(C_5H_3)_2]$, which was generated in THF solution from $[\mu\text{-}(Me_2Si)_2(C_5H_4)_2]$ and *n*-butyllithium (*n*-BuLi), with 2 equiv of Cp^*TiCl_3 ($Cp^* = \eta^5\text{-}C_5Me_5$) at room temperature produced LiCl and a mixture of *trans*- and *cis*-$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**1**, **2**), respectively. The isomers **1** and **2** were cleanly separated by crystallization to provide isolated yields of 37% (**1**) and 32% (**2**). Under similar conditions, $Li_2[\mu\text{-}(Me_2Si)_2(C_5H_3)_2]$ and $CpTiCl_3$ ($Cp = \eta^5\text{-}C_5H_5$) provided a 60% yield of only one isomer, *trans*-$[(\eta^5\text{-}C_5H_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**3**) (eq 1). Compounds **1** and **3** are air stable, and **2** slowly decomposes on exposure to air.



(1)

Treatment of **1**−**3** with 4.0 equiv of MeLi in THF at 0 °C and subsequent warming to room temperature provides the corresponding tetramethyl derivatives *trans*-$[(\eta^5\text{-}C_5Me_5)TiMe_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**4**), *cis*-$[(\eta^5\text{-}C_5Me_5)TiMe_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**5**), and *trans*-$[(\eta^5\text{-}C_5H_5)TiMe_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**6**) in yields from 75 to 93% (illustrated for the *cis*-isomer in eq 2). As with many methyl-substituted titanium compounds, **1**−**3** are all very air and moisture sensitive, making characterization by elemental analysis difficult.



(2)

The methyl derivatives **4**−**6** are very soluble in chlorinated, THF, and aromatic hydrocarbon solvents. Compounds **1** and **2** are moderately soluble in chlorinated and THF solvents with the solubility of **2** > **1**, and **2** is slightly soluble in aromatic hydrocarbons, while **1** is almost insoluble. It is this difference in solubility that allowed for the separation of **1** and **2** from the reaction mixture. Compound **3** is insoluble in chlorinated and THF solvents and only slightly soluble in DMSO. After a few hours, solutions of **3** in DMSO decompose with formation of an insoluble green solid.

The *cis*- and *trans*-isomers can be easily distinguished by the ^1H and ^{13}C-NMR signals for the bridging $SiMe_2$ units. For the *trans*-isomers **1**, **3**, **4**, and **6** all four methyl groups are equivalent and only one methyl resonance is observed. For the *cis*-isomers **2** and **5** there are two pairs of equivalent methyl groups; therefore, two methyl signals of equal intensity are observed. The protons for the bridged Cp's show the expected pseudo doublet and triplet in the ^1H-NMR for **1**−**6**. The methyls for $\eta^5\text{-}C_5Me_5$ in **1**, **2**, **4**, and **5** and the protons for $\eta^5\text{-}C_5H_5$ in **3** and **6** are equivalent, and each appear as sharp singlets in the ^1H-NMR. The ^{29}Si-NMR spectra for each of the six compounds indicate a single silicon environment.

The solid state structures of both **1** and **2** have been determined. Selected atomic coordinates and isotropic thermal parameters for both compounds are summarized in Table 1, and pertinent bond distances and angles are listed in Table 2. The ORTEP diagram for **1** is shown in Figure 1, and that for **2**, in Figure 2. Although the structure of **2** is of marginal quality, the basic features of the geometry are determined. The structures demonstrate that both metal units are bonded to opposite faces of the ligand in *trans*-**1** and to the same "face" in *cis*-**2**, and an additional feature that distinguishes the two complexes is the conformation of the central ring of the disilaindacene unit. In **1**, this six-membered ring is planar whereas in **2** the ring exhibits a boat conformation. The consequence of the fold along the Si••Si vector in **2** is to increase the separation between the metal sites compared to that observed in **1** and will be discussed in the next section. The bond distances and angles involving the disilaindacene ligand for **1** and **2** are similar except for the C−Si−C ring angle which is about 10° smaller in **2** compared to **1**.

Discussion

Synthesis of MLM. The development of ligands that contain a controlled separation between two metal sites is a considerable challenge. To define the distance between the metals will require a certain degree of ligand rigidity between the coordination sites. Ideally, some flexibility in the synthetic steps for the incorporation of the metal centers should be available. The reaction chemistry of the precursor, 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene, which provides two Cp rings for formation of metallocene complexes, allows different synthetic

Table 1. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)[a] for the Non-Hydrogen Atoms in *trans-* and *cis-*$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$, **1** and **2**

	compd **1**				compd **2**			
	x	*y*	*z*	*U*(eq)[b]	*x*	*y*	*z*	*U*(eq)[b]
Ti(1)	2366(1)	4706(1)	1687(1)	30(1)	1091(2)	5691(2)	373(1)	42(1)
Cl(1)	2932(1)	3863(1)	−172(1)	50(1)	2932(3)	6579(3)	123(1)	87(1)
Cl(2)	1885(1)	6033(1)	47(1)	49(1)	1755(3)	5556(3)	1072(1)	78(1)
Si(1)	−64(1)	5784(1)	1643(1)	39(1)	2996(3)	3610(3)	−535(1)	51(1)
C(1)	3063(3)	5444(3)	4194(4)	49(1)	−994(9)	6408(9)	519(3)	47(2)
C(2)	3387(3)	5973(3)	3123(5)	48(1)	−792(9)	6583(9)	76(3)	46(3)
C(3)	3913(3)	5375(4)	2456(5)	61(2)	165(9)	7490(9)	33(3)	49(3)
C(4)	3947(3)	4446(4)	3202(7)	78(2)	499(9)	7885(9)	438(3)	48(3)
C(5)	3422(3)	4508(3)	4261(5)	64(2)	−227(9)	7255(10)	729(3)	52(3)
C(11)	738(2)	4719(3)	1725(4)	34(1)	1871(9)	3949(9)	−98(3)	46(3)
C(12)	1301(2)	4260(3)	3064(4)	40(1)	591(10)	4170(9)	−144(3)	55(3)
C(13)	1683(2)	3399(3)	2632(4)	43(1)	−13(10)	3874(9)	217(4)	56(3)
C(14)	1338(2)	3309(2)	1023(4)	38(1)	852(11)	3523(8)	507(3)	58(3)
C(15)	768(2)	4115(2)	426(3)	33(1)	2077(9)	3571(8)	331(3)	44(3)
C(16)	−755(3)	5527(4)	3030(4)	62(2)	4188(11)	4770(10)	−657(4)	96(5)
C(17)	494(3)	6994(3)	2186(5)	63(2)	2061(11)	3280(12)	−1009(3)	93(4)

[a] Carbon atoms C(6) through C(10) associated with the Me groups on the Cp* are not included. See supplementary material. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **2**[a]

distances			angles		
	1	2		1	2
Ti(1)−Cl(1)	2.373(1)	2.319(3)	Cl(1)−Ti(1)−Cl(2)	92.7(1)	95.70(13)
Ti(1)−Cl(2)	2.334(1)	2.352(3)	Cp*−Ti(1)−Cp	131.7	132.5
Ti(1)−Cp*	2.112	2.106	Cp*−Ti(1)−Cl(1)	106.3	106.2
Ti(1)−Cp	2.089	2.105	Cp*−Ti(1)−Cl(2)	107.2	105.7
Si(1)−C(16)	1.859(5)	1.814(10)	Cp−Ti(1)−Cl(1)	105.3	106.4
Si(1)−C(17)	1.868(4)	1.851(10)	Cp−Ti(1)−Cl(2)	106.8	104.4
Si(1)−C(11)	1.884(4)	1.876(10)	C(16)−Si(1)−C(17)	106.6(2)	109.2(6)
Si(1A)−C(15)	1.873(3)	1.861(10)	C(11)−Si(1)−C(15A)	106.0(1)	96.8(4)
C(11)−C(15)	1.444(5)	1.450(11)	C(15)−C(11)−Si(1)	125.3(2)	123.9(7)
C(11)−C(12)	1.414(4)	1.391(13)	C(11)−C(15)−Si(1A)	128.7(2)	123.7(7)
C(12)−C(13)	1.426(5)	1.361(12)	C(11)−C(12)−C(13)	109.4(3)	109.4(10)
C(13)−C(14)	1.400(5)	1.360(13)	C(12)−C(13)−C(14)	107.1(3)	109.0(10)
C(14)−C(15)	1.413(4)	1.422(13)	C(13)−C(14)−C(15)	109.6(3)	109.9(9)
			C(14)−C(15)−C(11)	107.2(3)	104.3(9)
			C(15)−C(11)−C(12)	106.7(3)	107.2(9)

[a] Cp* is the centroid of C(1)−C(5). Cp is the centroid of C(11)−C(15).

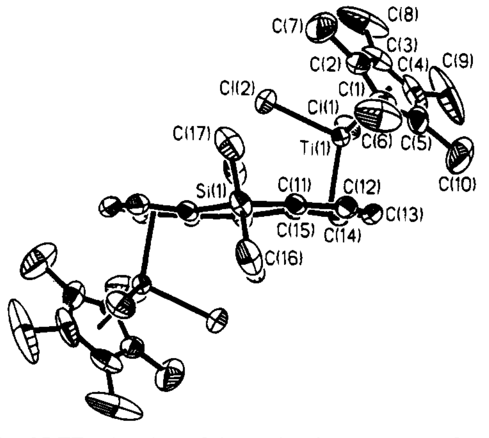


Figure 1. ORTEP drawing of the molecular geometry of *trans*-$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**1**) (without hydrogen atoms) and atom numbering as used in Tables 1 and 2. Displacement ellipsoids are at the 50% probability level.

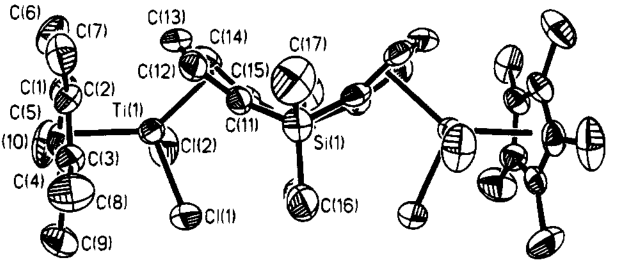
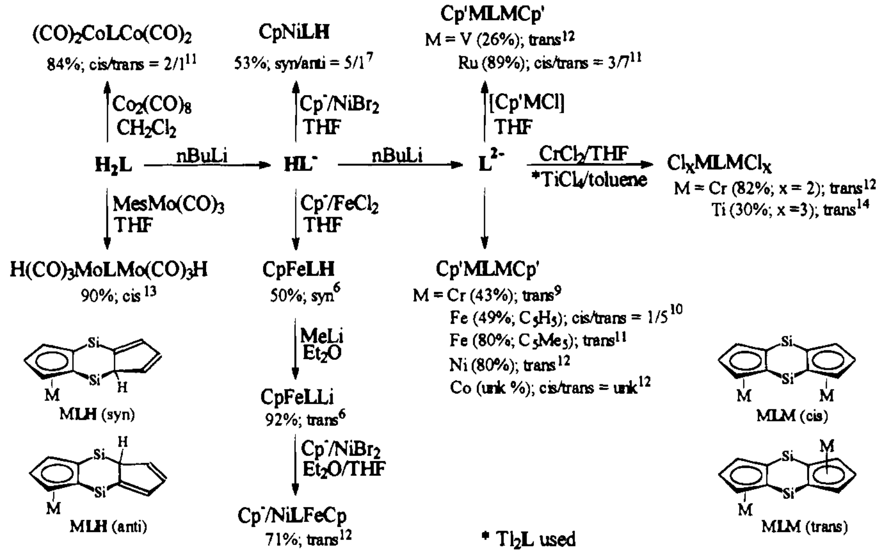


Figure 2. ORTEP drawing of the molecular geometry of *cis*-$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (**2**) (without hydrogen atoms) and atom numbering as used in Tables 1 and 2. Displacement ellipsoids are at the 50% probability level.

routes for the incorporation of two (or more) metals as outlined in Scheme 2. The neutral ligand can be deprotonated stepwise and thus provides for the possibility of incorporation of one metal at a time through the sequence $HL^- \rightarrow HLM \rightarrow LiLM \rightarrow M'LM$. The dianion, L^{2-} (as the Li^+, K^+,[13] or Tl^+ [14] salt), reacts with metal halides or metal halide derivatives to give the bis-metal sequence MLM. An alternative approach to the MLM sequence is provided from the neutral ligand which reacts with M(0) complexes, probably by oxidative addition.[11,13] Further flexibility for incorporating more than two metals has been demonstrated since it is also possible to trap HL^- with MCl_2 to give HLMLH. Subsequent reaction of HLMLH with M′(0)[8] or deprotonation to $[LML]^{2-}$ and reaction with metal halide[8] provides M′LMLM′.

Isomers of the bis-metal complexes, MLM, include *cis*-forms (metals coordinated to the same face) and *trans*-forms (metals coordinated to opposite faces). The nature of the reacting LiLLi species in THF solution is probably oligomeric, although the TMEDA complex is monomeric with a *trans*-distribution of the $[Li(TMEDA)]^+$ units in the solid state.[3b] The nature of K_2L[3b]

Scheme 2



and Tl_2L[14] used as alternatives to Li_2L has not been determined. The reactions of Li_2L are normally conducted in THF and provide, for the most part, *trans*-MLM products when reacted with MX_2 or "CpMX" either as a preformed reagent or generated *in situ* (see Scheme 2 for examples). Only in the reaction of Cp*RuCl[11] and CpMCl [M = Fe,[10] Co[12] (generated in situ from Cp^- and MX_2)] were minor *cis*-products observed and only in the case of CpFeLFeCp[10] was the *cis*-form actually separated from the *trans*. The yields of isolated MLM vary from about 25 to 90%. In general, when only the *trans*-form is reported, there is no indication that solutions remaining after crystallization of the *trans*-isomer contain a *cis*-form. In the synthesis of the mixed-metal derivative CpFeLNiCp (71%; *trans*-form only), a single isomer was obtained independent of the ether solvent used (Et_2O, Bu_2O, or THF).[12] It is possible that the temperature may play a role since in one of the few cases where a *cis*-form was observed in reaction of L^{2-} with "CpMCl" in THF, the *cis/trans* ratio varied from ~5 (−40 °C) to 2.8 (25 °C) to 4.5 (reflux).[10] Only in the two instances where the neutral ligand has been reacted with M(0) [$Co_2(CO)_8$[11] and $MesMo(CO)_3$[13]] is the *cis*-form either the exclusive (Mo) or the major product (Co), but in the cobalt case the *cis*- and *trans*-forms coprecipitated and were not separated.

In the current study, H_2L was deprotonated with *n*-BuLi (2 equiv) in THF and reacted with $Cp'TiCl_3$ [Cp' = C_5Me_5 (Cp*), C_5H_5 (Cp)] to give both the *trans*- and *cis*-isomers of Cl_2-$Cp^*TiLCp^*Cl_2$ (**1** and **2**, respectively) which were cleanly separated whereas only *trans*- $Cl_2CpTiLTiCpCl_2$ (**3**) was isolated. No evidence for a *cis*-form of **3** was obtained from the mother liquor after removal of the *trans*-isomer. In the only other study that involved a titanium derivative, Tl_2L was reacted with $TiCl_4$ in toluene to give only *trans*-$Cl_3TiLTiCl_3$ as a toluene solvate in 30% yield.[14] No attempts to detect the *cis*-form were described. The only other example of reaction of L^{2-} (as the Li salt) with a metal halide involved $CrCl_3(THF)_3$ in the presence of PEt_3 which gave *trans*-$(Et_3P)Cl_2CrLCrCl_2(PEt_3)$ in 82% yield.[12]

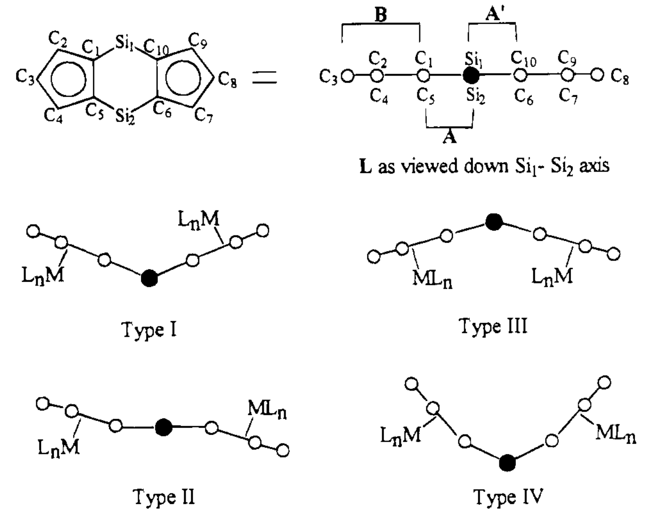


Figure 3. Simplified representations of the structural variations for MLM complexes and definition of planes that distinguish the structural types.

Structures of MLM. Two *trans*-forms and two *cis*-forms have been observed in the 11 crystallographically characterized complexes of the type MLM. The structural variations for MLM are illustrated in diagrammatic form in Figure 3. In general, the *trans*-forms of MLM have a center of inversion whereas the *cis*-forms contain a 2-fold axis which is perpendicular to the central six-membered ring. The central six-membered ring of the ligand exhibits either a boat form (types I, III, and IV) or is essentially planar (type II). The Cp "wings" are planar but can be coplanar with the Si atoms of the central ring, as in type I and type II, or can be "hinged" at the carbon atoms that are common to the fused five- and six-membered rings as in types II and IV. The complexes **1** and **2** are examples of structure types II and IV, respectively. The various structural types can also be described by a series of planes as shown in Figure 3. Plane B contains the five carbons atoms of the Cp ring, and planes A and A′ are defined by the best mean plane that contains the two silicon atoms and the two carbon atoms that are common to the five and six-membered rings. The angles between the planes are summarized in Table 3. The only mixed-metal derivative that has been characterized in the solid state, *trans*-(TMEDA)LiLFeCp, exhibits the type I structure.[6]

A ligand closely related to the disilaindane is the dianion derived from 4,8-ethano-2,4,6,8-tetrahydro-*s*-indacene [$(L')^{2-}$], where the carbon framework of the central ring is constrained to a rigid "boat" form. In this case, reaction with Cp^-/Fe_2Cl_4 provided both *cis*- and *trans*-CpFeL′FeCp (*cis/trans* ~ 1.3) which were separated by column chromatography.[15] The nature of the ligand imposes a small bridgehead angle which suggests

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(15) Atzkorn, H.; Huber, B.; Köhler, F. H.; Müller, G.; Müller, G. *Organometallics* **1991**, *10*, 238−244.

Table 3. Comparison of Angles between Sets of Planes for *cis*- and *trans*-Forms of L_nMLML_n[a]

ML_n	planes A/A′	planes A/B	type	M···M (Å)	ref
FeCp*	136	180	I	6.01	11
CrCp	134	180	I	5.83	9
[FeCp]b	123	171 (av)	I′	5.34	15
Li(TMEDA)	180	173	II	6.70	3b
$TiCl_2Cp^*$	180	171	II	6.94	this work
$TiCl_3$	180	176	II		14
$MoCl(CO)_3$	180	172	II	6.42	13
$Co(CO)_2$	157	180	III	4.25	11
$TiCp^*Cl_2$	130	163	IV	7.33	this work
$MoCl(CO)_3$	132	180	IV	6.54, 6.72[c]	14
[FeCp][b]	117	170	IV′	6.11	15

[a] See Figure 3 for definition of planes. Except where noted L = dianion of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene. [b] L = 4,8-ethano-2,4,6,8-tetrahydro-*s*-indacene-2,6-diyl dianion. Planes are defined as in Figure 3 except that the bridgehead carbons replace the silicon atoms. [c] The asymmetric unit contains two independent half-molecules.

that a structure similar to *cis*-III is unlikely and eliminates a *trans*-II structure. The *cis*-CpFeL′Cp exhibits a type IV structure and is closely related to the structure of **2**. Data for both these complexes are included in Table 3 for comparison. Planes A, A′, and B are defined in the same way as for the disilaindacenes except that planes A and A' include the bridgehead carbon atoms instead of the silicon atoms.

The distance between metal centers in MLM will vary as a function of the structure type and from the data in Table 3 are observed to increase in the order III < I < II < IV. Three systems exhibit the *cis*-IV structure, two of which are based on the disilaindacene, and these contain the more bulky groups Cp^*TiCl_2 and $Mo(CO)_3Cl$. For each of the systems that exhibits the *cis*-IV structure a *trans*-form has also been isolated. In each case the distance between metal centers is largest in the *cis*-form. Although an earlier study seemed to suggest that large metal–ligand fragments such as Cp*M (M = Fe, Ru) seem to favor a *trans* arrangement "for steric reasons",[11] the *cis*-IV form actually produces a complex in which the metal fragments are the furthest apart. Although Cp*RuLRuCp* is one of the few examples where *cis*- and a *trans*-isomers are formed (but not separated), the structure of neither was actually determined. In the present study, **1** (*trans*-II) and **2** (*cis*-IV) contain the bulky Cp^*MCl_2 unit and are formed in almost equal amounts in structures that maximize the separation between the metal. When the size of the Cp unit is reduced, as in **3**, only a *trans*-form is obtained although the nature of the *trans*-form is unknown. Only in the structure *cis*-III is the distance between metal atoms likely to be less than 5 Å; only one authenticated example of this structure type has been reported, and it contains the smallest metal unit, $Co(CO)_2$, formed from the reaction of $Co_2(CO)_8$ with H_2L. It may be possible to enforce a type III structure with a metal–metal-bonded fragment. This has been suggested for the product isolated in 2% yield from the reaction of H_2L with $Fe(CO)_5$ which appears to be consistent with the formulation $L[(OC)Fe(\mu\text{-}CO)_2Fe(CO)]$.[11] Synthetically a type III structure may be difficult to achieve since the two Cp units in the ligand, L^{2-}, can also function as a chelate to a single metal center as reported for the *ansa*-form $[L]MCl_2$ (M = Ti, Zr, Hf)[14] as well as the chiral zirconocene complexes of substituted disilaindacenes.[16]

The structure or conformation adopted in solution may not be the same as that found in the solid state and/or the structure in solution may vary with temperature. An inversion of the central ring could interconvert *trans*-I and *trans*-II or *cis*-III and *cis*-IV. This possibility has not been explored except in the case of CpMLMCp [M = Ni, Co (*cis*- and *trans*-forms); Cr (*trans*)].[12] On the basis of the temperature dependence of the ^1H NMR signal shifts, the authors proposed a structure similar to II for the *trans*-forms although the chromium derivative exhibits structure I in the solid. The authors also proposed a structure related to type III for the *cis*-form but with the two metals bound to the convex side. A variable-temperature NMR study of **1** showed essentially no change from 225 to 363 K, and no change for **2** was observed in the temperature range 190–340 K. However, **2** decomposes above 340 K. Therefore, the possibility of a *trans* to *trans* or a *cis* to *cis* conversion could not be demonstrated.

Conclusion

The dibridged cyclopentadienyl derivative 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene can be converted to bimetallic complexes of the form MLM either by reaction of the neutral ligand or through anions produced by successive deprotonation. Conversions of the neutral ligand tend to give predominantly *cis*-MLM whereas the anions favor predominantly *trans*-MLM, which may stem from the fact that both Li_2L and MLLi seem to also favor the *trans*-isomer. The yields of the MLM produced from the anionic route tend to vary considerably, but reports of the formation of *cis*-isomers are rare. By any synthetic route there was only one prior example of the actual separation of *cis*- and *trans*-forms when both were observed. In the present study, *cis*- and *trans* forms of $Cl_2Cp^*TiLTiCp^*Cl_2$ were formed in approximately equal amounts and could be separated due to the somewhat fortuitous insolubility of the *trans*-isomer in the reaction medium. Solutions of *cis*-**2** are not stable with mild heating or after periods of time at room temperature, and this may account, in some cases, for the isolation of only a *trans*-form.

Although the chemistry of H_2L provides for flexibility in synthetic routes to bimetallic (and higher oligomers), the structural variations observed for the MLM complexes produced suggests that it will be difficult to control the separation between metal sites although in some applications maintaining a particular distance between metal centers may not be a critical factor.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen with standard Schlenk techniques. Solvents were dried before use: THF (Na/benzophenone); CH_2Cl_2 and $CHCl_3$ (P_2O_5 after pretreatment with sulfuric acid and drying over CaH_2); hexanes (CaH_2). All glassware was flame dried prior to use. Commercial reagents, *n*-BuLi (in hexanes), MeLi (in Et_2O), $Ti(\eta^5\text{-}C_5H_5)Cl_3$, and $Ti(\eta^5\text{-}C_5Me_5)Cl_3$ were used as supplied. $[\mu\text{-}(SiMe_2)_2(C_5H_4)_2]$ was prepared by literature methods.[11]

^1H- and ^{13}C-NMR data were recorded in $CDCl_3$ (referenced to $CHCl_3$), C_6D_6 (referenced to C_6H_6), or d_6-DMSO (referenced to d_5-DMSO quintet) on either an XL-300 Varian spectrometer equipped with a four nucleus probe or a Bruker ARX500 equipped with either an inverse probe or a broad band probe. ^{29}Si-NMR data were recorded in either $CDCl_3$ or C_6D_6 (referenced to internal TMS) on the Bruker ARX500 spectrometer (99.36 Hz) using INEPTRD (with a ^1H refocusing pulse). Elemental analyses were performed by Schwartzkopf Laboratories.

Synthesis of *trans*- and *cis*-$[(\eta^5\text{-}C_5Me_5)TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (1, 2). An aliquot of *n*-BuLi (0.780 mL, 2.5 M in hexanes) was added to a cooled solution (0 °C) of $[(C_5H_4)_2(SiMe_2)_2]$ (0.237 g, 0.970 mmol) in THF (20 mL), and the solution was warmed to ambient temperature and stirred for 1 h. Subsequently, $(\eta^5\text{-}C_5Me_5)TiCl_3$ (0.563 g, 1.94 mmol) was added and the resulting dark red solution was stirred

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(16) Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H.-H. *Organometallics* **1993**, *12*, 1931–1935.

for 15 min and then allowed to stand overnight. The brown microcrystals that formed were separated from the reaction mixture by decantation, washed with hexanes, and dried in vacuo to provide the pure *trans*-isomer **1** (0.27 g, 37% yield). Recrystallization from $CHCl_3$ provided dark brown irregularly shaped plates which were suitable for the X-ray diffraction study.

The decantate from the reaction mixture was evaporated to dryness, CH_2Cl_2 (10 mL) was added, and the precipitated LiCl was removed by filtration. Concentration of the filtrate and addition of hexanes afforded dark red microcrystals, which were washed with hexanes and dried in vacuo to provide the pure *cis*-isomer **2** (0.27 g, 32% yield). After a series of recrystallization attempts, medium-quality dark red crystals were obtained from $CHCl_3$ which were used for the X-ray diffraction study.

trans-Isomer **1**: decomp > 350 °C. Anal. Calcd for $C_{30}H_{48}Ti_2Si_2Cl_4$: C, 54.41; H, 6.45. Found: C, 54.27; H, 6.68. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.42 (s, 12H, $SiMe_2$), 2.01 (s, 30H, C_5Me_5), 6.09 (t, J = 2.5 Hz, 2H, C_5H_3), 6.69 (d, J = 2.5 Hz, 4H, C_5H_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 2.94 ($SiMe_2$), 13.7 ($C_5\mathit{Me}_5$), 117.3, 131.9, 139.7 (C_5H_3), 129.7 (C_5Me_5). ^{29}Si-NMR (99 Hz, $CDCl_3$): δ −15.7 ($SiMe_2$).

cis-Isomer **2**: decomp > 275 °C ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.38 (s, 6H, $SiMe_2$), 0.65 (s, 6H, $SiMe_2$), 2.03 (s, 30H, C_5Me_5), 5.95 (t, J = 2.3 Hz, 2H, C_5H_3), 6.67 (d, J = 2.3 Hz, 4H, C_5H_3). ^{1}H-NMR (500 MHz, C_6D_6): δ 0.47 (s, 6H, $SiMe_2$), 1.12 (s, 6H, $SiMe_2$), 1.77 (s, 30H, C_5Me_5), 5.64 (t, J = 2.6 Hz, 2H, C_5H_3), 6.68 (d, J = 2.6 Hz, 4H, C_5H_3). ^{13}C-NMR (125 MHz, C_6D_6): δ 2.36, 3.11 ($SiMe_2$), 13.5 ($C_5\mathit{Me}_5$), 115.5, 132.6, 141.4 (C_5H_3), 129.3 (C_5Me_5). ^{29}Si-NMR (99 Hz, $CDCl_3$): δ −15.2 ($SiMe_2$).

Synthesis of *trans*-$[(\eta^5\text{-}C_5H_5)]TiCl_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (3). In a similar manner, $(\eta^5\text{-}C_5H_5)TiCl_3$ (1.00 g, 4.56 mmol) was added to a stirred THF solution (30 mL) of $Li_2[\mu_2\text{-}(C_5H_3)_2(SiMe_2)_2]$, which was prepared from *n*-BuLi (1.82 mL, 2.5 M) and $[\mu\text{-}(SiMe_2)_2\,(C_5H_4)_2]$ (0.560 g, 2.28 mmol). The reaction mixture immediately turned dark red, and pale red microcrystals began to form within 5 min. The reaction mixture was stirred for 15 min and then allowed to stand overnight. After this time, the microcrystals were separated by decantation, washed with THF and hexanes, and dried in vacuo to provide pure *trans*-isomer **3** (0.83 g, 60% yield). ^{1}H-NMR analysis of the decantate showed no distinguishable products.

trans-Isomer **3**: decomp > 300 °C. Anal. Calcd for $C_{24}H_{28}Ti_2Si_2Cl_4$: C, 47.24; H, 4.62. Found: C, 47.68; H, 4.70. ^{1}H-NMR (300 MHz, d_6-DMSO): δ 0.40 (s, 12H, $SiMe_2$), 6.61 (s, 10H, C_5H_5), 6.75 (t, J = 2.5 Hz, 2H, C_5H_3), 7.39 (d, J = 2.5 Hz, 4H, C_5H_3). ^{29}Si-NMR (99 Hz, d_6-DMSO): δ −15.8 ($SiMe_2$).

Synthesis of *trans*- and *cis*-$[(\eta^5\text{-}C_5Me_5)TiMe_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (4, 5) and *trans*-$[(\eta^5\text{-}C_5H_5)TiMe_2]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2]$ (6). The same basic procedure was used to prepare each of these three tetramethylated derivatives. Consequently, only the preparation of **4** will be described.

An aliquot of MeLi (0.550 mL, 1.4 M) was added to a cooled (0 °C) suspension of **1** (0.144 g, 0.192 mmol) in THF (10 mL). After the mixture was stirred at this temperature for 5 min, the ice bath was removed and the reaction mixture was allowed to warm to room temperature. As the mixture warmed, the solution changed from brown/red to dark yellow. After the solution was stirred for 30 min at room temperature, the THF was removed under reduced pressure, and the resulting yellow residue was dissolved in CH_2Cl_2 (10 mL). The LiCl that precipitated was removed by filtration through a fine frit. The CH_2Cl_2 was removed from the filtrate under reduced pressure, and the resulting yellow powder was washed with cold hexanes and dried in vacuo to provide the *trans*-derivative **4** (0.12 g, 93% yield). Attempts to obtain satisfactory analyses failed. ^{1}H-NMR (500 MHz, $CDCl_3$): δ −0.56 (s, 12H, $TiMe_2$), 0.37 (s, 12H, $SiMe_2$), 1.81 (s, 30H, C_5Me_5), 5.21 (t, J = 2.3 Hz, 2H, C_5H_3), 6.05 (d, J = 2.6 Hz, 4H, C_5H_3). ^{1}H-NMR (500 MHz, C_6D_6): δ −0.15 (s, 12H, $TiMe_2$), 0.63 (s, 12H, $SiMe_2$), 1.68 (s, 30H, C_5Me_5), 5.14 (t, J = 2.4 Hz, 2H, C_5H_3), 6.12 (d, J = 2.3 Hz, 4H, C_5H_3). ^{13}C-NMR (125 MHz, C_6D_6): δ 3.1 ($SiMe_2$), 12.4 (C_5Me_5), 47.3 ($TiMe_2$), 115.4, 124.6, 132.0 (C_5H_3), 120.2 (C_5Me_5). ^{29}Si-NMR (99 Hz, C_6D_6): δ −16.9 ($SiMe_2$).

cis-Derivative **5** (75% yield): ^{1}H-NMR (500 MHz, $CDCl_3$) δ −0.40 (s, 12H, $TiMe_2$), 0.28 (s, 6H, $SiMe_2$), 0.56 (s, 6H, $SiMe_2$), 1.81 (s, 30H, C_5Me_5), 5.14 (t, J = 2.5 Hz, 2H, C_5H_3), 6.12 (d, J = 2.6 Hz, 4H, C_5H_3). ^{1}H-NMR (500 MHz, C_6D_6) δ 0.02 (s, 12H, $TiMe_2$), 0.61 (s, 6H, $SiMe_2$), 0.67 (s, 6H, $SiMe_2$), 1.68 (s, 30H, C_5Me_5), 5.11 (t, J = 2.7 Hz, 2H, C_5H_3), 6.21 (d, J = 2.7 Hz, 4H, C_5H_3): ^{13}C-NMR (125 MHz, C_6D_6) δ 2.3, 3.8 ($SiMe_2$), 12.4 (C_5Me_5), 47.8 ($TiMe_2$), 114.3, 125.7, 134.1 (C_5H_3), 120.2 (C_5Me_5): ^{29}Si-NMR (99 Hz, C_6D_6) δ −16.1 ($SiMe_2$).

trans-Derivative **6** (87% yield): ^{1}H-NMR (500 MHz, $CDCl_3$) δ −0.16 (s, 12H, $TiMe_2$), 0.32 (s, 12H, $SiMe_2$), 5.96 (t, J = 2.7 Hz, 2H, C_5H_3), 6.01 (s, 10H, C_5H_5), 6.37 (d, J = 2.7 Hz, 4H, C_5H_3): ^{1}H-NMR (500 MHz, C_6D_6) δ 0.13 (s, 12H, $TiMe_2$), 0.35 (s, 12H, $SiMe_2$), 5.50 (t, J = 2.7 Hz, 2H, C_5H_3), 5.77 (s, 10H, C_5H_5), 6.13 (d, J = 2.7 Hz, 4H, C_5H_3): ^{13}C-NMR (125 MHz, C_6D_6) δ 2.1 ($SiMe_2$), 46.9 ($TiMe_2$), 113.7 (C_5H_5), 114.3, 125.7, 134.1 (C_5H_3); ^{29}Si-NMR (99 Hz, C_6D_6) δ −16.3 ($SiMe_2$).

Table 4. Crystallographic Data for **1** and **2**

	1	2
formula	$C_{34}H_{48}Cl_4Si_2Ti_2$	$C_{34}H_{48}Cl_4Si_2Ti_2$
fw	750.5	750.5
space group	$P2_1/c$	$P4_32_12$
a, Å	14.967(2)	10.648(2)
b, Å	13.772(2)	10.648(2)
c, Å	8.983(2)	32.030(8)
α, deg	90	90
β, deg	105.92	90
γ, deg	90	90
V, Å^3	1780.4(3)	3631.6(13)
Z	2	4
D_c, g/cm^3	1.400	1.373
T, 25 °C	25	25
λ, Å	0.710 73	0.710 73
μ, mm^{-1}	0.839	0.823
R^a	4.60	8.07
$R_w{}^a$	4.77	13.69
GOF^a	1.23	1.05

^{a} $R = \sum F_o - F_c/\sum F_o$; $R_w = \sum[(F_o - F_c)\sqrt{w}]/\sum[F_o\sqrt{w}]$; GOF = S = $[\sum w(F_o - F_c)^2/(\text{no. of obsd reflns} - \text{no. of params})]^{1/2}$.

Crystallographic Data Collection and Structure Determination for 1 and 2. A plate of dimensions 0.30 × 0.10 × 0.03 mm for **1** and 0.50 × 0.30 × 0.10 mm for **2** was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed using a Siemens P4RA automated single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 25 °C.[17] Autoindexing of 15 centered reflections from the rotation photographs indicated monoclinic (**1**) and tetragonal (**2**) lattices. Equivalent reflections were checked to confirm the Laue symmetry, and a fractional index search was conducted to confirm the cell lengths (XSCANS, Siemens Analytical Instruments, Madison, WI, 1994). Final cell constants and orientation matrix for data collection were calculated by least squares refinement of the setting angles: 39 reflections (10° < 2θ < 25°) for **1**; 39 reflections (5° < 2θ < 15°) for **2**. Intensity data were collected using $2\theta/\omega$ (**1**) and ω (**2**) scans with variable scan speed. Three representative reflections measured every 97 reflections showed <2% (**1**) and 17% (**2**) variation during data collection. Crystal data and intensity data collection parameters are listed in Table 4.

Data reduction was carried out using XSCANS, and structure solution and refinement were carried out using the SHELXTL-PLUS (VMS) software package (Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1991). An empirical absorption correction was applied to the data using ψ-scan reflections. The structures were solved by Patterson methods and refined successfully in the space groups $P2_1/c$ (**1**) and $P4_32_12$ (**2**). Full-matrix least-squares refinement was carried out minimizing $\sum w(F_o - F_c)^2$. The non-hydrogen atoms were refined anisotropically to convergence. For **1**, all hydrogen atoms were located from the difference Fourier peaks, but as they did not refine, hydrogen atoms were included in the final refinement in their idealized positions. For **2**, all hydrogen atoms were added in the final refinement using the

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(17) Data collection for compound **2** was performed by Siemens at the University of Wisconsin—Madison.

appropriate riding model, and absolute structure was confirmed using Flack x parameter, $x = -0.02$.[18]

For **1**, there was disorder in the Me groups of the η^5-C_5Me_5 groups which could not be resolved using F^2 refinement (SHELXL-93). For **2**, there was partial twinning in the crystal which resulted in a high $R1$.

Projection views of the molecules with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling are presented in Figures 1 (**1**) and 2 (**2**). Complete lists of bond distances and bond angles, positional and isotropic displacement coefficients for the non-hydrogen atoms, and anisotropic thermal parameters are submitted as supplementary material.

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Supplementary Material Available: For compounds **1** and **2**, tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

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[18] Flack, H. D. *Acta Crystallogr.* **1983,** *A39*, 876−881.