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Synthesis and Characterization of the Five-Coordinate Scandium Dialkyl Complexes ScR$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (R = Me, Et, CH$_2$SiMe$_3$)

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The preparation of new scandium phosphine complexes that contain two hydrocarbyl groups is reported. Thus, reaction of the amido diphosphine ligand precursor LiN(SiMe$_2$CH$_2$PPr$^i_2$)$_2$ with ScCl$_3$(THF)$_3$ in toluene at 100 °C leads to the formation of ScCl$_2$(THF)[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] for which the THF molecule can be removed by pumping in the solid state. The X-ray crystal structure of this molecule shows it to be monomeric with a distorted octahedral geometry having trans-disposed chloride ligands and the tridentate ligand meridionally bound. The solution NMR spectra are also consistent with this geometry. Addition of the alkyllithium reagents RLi (where R = Me, Et, and CH$_2$SiMe$_3$) leads to the formation of bis(hydrocarbyl) derivatives of the formula ScR$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]. These are the first dialkyl-substituted scandium complexes that have been characterized. The solid-state X-ray structures of ScEt$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] and Sc(CH$_2$SiMe$_3$)$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] show that these molecules are mononuclear in the solid state with distorted trigonal bipyramidal geometries. In solution, the NMR spectroscopic parameters are consistent with overall C_{2v} symmetry. A number of reactions were attempted such as addition of CO, H$_2$, CH$_3$I, nitriles, isocyanides, and silanes: in all cases, complete decomposition to a mixture of unidentifiable products was observed. The reaction of ethylene with these bis(hydrocarbyl) species did result in the formation of polyethylene, but the nature of the catalytically active species could not be determined. For the reaction with CO$_2$, insertion was observed to be competitive with decomposition. Molecular orbital calculations show that the frontier orbitals of the five-coordinate, symmetrized complex Sc(CH$_3$)$_2$[N(SiMe$_2$CH$_2$PH$_2$)$_2$] (isopropyl groups at phosphorus replaced with H's) have a different symmetry than that of metallocene systems; in addition, the HOMO was found to be largely the amido nitrogen lone pair of the Sc−N interaction.

Introduction

Compared to most metals in the transition series and the other group 3 elements, the organometallic chemistry of scandium is still largely unexplored. However, recently there has been a surge of activity in this area[1−4] mostly due to the recognition that the enhanced Lewis acidity of Sc(III) can result in new reactivity patterns with small molecules.[5] Although a number of homoleptic alkyls and aryls of scandium have been reported,[6,7] by far the vast majority of organometallic complexes of this element utilize modified-cyclopentadienyl ancillary ligands to stabilize particular coordination geometries.[1,8−14] For example, the σ-bond metathesis reaction owes its existence to early work[15] with bis(pentamethylcyclopentadienyl) systems such as Cp*$_2$ScR; in fact, the combination of two substituted cyclopentadienyl supporting ligands is a common theme in the recent chemistry of scandium.[5,16−20]

Our approach to examining the chemistry of the early transition metals and the elements of group 3 has been to use the tridentate, mixed ligand system $^-$N(SiMe$_2$CH$_2$PR$_2$)$_2$;[21−24] the hard amido donor serves

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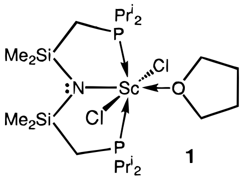
to anchor the ligand to those electropositive metal centers, and this forces the phosphine donors to bind by virtue of their proximity. In this way, we have been able to prepare phosphine complexes of many metals for which the phosphine ligand may not be especially well suited, for example, phosphine complexes of the heavier elements of group 3, yttrium and lanthanum.[25,26] In this paper, we describe our efforts in the coordination chemistry with Sc(III) particularly in the formation of dialkyl derivatives.

Results and Discussion

The reaction of the lithium salt of the ligand, $LiN(SiMe_2CH_2PPr^i_2)_2$,[27] with $ScCl_3(THF)_3$ in toluene at 100 °C for 24 h generates good yields of the monoligand starting material $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**).



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The use of toluene appears to be important since THF fails completely to produce any of **1**. The coordinated THF can be removed by pumping the solid under vacuum as evidenced by the elemental analysis; the coordinated THF however can be detected by NMR spectroscopy and was also evident in the particular crystal used for the solid-state analysis (see later). The solution spectroscopic data for the dichloro derivative **1** is consistent with a meridional coordination of the tridentate ancillary ligand and a trans orientation of the two chloride ligands with the coordinated THF ligand thus trans to the amide donor; this is evident from the fact that the silyl methyl protons resonances in the ^1H NMR spectrum appear as a singlet indicating C_{2v} symmetry. The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a broad singlet slightly shifted from that of the free ligand; the broadness of the peak persists at all temperatures and is a result of the quadrupolar ^{45}Sc nucleus (^{45}Sc, $I = {}^7/_2$, 100% natural abundance). The THF adduct **1** is the preferred starting reagent over the THF-free material $ScCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ simply because the latter is less soluble in hydrocarbon solvents than **1**.

The formation of hydrocarbyl derivatives of scandium using **1** as a starting material proceeds smoothly as long as certain conditions are met. The reaction solvent turns out to be rather important. By using certain alkyllithium (RLi) reagents, dialkyl derivatives could be isolated in pure form, although these species showed a propensity for incorporation of LiCl (eq 1); the use of Grignard or organozinc reagents did not result in the formation of characterizable materials. The solvent for

$$\underset{\mathbf{1}}{ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]} + 2\,RLi \longrightarrow ScR_2[N(SiMe_2CH_2PPr^i_2)_2]\bullet(LiCl)_x \quad (1)$$

2 : R = Me
3 : R = Et
4 : R = CH_2SiMe_3

the metathesis reaction generally was toluene which worked nicely for the diethyl, **3**, and the bis((trimethylsilyl)methyl), **4**; however, for the formation of the dimethyl complex, **2**, the use of hexanes/Et_2O was necessary. The colorless dialkyl derivatives are extremely soluble in all hydrocarbon solvents and can only be crystallized with difficulty from $O(SiMe_3)_2$. These bis(hydrocarbyl)scandium complexes can be stored for months under N_2 at room temperature without decomposition. The elemental analyses are indicative of incorporation of variable amounts of LiCl; although this impurity can be reduced by repeated recrystallizations as evidenced by improved analytical results, the yields are progressively worse. The NMR spectroscopic parameters for these species are quite simple: the ligand backbone resonances are consistent with a highly symmetric environment (one silyl methyl resonance in the ^1H NMR spectrum), and the equivalent hydrocarbyl groups show coupling of equivalent phosphorus-31 nuclei to the α-H's in the ^1H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectra of these species show very broad singlets that are not particularly sensitive to temperature. There is no feature that corresponds directly to the presence of LiCl, nor do any of the single crystals show evidence of regular LiCl incorporation in the lattice. Addition of excess LiCl to a toluene solution of the bis((trimethylsilyl)methyl) derivative **4** resulted in the formation of the THF-free dichloride $ScCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ or a LiCl adduct of this material; no attempt was made to characterize this mixture further.

The dialkyl complexes $ScR_2[N(SiMe_2CH_2PPr^i_2)_2]$ isolated can be considered as 12-electron species assuming that the amido ligand is a four-electron donor. Such coordinative unsaturation might be expected to lead to agostic interactions[16,19,28] with either the α-C−H's of the dimethyl complex **2** and the bis((trimethylsilyl)methyl) derivative **4** or *β*-C−H's of the diethyl complex **3**. Unfortunately, all of our attempts to observe an agostic interaction proved unsuccessful; ^1H NMR data of the diethyl complex **3** are not diagnostic of a static or rapidly fluxional agostic structure, and solid or solution IR spectroscopy reveals no low-energy C−H bands indicative of such an interaction. In addition, the carbon−hydrogen coupling constants $^1J_{C-H}$ for the diethyl derivative **3** are typical for sp^3 C−H bonds, further support that no additional interaction with the unsaturated Sc center is occurring.

As already mentioned in the Introduction, homoleptic trialkyl derivatives of scandium are known; complexes of the empirical formula ScR_3 can be prepared although many of these species are polymeric in nature.[6] With sufficiently bulky hydrocarbyl groups such as neopentyl or (trimethylsilyl)methyl, monomeric species can be isolated as THF adducts, for example, $Sc(CH_2CMe_3)_3(THF)_2$.[7] However, the most well-studied systems are those having one hydrocarbyl group per scandium

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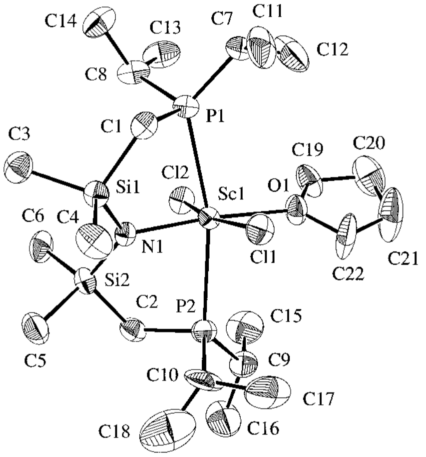

Figure 1. Molecular structure and numbering scheme for $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**).

Table 1. Selected Bond Distances (Å) for $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (1), $ScEt_2[N(SiMe_2CH_2PPr^i_2)_2]$ (3), and $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (4)

1		3		4	
Sc−P1	2.752(3)	Sc−P1	2.779(2)	Sc−P1	2.794(2)
Sc−P2	2.756(3)	Sc−P1*	2.779(2)	Sc−P2	2.788(2)
Sc−N	2.101(7)	Sc−N	2.103(3)	Sc−N	2.126(4)
Sc−Cl1	2.448(3)				
Sc−Cl2	2.418(3)				
Sc−O1	2.271(7)				
		Sc−C10	2.242(3)	Sc−C19	2.224(5)
		Sc−C10*	2.242(3)	Sc−C23	2.204(5)
N−Si1	1.731(7)	N−Si1	1.716(2)	N−Si1	1.718(4)
N−Si2	1.699(8)	N−Si1*	1.716(2)	N−Si2	1.715(4)
		C10−C11	1.485(4)	C19−Si3	1.838(5)
				C23−Si4	1.837(5)

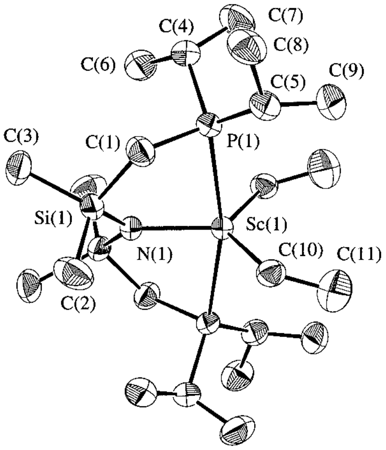

Figure 2. Molecular structure and numbering scheme for $ScEt_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**3**).

stabilized by two cyclopentadienyl or modified cyclopentadienyl ligands; typical examples are Cp^*_2ScR and $[Me_2Si(C_5H_3\text{-3-t-Bu})_2]ScR$.[1,5] The dialkyl species reported here thus represent a new class of organoscandium derivatives.

Crystallographic Studies of Scandium Phosphine Complexes. Three crystal structures are reported in this work: the starting dichloride−THF adduct **1** and two dialkyl complexes, the diethyl **3** and the bis((trimethylsilyl)methyl) derivative **4**. Relevant bond distances and bond angles are found in Tables 1 and 2, respectively.

Slow evaporation of a toluene solution of $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**) yielded colorless plates that were suitable for single-crystal X-ray diffraction. The molecular structure and numbering scheme are illustrated in Figure 1. The coordination environment around the Sc center can best be described as distorted octahedral, with trans-disposed chlorides and the THF molecule trans to the amide nitrogen of the ancillary tridentate ligand. The PNP ligand is bound in a meridional fashion with the P(1)−Sc(1)−P(2) angle bent back to 164.6(1)°. The distorted octahedral geometry is evidenced by both the Cl(1)−Sc(1)−Cl(2) bond angle of 168.1(1)° and the O(1)−Sc(1)−N(1) bond angle of 174.4(3)°. In addition, the backbone of the ancillary amido diphosphine ligand is twisted with respect to the plane defined by the NPScP atoms; the dihedral angle between the NSi_2 and NPScP planes is 34.43° for **1**. The scandium−chlorine distances of 2.448(3) and 2.418(3) Å are slightly longer than those reported for the only other characterized compound containing terminal scandium−chlorine bonds, $ScCl_3(THF)_3$, for which a Sc−Cl distance of 2.413 Å was cited.[29] By comparison, Cp_2ScCl, which is known to have a dimeric structure in the solid state, contains bridging Sc−Cl bond lengths of 2.575 Å, the lengthening of a bond to a bridging halide being quite common.[29] The scandium−phosphorus bond lengths of 2.752(3) and 2.756(3) Å are comparable to those found in $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ScH(PMe_3)$ (2.752(1) Å).[30] As is the case with $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]ScH(PMe_3)$, it appears that the Sc−P bond distance, approximately 0.21 Å larger than the sum of the covalent radii, is indicative of a weak Sc−P bond. It is noteworthy that the two other previously characterized phosphine complexes of scandium, $[(Cp^*SiNR)(PMe_3)Sc]_2(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-}C_2H_4)$ and $[(Cp^*SiNR)(PMe_3)Sc]_2(\mu\text{-H})_2$, each possess uncharacteristically long Sc−P bonds (2.825 and 2.996 Å, respectively[10,31]); however, in each of these cases, PMe_3 dissociation was determined to be rapid. The complex **1** also contains an unremarkable scandium−amide bond distance of 2.101(7) Å which is intermediary between those reported for Cp*-based systems[10] and the somewhat longer Sc−N bonds found in (OEP)ScR (OEP = octaethylporphyrinato; R = alkyl, aryl) derivatives.[2,32]

Both of the bis(hydrocarbyl) derivatives **3** and **4** are isolated as colorless prisms after slow evaporation of hexamethyldisiloxane solutions. The results of the single-crystal X-ray diffraction analyses are presented in Figures 2 and 3, respectively. In both cases, the dialkyls are isolated free from the interaction of a THF donor molecule and thus can best be described as possessing a distorted trigonal bipyramidal geometry in the solid state. The diethyl derivative **3** maintains exact C_2 symmetry and, thus, has two N(1)−Sc(1)−C(10) bond angles measuring 117.59(8)°. Again, as in **1**, the backbone of the ancillary ligand is twisted out of the axial plane (defined by the NPScP atoms) with a dihedral angle of 36.62°; in the equatorial plane, the C(10)−Sc(1)−C(10)* bond angle is 124.8(2)°. The scandium−phosphorus bonds are in the axial positions with a P(1)−Sc(1)−P(1)* bond angle of 166.95(4)°; here again,

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Table 2. Selected Bond Angles for $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (1), $Sc(CH_2CH_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (3), and $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (4)

1		3		4	
P1−Sc−P2	164.6(1)	P1−Sc−P1*	166.95(4)	P1−Sc−P2	154.92(6)
P1−Sc−N	83.2(2)	P1−Sc−N	83.48(2)	P1−Sc−N	76.6(1)
P2−Sc−N	81.5(2)			P2−Sc−N	78.9(1)
P1−Sc−Cl1	85.2(1)	P1−Sc−C10	88.72(8)	P1−Sc−C19	92.2(2)
P1−Sc−Cl2	99.0(1)	P1−Sc−C10*	97.33(7)	P1−Sc−C23	99.7(2)
P2−Sc−Cl1	95.1(1)			P2−Sc−C19	102.3(1)
P2−Sc−Cl2	88.8(1)			P2−Sc−C23	93.1(1)
N−Sc−Cl1	96.8(2)	N−Sc−C10	117.59(8)	N−Sc−C19	113.2(2)
N−Sc−Cl2	94.9(2)			N−Sc−C23	133.3(2)
Cl1−Sc−Cl2	168.1(1)	C10−Sc−C10*	124.8(2)	C19−Sc−C23	113.5(2)
Si1−N−Si2	121.6(4)	Si1−N−Si2	123.6(2)	Si1−N−Si2	122.3(2)
		Sc−C10−C11	115.5(2)	Sc−C19−Si3	131.4(3)
				Sc−C23−Si4	149.8(3)
Sc−N−Si1	118.7(4)	Sc−N−Si1	118.20(8)	Sc−N−Si1	117.6(2)
Sc−N−Si2	119.6(4)			Sc−N−Si2	120.1(2)
P1−Sc−O1	102.4(2)				
P2−Sc−O1	93.0(2)				
Cl1−Sc−O1	84.3(2)				
Cl2−Sc−O1	84.2(2)				
N−Sc−O1	174.4(3)				

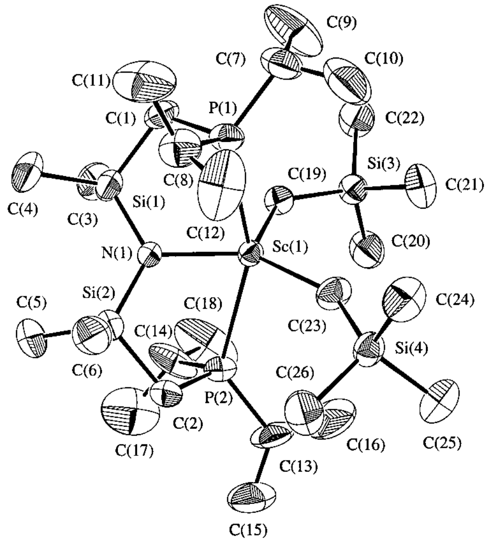

Figure 3. Molecular structure and numbering scheme for $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**4**).

the phosphines are cantilevered slightly back from a purely trans disposition although less than that observed for the octahedral geometry found in **1**. **3** also exhibits scandium−carbon bond lengths of 2.242(3) Å, almost identical to those reported for $Cp^*{}_2ScMe$,[1,15] (OEP)ScMe and $(OEP)ScCH(SiMe_3)_2$.[2] What is remarkable is the lack of any evidence for an agostic interaction between the coordinately unsaturated scandium center and the β-hydrogens of the two ethyl groups. In our systems, the dialkyl derivatives $ScR_2[N(SiMe_2CH_2PPr^i_2)_2]$ are formally 12-electron compounds and, hence, are electron deficient. As **3** is isolated free from Lewis-base interactions, and given the Lewis-acidic nature of scandium, it would be reasonable to expect **3** to harbor an agostic Sc−C−C−H interaction. Previously, the monoethyl derivative $Cp^*{}_2ScCH_2CH_3$ was inferred to possess an agostic β-C−H bond interaction, although disorder in the crystal prevented an accurate determination of the relevant bond lengths and angles.[15] However, the Sc−C(10)−C(11) angle in **3** is 115.5(2)° and not acute enough to suggest a β-C−H interaction.

The solid-state structure of the bis((trimethylsilyl)methyl) complex **4** is similar to that of **3** in that it too exhibits a coordination sphere that can best be described as trigonal bipyramidal, although deviations from this ideal geometry are more pronounced. The twist angle of the NSi_2 portion of the backbone is found to be 40.82°. **4** possesses N(1)−Sc(1)−C(19,23) bond angles of 133.3(2) and 113.2(2)°, which are the greatest indication of dissymmetry in the molecule. Also of note is the reduced P(1)−Sc(1)−P(2) bond angle of 154.92(6)° as compared with that of 166.95(4)° for **3**. This is undoubtedly due to the greater steric demands of the CH_2SiMe_3 moiety as compared to that of CH_2CH_3. It should also be noted that the Sc−C(19)−Si(3) bond angle of 131.4(3)° is probably a result of steric crowding around Sc and not due to any α-agostic interaction. **3** and **4** both contain comparable scandium−amide and scandium−phosphorus bond lengths; as was found for **1**, the latter are indicative of weak Sc−P bonds.

Reactivity of Scandium Dialkyl Complexes. In an effort to probe the reactivity of these species, we performed a number of standard reactions with the dialkyl complexes $ScR_2[N(SiMe_2CH_2PPr^i_2)_2]$ to test their ability to activate small molecules. Unfortunately, in every case that we examined, the complex decomposed to give a mixture of intractable materials including some free ligand, $HN(SiMe_2CH_2PPr^i_2)_2$. For example, reaction with H_2 gave elimination of alkane (observed by ^1H NMR spectroscopy) but no hydrides could be detected and the $^{31}P\{^1H\}$ NMR spectrum of the crude material indicated a complex mixture of products. Similar results were obtained when the dialkyl complexes were allowed to react with CH_3I, with CO, with nitriles, with isocyanides, and with silanes. In the presence of olefins such as ethylene, polyethylene was observed as a product; however, in this case, no new organoscandium products could be observed as growing in. On a slightly positive note, the reaction of the diethyl complex **3** with CO_2 did show evidence for the formation of $Sc(O_2CEt)$ type residues[2,33,34] by ^1H NMR spectroscopy; however, substantial decomposition was also observed and we were unable to determine if CO_2 insertion into the Sc−N bond was also occurring.

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Attempts were made to try to characterize some of the decomposition products. Thus, in the reaction of the bis((trimethylsilyl)methyl) complex **4** with CO, head space, volatiles and involatiles were subjected to NMR analyses, GC-MS, and IR spectroscopy; the only products detected were $Si(CH_3)_4$ (by ^1H NMR spectroscopy and GC-MS) and $HN(SiMe_2CH_2PPr^i{}_2)_2$ (by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy).[35,36] The fate and function of the CO in this decomposition process remain unknown as does the whereabouts of the Sc.

Electronic Structure of Scandium Dimethyl Complexes Stabilized by Amido Diphosphine Ligands. The singular lack of controllable reactivity of these particular organoscandium complexes was disappointing. The compounds would appear to be kinetically stable enough to be isolated and handled under certain conditions, but in the presence of a variety of small molecules, these five-coordinate, dialkylscandium complexes apparently self-destruct. The question we asked was why. It is well established that the bis(cyclopentadienyl) ligand ancillary set is remarkable in terms of generating reactive early metal fragments; the frontier orbitals[37] of the bent Cp_2M unit have a symmetry that allows the interaction of certain small molecules with the fragment in a way that promotes insertion and metathesis reactions. We therefore examined our complex to determine if the frontier orbitals of these mononuclear bis(hydrocarbyl)'s showed any peculiarities. We performed INDO/1 level calculations using the ZINDO program on the CAChe system; the model we used was symmetrized to C_{2v}, and the isopropyl substituents at phosphorus were replaced with hydrogens. The parameters are those developed in the literature and are generally applicable for first- and second-row transition elements.[38] The orbital diagram is shown in Figure 4. The orbitals of interest are the sets of highest occupied and lowest unoccupied MO's. The HOMO corresponds to the lone pair of electrons on the amide nitrogen p orbital; the next two occupied orbitals, HOMO − 1 and HOMO − 2, are essentially the Sc−C σ bonds and are more stabilized by 1.4 eV. The two lowest unoccupied orbitals are two d orbitals at Sc. By comparison to bent metallocene complexes, the frontier orbitals of these bis(hydrocarbyl) systems are noticeably different. Instead of the characteristic a_1 and b_2 unoccupied orbitals of the metallocene systems (Scheme 1), one can see that the comparable LUMO's of the Sc[PNP] system are d orbitals of π-symmetry (a_2 and b_1) and cannot accept electron density from filled orbitals of molecules like CO. Thus from a symmetry point of view, one can rationalize that the two important empty orbitals at Sc are not appropriate for overlap with typical small molecules. In addition, the steric bulk of the ancillary amido diphosphine ligand is such that approach to the LUMO at Sc perpendicular to the plane defined by $ScNP_2$ is impeded by the backbone of the tridentate ligand, while approach to LUMO + 1 is opposite to the Sc−N bond, and here the large isopropyl groups at phosphorus are possibly in the way. Nevertheless, it is probably the symmetry aspect that is the overriding feature of these systems. As a caveat, we point out that rehybridization of these MO's upon interaction with a small molecule is possible and thus these simple ideas do suffer from lack of sophistication. In addition, such an analysis completely ignores kinetic issues and these may be the important reasons for the reactivity differences for the bis(hydrocarbyl) complexes of Sc versus the bent metallocene derivatives. For example, if there is phosphine dissociation, new orbitals would become available that have correct symmetry requirements for interaction with typical small molecules; moreover, phosphine dissociation might also be the trigger to decomposition under certain conditions.

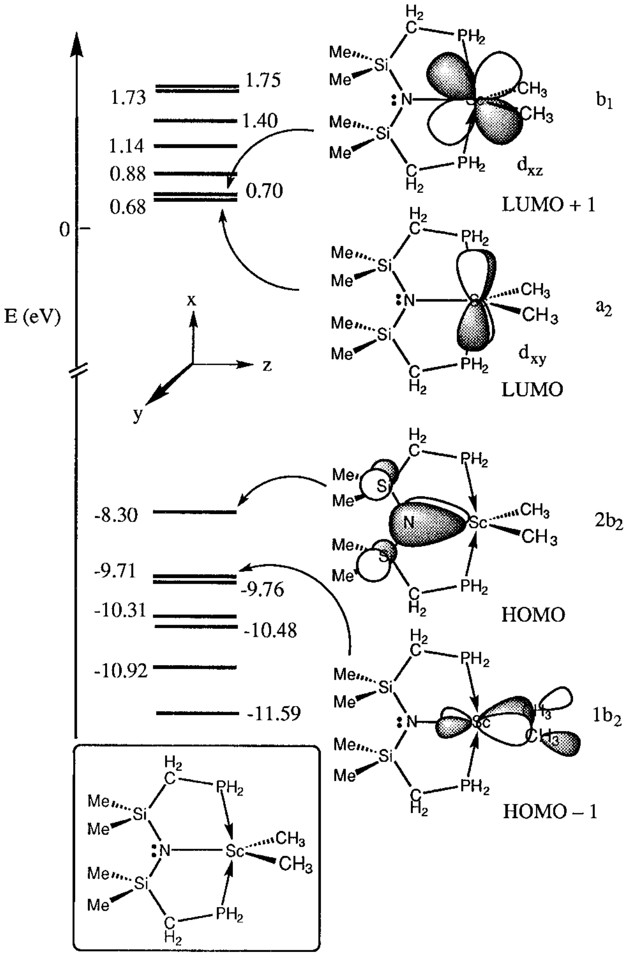
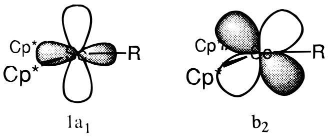


Figure 4. Molecular orbital diagram for the model compound $Sc(CH_3)_2[N(SiMe_2CH_2PH_2)_2]$.

Scheme 1



One final point should be mentioned regarding the frontier orbitals of this fragment. We note that there are no appropriate empty orbitals that can overlap with the existing α-C−H or β-C−H bonds in the ground-state structures; both the LUMO and the LUMO + 1 are too far away to interact with these alkyl groups without considerable distortion of Sc−C−C angles. In other

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words, the lack of agostic interactions from both solution and solid-state structures is supported by this MO analysis.

Conclusions

The use of the bulky amido diphosphine ancillary ligand $N(SiMe_2CH_2PPr^i_2)_2$ has allowed for the isolation of a series of mononuclear, dialkyl complexes of Sc(III). In particular, both the diethyl and the bis((trimethylsilyl)methyl) complexes **3** and **4** were characterized in solution and in the solid state. No evidence for agostic interactions was observed either in solution or in the solid state. Reactivity studies were attempted, but in all cases studied, decomposition of the dialkyl complexes was observed. Semi-empirical molecular orbital calculations (INDO/1) suggest that the HOMO is in fact concentrated on the lone pair of the amide nitrogen rather than on the Sc−C bonds. It would appear that the ancillary ligand allows for the kinetic stabilization of these 12-electron species but they are poised to self-destruct in the presence of small molecules.

Experimental Section

Procedures. Unless otherwise stated all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 model equipped with a MO-40-2H purification system and a −40 °C freezer. ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR spectroscopy were performed on a Varian XL-300 instrument operating at 299.9, 121.4, and 75.48 MHz, respectively. ^1H NMR spectra were referenced to internal $C_6D_5\mathit{H}$ (7.15 ppm) or $C_6D_5CD_2\mathit{H}$ (2.09 ppm). $^{31}P\{^1H\}$ NMR spectra were referenced to external $\mathit{P}(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). ^{13}C spectra were referenced to internal C_6D_6 (128.0 ppm). Mass spectral studies were carried out on a Kratos MS 50 using an EI source. Infrared spectra were recorded on a BOMEM MB-100 spectrometer. Solution samples were recorded on a 0.1 mm KBr cell, and solid samples were recorded as KBr pellets. Microanalyses (C, H, N, Cl) were performed by Mr. P. Borda of this department. Low carbon analyses may in part be due to the metal-catalyzed formation of silicon carbide, which does not burn completely during combustion analysis.

Materials. $LiN(SiMe_2CH_2PPr^i_2)_2$ was prepared by a published procedure.[27] MeLi (1.4 M solution in ether) was purchased from Aldrich and used as received. $ScCl_3(THF)_3$, EtLi, and $LiCH_2SiMe_3$ were prepared according to published procedures.[5,39,40]

Hexanes, toluene, Et_2O and hexamethyldisiloxane were refluxed over CaH_2 prior to a final distillation from either sodium metal or sodium benzophenone ketyl under an Ar atmosphere. Deuterated solvents were dried by distillation from sodium benzophenone ketyl; oxygen was removed by 3 freeze−pump−thaw cycles. CO was purchased from Praxair and used as received. CO_2 was purchased from Praxair and subjected to 3 freeze−pump−thaw cycles to remove oxygen followed by transfer from a −50 °C dry ice/ethanol bath to remove residual water.

$ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (1). To a slurry of $ScCl_3(THF)_3$ (992 mg; 2.70 mmol) in toluene (10 mL) was added a toluene solution (10 mL) of $LiN(SiMe_2CH_2PPr^i_2)_2$ (985 mg; 2.48 mmol). The reaction vessel was then heated at 100 °C for 24 h. The reaction mixture was then cooled and passed through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield a yellow waxy solid. The residue was taken up in a minimum amount of toluene (approximately 4 mL). Slow evaporation of the solvent afforded large colorless plates (1.193 g; 83% yield). ^1H NMR (C_6D_6): δ 4.08 (t, 4H, $O(C\mathit{H}_2CH_2)_2$, $^3J_{H-H} = 6.5$ Hz), 1.91 (d of sept, 4H, $C\mathit{H}Me_2$, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-P} = 4.8$ Hz), 1.36 (t, 4H, $O(CH_2C\mathit{H}_2)_2$, $^3J_{H-H} = 6.5$ Hz), 1.20 and 1.10 (dd, 24H, $CH\mathit{MeMe'}$, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-P} = 7.0$ Hz), 1.05 (d, 4H, $C\mathit{H}_2P$, $^2J_{H-P} = 9.7$ Hz), 0.45 (s, 12H, $Si\mathit{Me}_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.8 (480 Hz peak width at half height). MS: *m/e* 507 ($M^+ -$ THF). The THF can be removed by pumping in vacuo. ^1H NMR (C_6D_6) for $ScCl_2[N(SiMe_2CH_2PPr^i_2)_2]$: δ 1.59 (d of sept, 4H, $C\mathit{H}Me_2$, $^3J_{H-H} = 6.9$ Hz, $^2J_{H-P} = 1.5$ Hz), 1.04 and 1.02 (dd, 24H, $CH\mathit{Me_2}'$, $^3J_{H-H} = 6.9$ Hz, $^3J_{H-P} = 7.0$ Hz), 0.47 (d, 4H, $C\mathit{H}_2P$, $^2J_{H-P} = 3.7$ Hz), 0.29 (s, 12H, $Si\mathit{Me}_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −4.9. .Anal. Calcd for $C_{18}H_{44}Cl_2NP_2ScSi_2$(THF-free material): C, 42.51; H, 8.72; N, 2.75. Found: C, 42.33; H, 8.65; N, 2.58.

$Sc(CH_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (2). To a hexanes solution (5 mL) of $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (252 mg; 0.434 mmol) was added MeLi (0.65 mL of a 1.4 M Et_2O solution, diluted with 5 mL of ether; 0.910 mmol) dropwise. The reaction mixture was then stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield an orange-yellow waxy solid (197 mg; 97% yield). Purification by recrystallization was not possible either due to the compound's extreme solubility in hydrocarbon solvents or because it was low melting; as a result, characterization by MS or elemental analysis was not possible. ^1H NMR (C_6D_6): δ 1.84 (d of sept, 4H, $C\mathit{H}Me_2$, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-P} = 5.6$ Hz), 1.12 and 1.08 (dd, 24H, $CH\mathit{MeMe'}$, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-P} = 8.0$ Hz), 0.80 (d, 4H, $C\mathit{H}_2P$, $^2J_{H-P} = 6.8$ Hz), 0.31 (s, 12H, $Si\mathit{Me}_2$), 0.27 (t, 6H, $Sc\mathit{Me}_2$, $^3J_{H-P} = 2.1$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.0 (160 Hz peak width at half-height).

$ScEt_2[N(SiMe_2CH_2PPr^i_2)_2]$ (3). To a toluene solution (10 mL) of $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (569 mg; 0.980 mmol) was added EtLi (74 mg; 2.06 mmol) in toluene (10 mL). The reaction mixture was left to stir overnight and then filtered through a frit lined with Celite to remove LiCl, followed by solvent removal *in vacuo*. The residue was taken up in a minimum amount of hexamethyldisiloxane (approximately 5 mL). Subsequent slow evaporation resulted in the formation of colorless prisms (335 mg; 69% yield). ^1H NMR (C_6D_6): δ 1.86 (d of sept, 4H, $C\mathit{H}Me_2$, $^3J_{H-H} = 7.5$ Hz, $^2J_{H-P} = 4.7$ Hz), 1.82 (t, 6H, $ScCH_2\mathit{Me}$, $^3J_{H-H} = 8.4$ Hz), 1.13 and 1.08 (dd, 24H, $CH\mathit{MeMe'}$, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-P} = 6.6$ Hz), 0.81 (d, 4H, $C\mathit{H}_2P$, $^2J_{H-P} = 6.6$ Hz), 0.55 (t of q, 4H, $ScC\mathit{H}_2Me$, $^3J_{H-H} = 8.4$ Hz, $^3J_{H-P} = 4.0$ Hz), 0.31 (s, 12H, $Si\mathit{Me}_2$). ^{13}C NMR (C_6D_6): δ 23.25 (mult, 4C, $\mathit{C}HMe_2$), 19.78 and 19.20 (mult, 8C, $CH\mathit{MeMe'}$,), 12.56 (mult, 2C, $\mathit{C}H_2P$), 8.66 (mult, 2C, $Sc\mathit{C}H_2Me$, $^1J_{C-H} = 125$ Hz), 6.25 (mult, 4C, $Si\mathit{Me}_2$), 6.00 (mult, 2C, $ScCH_2\mathit{Me}$, $^1J_{C-H} = 119$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.8 (230 Hz peak width at half-height). MS: *m/e* 496 (M^+). Anal. Calcd for $C_{22}H_{54}NP_2ScSi_2$ (+0.5 equiv of LiCl): C, 51.12; H, 10.53; N, 2.71. Found: C, 51.17; H, 10.58; N, 3.11.

$Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (4). A solution of Me_3SiCH_2Li (164 mg; 1.74 mmol) in toluene (10 mL) was added to a toluene solution (15 mL) of $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$ (500 mg; 0.862 mmol). The reaction mixture was stirred overnight, after which it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* and the residue taken up in a minimum amount of hexamethyldisiloxane (approximately 5 mL). Slow evaporation of the solvent resulted in the formation of colorless prisms (380 mg; 72% yield). ^1H NMR (C_6D_6): δ 1.96 (d of sept, 4H, $C\mathit{H}Me_2$, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-P} = 4.8$ Hz), 1.18 and 1.14 (dd, 12H, $CH\mathit{MeMe'}$, $^3J_{H-H} = 7.2$ Hz, $^3J_{H-P} = 5.8$), 0.84 (d, 4H, $C\mathit{H}_2P$, $^2J_{H-P} = 12.0$ Hz), 0.41 (s, 18H, $CH_2Si\mathit{Me}_3$), 0.35 (s, 12H, $Si\mathit{Me}_2$), 0.21 (t, 4H, $C\mathit{H}_2SiMe_3$, $^3J_{H-P} = 5.0$ Hz). $^{31}P\{^1H\}$ NMR

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[40] Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691−693.

Table 3. Crystallographic Data[a]

compd	$ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$, **1**	$ScEt_2[N(SiMe_2CH_2PPr^i_2)_2]$, **3**	$Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$, **4**
formula	$C_{22}H_{52}Cl_2NOP_2ScSi_2$	$C_{22}H_{54}NP_2ScSi_2$	$C_{26}H_{66}NP_2ScSi_4$
fw	580.64	493.75	612.06
color, habit	colorless, plate	colorless, prism	colorless, prism
cryst size, mm	0.05 × 0.35 × 0.40	0.10 × 0.20 × 0.35	0.25 × 0.30 × 0.35
cryst system	orthorhombic	monoclinic	monoclinic
space group	$Pca2_1$	$C2/c$	$P2_1/c$
a, Å	21.482(4)	19.316(1)	12.862(2)
b, Å	10.597(5)	10.3386(9)	12.515(3)
c, Å	14.668(3)	15.832(1)	24.582(3)
β, deg	90	104.843(4)	91.15(1)
V, Å^3	3339(1)	3056.1(4)	3956(1)
Z	4	4	4
T, °C	21	21	21
D_c, g/cm^3	1.155	1.077	1.028
F(000)	1248	1088	1344
radiation	Mo	Cu	Mo
μ, cm^{-1}	5.61	39.24	4.01
transm factors	0.90−1.00	0.60−1.00	0.97−1.00
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan range, deg in ω	$0.89 + 0.35 \tan \theta$	$0.73 + 0.20 \tan \theta$	$0.82 + 0.35 \tan \theta$
scan speed, deg/min	16 (up to 8 rescans)	16 (up to 8 rescans)	16 (up to 8 rescans)
data collcd	$+h,+k,+l$	$+h,+k,\times$b1l	$+h,+k,\times$b1l
$2\theta_{max}$, deg	45	155	50
crystal decay, %	12.9	negligible	1.8
tot. no. of reflcns	2514	3387	7679
unique reflcns	2514	3287	7320
R_{merge}		0.023	0.043
no. with $I \geq 3\sigma(I)$	1255	2314	2643
no. of variables	279	129	317
R	0.035	0.038	0.043
R_w	0.034	0.046	0.036
gof	1.39	2.72	1.85
max Δ/σ (final cycle)	0.003	0.0005	0.02
resid density, e/Å^3	−0.19, 0.18	−0.20, 0.20	−0.21, 0.19

[a] Rigaku AFC6S diffractometer, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), Mo $K\alpha$ radiation (λ = 0.710 69 Å) or Cu $K\alpha$ radiation (λ = 1.541 78 Å), graphite monochromator, $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan speed, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

(C_6D_6): δ −0.7 (90 Hz peak width at half-height). MS: m/e 524 ($M^+ - CH_2SiMe_3$). Anal. Calcd for $C_{26}H_{66}NP_2ScSi_4$ (+0.80 equiv of LiCl): C, 48.34; H, 10.30; N, 2.17. Found: C, 48.57; H, 10.48; N, 2.28. Analysis after an additional recrystallization: Calcd for $C_{26}H_{66}NP_2ScSi_4$ (+0.58 equiv of LiCl): C, 49.05; H, 10.45; N, 2.20. Found: C, 49.06; H, 10.28; N, 2.36. Analysis after a 3rd recrystallization: Calcd for $C_{26}H_{66}NP_2ScSi_4$ (+0.43 equiv of LiCl): C, 49.55; H, 10.55; N, 2.22; Cl, 2.42. Found: C, 49.96; H, 10.27; N, 2.38; Cl, 2.45.

Reaction of $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ with CO. Method 1. In the glovebox, approximately 20 mg of **4** was dissolved in 0.5 mL of C_6D_6 and placed in a sealable NMR tube equipped with a Kontes-valve needle adapter. The NMR tube assembly was then attached to a second sealable NMR tube by means of a glass bridge. The apparatus was then taken onto the line, and the solution of **4** was subjected to 3 freeze−pump−thaw cycles. The solution was then exposed to 1 atm of CO under which it was left to stand for 12 h. The volatiles were then condensed at liquid-N_2 temperature into the second NMR tube under static vacuum. The second NMR tube containing the volatiles was then flame-sealed. C_6D_6 was then added to the first NMR tube via syringe and the tube flame-sealed. The contents of both tubes were then analyzed by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy.

Method 2. In the glovebox, approximately 100 mg of **4** was dissolved in 10 mL toluene and placed in a small reactor bomb, which was then attached to a second reactor bomb by means of a glass bridge. The apparatus was then taken onto the line, and the solution of **4** was subjected to 3 freeze−pump−thaw cycles. The solution was then exposed to 1 atm of CO under which it was left to stand for 12 h. The volatiles were then condensed at liquid-N_2 temperature into the second bomb under static vacuum. The contents of the second bomb were then analyzed by GC-MS and solution IR spectroscopy. Toluene was then added to the first bomb via syringe and the contents examined by GC-MS and solution IR spectroscopy.

Reaction of $Sc(CH_2CH_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$ with CO_2. In the glovebox, 184 mg of **3** was dissolved in 10 mL of toluene and placed in a small reactor bomb. The bomb was then attached to the line by means of a constant-volume glass bulb (9.1 mL) equipped at either end with a Kontes needle valve. The yellow solution of **3** was then subjected to 3 freeze−pump−thaw cycles. With the solution frozen, the apparatus was evacuated and CO_2 introduced to the glass bulb. The bulb was then closed to the CO_2 source and opened to the evacuated bomb, and the CO_2 was condensed into the bomb over a period of 30 min. The bomb was then sealed and left to stir overnight, during which time the solution turned colorless. The toluene was then removed *in vacuo* to yield a slightly yellow oil. This reaction was repeated using varying amounts of **3** and/or glass bulbs of differing volume. ^1H NMR (C_6D_6): δ 3.26 (q, 4H, $ScCO_2CH_2Me$, $^3J_{H-H}$ = 7.0 Hz), 1.47 (d of sept, 4H, $CHMe_2$, $^3J_{H-H}$ = 7.1 Hz, $^2J_{H-P}$ = 1.5 Hz), 1.11 (t, 6H, $ScCO_2CH_2Me$, $^3J_{H-H}$ = 7.0 Hz), 0.91 and 0.90 (dd, 24H, $CHMeMe'$, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-P}$ = 4.5 Hz), 0.30 (d, 4H, CH_2P, $^2J_{H-P}$ = 3.0 Hz), 0.08 (s, 12H, $SiMe_2$).

Molecular Orbital Calculations. All molecular orbital calculations were performed on the CAChe Worksystem, a product developed by Tektronix. The parameters used in the INDO/1 semiempirical molecular orbital calculations on the model compound $Sc(CH_3)_2[N(SiMe_2CH_2PH_2)_2]$ were taken from the literature.[38] A full list of eigenvalues and symmetry labels can be found in the Supporting Information. The bond lengths were taken from the X-ray crystal structure analysis of **3**, and the model was restricted to C_{2v} symmetry. The $-PPr^i_2$ groups were replaced with $-PH_2$ groups and the $-CH_2CH_3$ groups replaced with their methyl analogues. The $-PH_2$, $-CH_3$, and $-SiMe_2$ moieties were all eclipsed to effect maximum symmetry. The Cartesian coordinates of the model can be found in the Supporting Information. For the model, the following standard bond lengths were used: P−H, 1.380 Å; C−H, 1.090 Å.

X-ray crystallographic Analyses of $ScCl_2(THF)[N(SiMe_2CH_2PPr^i_2)_2]$, 1, $ScEt_2[N(SiMe_2CH_2PPr^i_2)_2]$, 3, and $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2PPr^i_2)_2]$, 4. Crystallographic data appear in Table 3. The final unit-cell parameters were obtained by least-squares fitting of the setting angles for 25 reflections with $2\theta = 15.4-27.7°$ for **1**, 65.7−73.2° for **3**, and 20.0−30.4° for **4**. The intensities of three standard reflections, measured every 200 reflections, decayed uniformly by 12.9% for **1** and by 1.8% for **4** and showed only small random fluctuations for **3**. The data were processed,[41] corrected for Lorentz and polarization effects, decay (for **1** and **4**), and absorption (empirical: based on azimuthal scans for three reflections).

The structure of **1** was solved by direct methods, and those of **3** and **4** were solved by conventional heavy atom methods. The structure analysis of **1** was initiated in the noncentrosymmetric space group $Pca2_1$, and that of **3**, in the centrosymmetric space group $C2/c$ on the basis of the *E*-statistics and the appearances of the Patterson functions. These choices were confirmed by the subsequent successful solutions and refinements of the structures. The point group for **4** was uniquely determined to be $P2_1/c$ due to systematic absences. Complex **3** has exact C_2 symmetry, the Sc and N atoms lying on the crystallographic 2-fold axis. The non-hydrogen atoms of all three structures were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C−H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Secondary extinction corrections (Zachariasen type) were applied for **3** and **4**, the final values of the extinction coefficients being $1.79(9) \times 10^{-6}$ and $1.03(15) \times 10^{-7}$, respectively. Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref 42. A parallel refinement of the structure of **1** having the opposite polarity gave identical residuals; thus, the polarity of **1** could not be established. Final atomic coordinates and equivalent isotropic thermal parameters are given in the Supporting Information. Selected bond lengths and angles appear in Tables 4 and 5. Complete tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

Acknowledgment. Financial support was generously provided by the NSERC of Canada in the form of grants to M.D.F. and a postgraduate scholarship to G.G.

Supporting Information Available: Cartesian coordinates for molecular orbital calculation model, complete tables of bond lengths and bond angles, complete atomic parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (39 pages). Ordering information is given on any current masthead page.

OM960052Q

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