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Synthesis and Molecular Structure of Bis(pentamethylcyclopentadienyl) Phospholyl- and Arsolylsamarium(III) Complexes: Influence of Steric and Electronic Factors

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The title complexes could be easily synthesized respectively from the following biphospholyls: 2,3,4,5,2′,3′,4′,5′-octamethylbi-1,1′-phospholyl (**1**); 3,4,3′,4′-tetramethylbi-1,1′-phospholyl (**2**); 2,5,2′,5′-tetra-*tert*-butylbi-1,1′-phospholyl (**3**), and Cp^*_2Sm or $Cp^*_2Sm(Et_2O)$ (Cp* = pentamethylcyclopentadienyl). 3,4,3′,4′-Tetramethylbi-1,1′-arsolyl (**4**), a precursor of the new 3,4-dimethylarsolyl ligand, was prepared in three steps from the known 1-chloro-2,5-di(trimethylsilyl)-3,4-dimethylarsole (**5**). The reaction of **4** with Cp^*_2Sm afforded the title complex **12**. Although the unsubstituted bi-1,1′-phospholyl could be observed by NMR, it decomposed during the isolation, and thus the title complex **13** with the unsubstituted phospholyl was prepared from $Cp^*_2Sm(Et_2O)$ and the new thallium phospholide **8**, synthesized by metathesis of lithium phospholide with thallous ethoxide. Compounds **8**−**13** were characterized by X-ray crystallography. The solid state structures of complexes **9**−**13** vary depending on the substitution pattern on the phospholyl ligand. They can be η^1- or η^5-coordinated monomers (respectively **9** and **12**), a μ:η^1,η^5- symmetrical dimer (**13**), or even unsymmetrical dimers where both the η^1- and the μ:η^1,η^5-coordination modes are found (**10** and **11**). These structures are discussed by taking into account the electronic and steric properties of the phospholyl and arsolyl ligands.

Introduction

The pentamethylcyclopentadienyl (Cp*) ligand has been much employed in organolanthanide chemistry.[1] For instance, it has been successfully used to synthesize stable seven-coordinated alkyllanthanoid compounds such as $[Cp^*_2LnCH(SiMe_3)_2]$.[2] However, when two Cp* ligands are coordinated to a lanthanoid metal, the optimum coordination number is generally 8; thus, ate-complexes such as $[Cp^*_2LnCl_2Li(solv)_n]$ are very common and are known for all the lanthanoids.[1] In contrast with lesser-substituted Cp ligands, no $[Cp^*_3Ln]$ complexes had been prepared until Evans et al. demonstrated the existence of overcrowded nine-coordinated Cp^*_3Sm[3] and Cp^*_3Nd.[4] In the actinide chemistry, even 10-coordinated complexes such as $[Cp^*_3UX]$ (X = halogen)[5] could be isolated.

In organolanthanoid chemistry, we have developed the use of phospholyl (or phosphacyclopentadienyl) ligands as an alternative to cyclopentadienyl ligands. For instance, with the tetramethylphospholyl (C_4Me_4P) ligand, we have recently been able to isolate $[(C_4Me_4P)_2LnCH(SiMe_3)_2]$ (Ln = La, Nd, Sm).[6] However, the reaction of C_4Me_4PK with $SmCl_3$ in toluene did not afford the expected $[(C_4Me_4P)_3Sm)]$ but a polymeric ate-complex: $[\{(C_4Me_4P)_3SmClK(toluene)_{1.5}\}_n]$, in which all three C_4Me_4P groups have different coordination behavior: one is only η^5-bonded to samarium, another is bonded both η^5- to samarium and η^1- to potassium, and the third one is η^5-bonded to potassium and only η^1-ligated to samarium.[7] Thus, the lone pair at phosphorus imparts additional functionality to the phospholyl ligand. To gain more insight into the versatile behavior of this ligand in lanthanide chemistry, we studied its coordination by varying the substitution pattern on the phospholyl ring, in a sterically demanding environment provided by the presence of two Cp* ligands coordinated to a lanthanide metal. We hereafter report the synthesis and crystal structure of four $[Cp^*_2Sm(phospholyl)]$ complexes, one $[Cp^*_2Sm(arsolyl)]$ complex, and two ligand precursors: a biarsolyl and a phospholylthallium, with the crystal structure of the latter.

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Results and Discussion

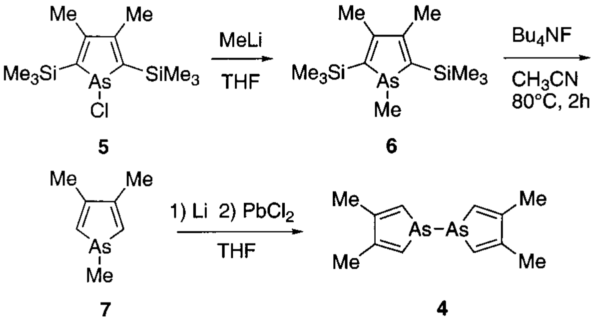
Several pathways are possible for the synthesis of Cp*$_2$Ln(phospholyl) complexes, the most obvious being the metathetical reaction of a Ln(III) precursor such as [Cp*$_2$LnCl$_2$Li(solv.)$_n$] with an alkali metal phospholide. However, these reactions are usually conducted in THF, and in our case this is a drawback, since this solvent is likely to remain coordinated to the lanthanide metal in the product; it can even further react with ring opening, as it has previously been shown by Schumann et al.[8] and by Evans et al.[9] Several other pathways are possible: For instance, Evans et al. have shown that [Cp*$_2$Sm] could be oxidized by tetraphenylbiphosphines or -biarsines in a nonpolar solvent to give [Cp*$_2$Sm(EPh$_2$)] (E = P, As);[9] Deacon et al. have also demonstrated that [Cp*$_2$Sm(THF)$_2$] could be oxidized by a Tl(I) triphospholide into [Cp*$_2$Sm(THF)(triphospholide)].[10] A simple transposition of Evans' method would then involve the synthesis of the desired [Cp*$_2$Sm(phospholyl)] complexes by reaction of [Cp*$_2$Sm] with a 1,1′-biphospholyl as phospholyl ligand precursor. This method is appealing since several such biphospholyls are known in the literature. Since the As−As bond of a biarsine can also be cleaved, a 1,1′-biarsolyl could be similarly used as reagent for the synthesis of a [Cp*$_2$Sm(arsolyl)] complex. Alternatively, a variation of Deacon's procedure would imply the reaction of a Cp*$_2$Sm precursor with a thallium phospholide.

Synthesis of the Phospholyl and Arsolyl Ligand Precursors. The precursors 2,3,4,5,2′,3′,4′,5′-octamethylbi-1,1′-phospholyl [(C$_4$Me$_4$P)$_2$ (**1**)],[11] 3,4,3′,4′-tetramethylbi-1,1′-phospholyl [(C$_4$H$_2$Me$_2$P)$_2$ (**2**)],[12] and 2,5,2′,5′-tetra-*tert*-butylbi-1,1′-phospholyl [(C$_4$*t*-Bu$_2$H$_2$P)$_2$ (**3**)][13] are known in the literature and have been prepared in our laboratory. Their variation in steric properties is interesting: **1** has methyl subtituents at all available positions; **2** has free 2,5 positions, and **3** has bulky substituents at the 2,5 positions and free 3,4 positions. It also appeared desirable to include an arsolyl ligand around samarium because of its resemblance with the phospholyl ligand and to also study the complexation of the parent, unsubstituted phospholyl ligand.

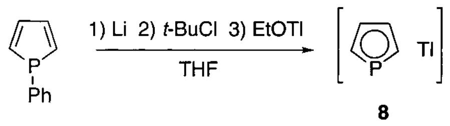
We introduced the new 3,4-dimethylarsolyl (C$_4$H$_2$Me$_2$As) ligand, a homologue to the well-known 3,4-dimethylphospholyl ring system. The synthesis of 3,4,3′,4′-tetramethylbi-1,1′-arsolyl [(C$_4$H$_2$Me$_2$As)$_2$ (**4**)] is outlined in Scheme 1.

Reaction of the known 1-chloro-2,5-di(trimethylsilyl)-3,4-dimethylarsole (**5**)[14] with methyllithium afforded a good yield of 1-methyl-2,5-di(trimethylsilyl)-3,4-dimethylarsole (**6**), which was desilylated into 1-methyl-3,4-dimethylarsole (**7**) in standard conditions. Small-scale experiments established that lithium cleavage of the As−Me bond was quantitative after 2.5 h. ^{1}H NMR (in THF-d_8) of the toluene-insoluble solid showed the formation of a 1:1 mixture of 3,4-dimethylarsolyllithium (δ 2.05, s, 6H; 7.24, s, 2H) and methyllithium (δ −2.05, s, 3H). Treatment of 1 equiv of this mixture with 0.5 equiv of PbCl$_2$ resulted in selective reaction of PbCl$_2$ with MeLi: after filtration and evaporation to dryness, only the signal of 3,4-dimethylarsolyllithium was observed in the proton spectrum. Addition of another 0.5 equiv of PbCl$_2$ then resulted in the clean oxidative coupling of 3,4-dimethylarsolyllithium into **4**. Therefore, in a full-scale experiment, 1 equiv (in fact, a slight excess) of PbCl$_2$ was added to the solid resulting from lithium cleavage of **7** to yield **4** in high conversion. Analytically pure product was obtained after recrystallization from hexane. Initial attempts at the synthesis of **4** by oxidation of 3,4-dimethylarsolyllithium generated from lithium cleavage of 1-phenyl-3,4-dimethylarsole, which could be synthesized analogously to **7**, resulted in a low yield of impure **4**.

Scheme 1



Scheme 2



Next, we attempted to prepare the parent 1,1′-biphospholyl (C$_4$H$_4$P)$_2$, potentially available by oxidation of the already described parent lithium phospholide.[15] Lithium cleavage of 1-phenylphosphole followed by iodine oxidation of the lithium phospholide presumably afforded the parent 1,1′-biphospholyl, characterized by its ^{31}P chemical shift at −19.2 ppm; however, attempted isolation of this compound invariably resulted in decomposition. Therefore, we used another route to synthesize the desired product using thallium phospholide [Tl(C$_4$H$_4$P)], **8** (Scheme 2).

Lithium cleavage of 1-phenylphosphole was followed by standard neutralization of the concomitantly created phenyllithium with *t*-BuCl. The resulting lithium phospholide was then treated with thallous ethoxide, a soluble Tl(I) reagent, whereupon a yellow precipitate of **8** appeared, which was isolated after hydrolysis of the reaction mixture since **8** is not water-sensitive. Like [TlCp], **8** is volatile, and thus it could be purified by slow vacuum sublimation at 80 °C/0.1 Torr and was eventually obtained in fair yield as air-stable yellow crystals. Complex **8** is not light-sensitive and is only slightly

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Table 1. X-Ray Diffraction Summary

	8	**9**	**10**	**11**	**12**	**13**
formula	C_4H_4PTl	$C_{28}H_{42}PSm$	$C_{52}H_{76}P_2Sm_2$	$C_{32}H_{50}PSm$	$C_{52}H_{76}As_2Sm_2$	$C_{24}H_{34}PSm$
molecular weight	287.41	559.94	1063.76	616.04	1151.67	503.83
cryst color, habit	yellow needle	orange plate	red cube	red plate	red cube	red plate
cryst dimens, mm	0.20 × 0.12 × 0.12	0.20 × 0.18 × 0.04	0.12 × 0.12 × 0.12	0.22 × 0.20 × 0.16	0.16 × 0.16 × 0.16	0.22 × 0.18 × 0.12
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic
space group (#)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)
a, Å	6.201(5)	9.943(5)	10.7820(2)	9.7016(2)	10.773(5)	13.738(5)
b, Å	9.563(5)	33.367(5)	19.5920(4)	11.8348(3)	19.633(5)	9.084(5)
c, Å	9.149(5)	16.209(5)	22.7530(3)	13.0392(3)	22.898(5)	17.827(5)
α, deg	90	90	90	90.0520(10)	90	90
β, deg	98.820(5)	103.100(5)	90	96.0300(10)	90	104.110(5)
γ, deg	90	90	90	99.9610(10)	90	90
V, Å^3	536.1(6)	5238(3)	4806.37(15)	1466.11(6)	4843(3)	2157.6(15)
Z	4	8	4	2	4	4
d, g·cm^{-3}	3.561	1.420	1.470	1.395	1.579	1.551
F(000)	496	2296	2168	638	2312	1020
μ, cm^{-1}	30.261	2.315	2.519	2.075	3.790	2.801
max. θ	30.07	30.03	29.98	30.01	30.02	30.03
h index range	−8 to 8	−14 to 10	−15 to 15	−13 to 13	−15 to 14	−19 to 19
k index range	−10 to 13	−46 to 44	−27 to 27	−16 to 16	−21 to 27	−12 to 11
l index range	−12 to 12	−13 to 22	−31 to 31	−18 to 15	−32 to 23	−25 to 25
no. of reflns measd	2569	29 060	13 737	12 390	33 515	10 541
indep reflns	1565	14 440	13 737	8492	13 916	6220
no. of reflns used ($I > 2\sigma(I)$)	1305	12 335	12 640	8155	12 779	4866
wR2 (all data)	0.1015	0.1295	0.0592	0.0921	0.0516	0.1114
R1	0.0364	0.0319	0.0276	0.0332	0.0252	0.0419
GoF	1.062	1.135	0.998	1.203	1.019	1.096

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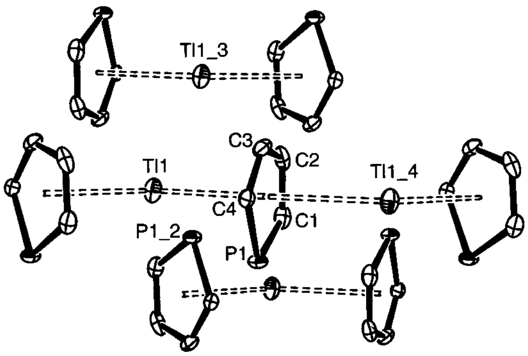

Figure 1. ORTEP plot of part of the solid state polymeric structure of **8** together with the numbering scheme used (50% ellipsoids, hydrogens omitted). Selected interatomic distances (Å): Tl(1)−P(1) 3.163(2), Tl(1)−C(1) 3.075(6), Tl(1)−C(2) 3.091(6), Tl(1)−C(3) 3.098(6), Tl(1)−C(4) 3.071(6), P(1)−Tl(1)#4 3.298(3), C(1)−Tl(1)#4 2.986(6), C(2)−Tl(1)#4 2.972(6), C(3)−Tl(1)#4 3.126(6), C(4)−Tl(1)#4 3.267(6), P(1)#2−Tl(1) 3.673(2), Tl(1)−Tl(1)#3 3.7953(3).

soluble at room temperature even in polar solvents such as THF, but it could be recrystallized from this solvent at 100 °C in a sealed tube (a summary of the X-ray data collection and solution parameters is presented in Table 1).

The polymeric solid state structure of **8** (Figure 1) consists of parallel zigzag strands in which the thallium atoms are η^5-bonded to both sides of the phospholyl ring. This structure is similar to that of $[(TlCp)_n]$[16] as well as that of $[\{Tl(1,4,2\text{-}P_2SbC_2t\text{-}Bu_2)\}_n]$.[17] There are two noticeable interstrand close contacts in **8**. One involves two thallium atoms ($d_{Tl-Tl} = 3.7953(3)$ Å), this distance being intermediate between that found in $[(TlCp)_n]$ (3.94 Å) and that measured in the $[\{Tl[C_5(CH_2Ph)_5]\}_2]$ dimer[18] (3.63 Å), and the other is observed between a thallium atom and a phosphorus atom ($d_{Tl-P} = 3.673(2)$ Å), this one being longer than that observed in $[\{Tl(1,4,2\text{-}P_2SbC_2t\text{-}Bu_2)\}_n]$[17] (3.39 Å) as well as that found in $[\{Tl(C_5H_4PPh_2)\}_n]$[19] (3.58 Å). Although the strength of the Tl(I)−Tl(I) closed shell interaction has been a subject of controversy,[20] it is possible that this interaction together with the P−Tl interstrand contact could contribute to the low solubility of **8**. The other geometrical parameters of **8** are unexceptional.

Synthesis and Crystal Structures of the Samarium Complexes. The P−P (and As−As)-bonded precursors **1**−**4** were reacted with $[Cp^*_2Sm]$ as described by Evans for $[Cp^*_2Sm(EPh_2)]$[9] (E = P, As), and the corresponding complexes $[(Cp^*_2Sm)(C_4Me_4P)]$ (**9**), $[(Cp^*_2Sm)(C_4H_2Me_2P)]$ (**10**), $[(Cp^*_2Sm)(C_4t\text{-}Bu_2H_2P)]$ (**11**), and $[(Cp^*_2Sm)(C_4H_2Me_2As)]$ (**12**) were isolated in moderate to fair yields. We found that $[(Cp^*_2Sm)(Et_2O)]$ could be employed as starting material in the same conditions as $[Cp^*_2Sm]$; the final products did not contain coordinated diethyl ether (Scheme 3).

$[(Cp^*_2Sm)(C_4H_4P)]$ (**13**) was then prepared by a procedure similar to that used by Deacon.[10] Although the reaction of $[Cp^*_2Sm]$ with $[Tl(C_4H_4P)]$ (**8**) gave the expected compound **13**, the reaction was not clean and **13** could not be efficiently purified. The reaction of $[(Cp^*_2Sm)(Et_2O)]$ with **8** gave a much better result, and **13** was obtained in fair yield (Scheme 4).

^{1}H and ^{13}C NMR spectra for all complexes agreed with their expected compositions and are consistent with

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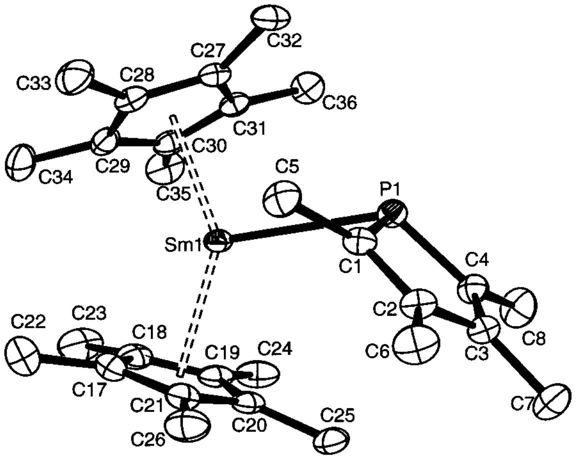
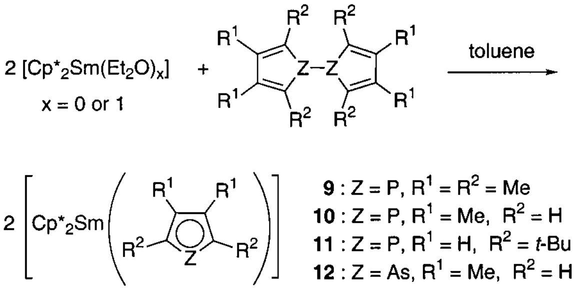
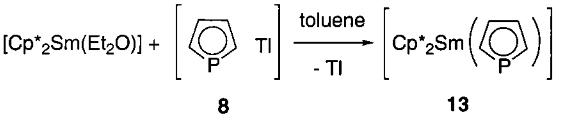


Figure 2. ORTEP plot of **9** (molecule 1) together with the numbering scheme used (50% ellipsoids, hydrogens omitted). Selected interatomic distances (Å) and angles (deg): Sm(1)−P(1) 2.856(1), Sm(1)−C(1) 3.021(4), Sm(1)−C(5) 3.034(4), Sm(2)−P(2) 2.891(1), Sm(2)−C(9) 2.983(4), Sm(2)−C(13) 2.914(4), Sm−C(Cp*) (av.) 2.70(1); C(4)−P(1)−C(1) 91.3(2), C(4)−P(1)−Sm(1) 127.4(1), C(1)−P(1)−Sm(1) 77.4(1), C(12)−P(2)−C(9) 91.2(2), C(12)−P(2)−Sm(2) 131.1(1), C(9)−P(2)−Sm(2) 75.1(1).

Scheme 3



Scheme 4



symmetrical structures (from the equivalence of the Cp* rings and of the α/α′ and β/β′ positions to the heteroatom in the heterocyclopentadienyl ligand). No ^{31}P signals could be measured, except for **11**, which exhibited a very broad signal ($w_{1/2} \approx 2000$ Hz) at ca. −40 ppm.

Complexes **9**−**13** were analyzed by X-ray crystallography (Table 1). As expected, they all have two η^5-coordinated Cp* ligands around samarium. However, their structures are very different, as the substitution scheme is varied on the heterocyclic ligand.

Compound **9** is monomeric; there are two independent molecules (1 and 2) per unit cell, which have similar conformations. Only molecule 1 is represented in Figure 2 for the sake of clarity.

In **9**, the phospholyl ligand is η^1- (σ) bonded to samarium via the phosphorus atom. The P−Sm bonds (2.856(1) and 2.891(1) Å, respectively, for molecules 1 and 2) are relatively short when compared to other Sm(III) complexes.[21] The C−Sm π bonds span a range (2.67−2.73 Å) similar to that found in other seven-coordinated Cp*$_2$Sm(III) complexes such as [Cp*$_2$Sm(OC$_6$Me$_4$H)][22] or [Cp*$_2$Sm(C≡CMe)].[23] Also, the centroid(Cp)*−Sm−centroid(Cp)* angle (136°) has nothing unusual. The most striking feature of **9** is the dissymmetry of the coordination of the C$_4$Me$_4$P ligand to samarium, as indicated by the great difference between the two coordination angles around this metal: Cα−P−Sm (127.4(1)° and 131.1(1)°) and Cα′−P−Sm (77.4(1)° and 75.1(1)°, respectively, for molecules 1 and 2). This is due to close contact interactions of the samarium atom with the Cα atom (2.983(4) and 3.021(4) Å) and the Cα methyl group (2.914(4) and 3.034(4) Å, respectively, for 1 and 2). These interactions are probably due to coordinative unsaturation in complex **9** (coordination number (c.n.) = 7), which causes the samarium metal to become more electrophilic. A similar effect has already been described in other seven-coordinated bis(Cp*) lanthanoid complexes such as [Cp*$_2$LnCH(SiMe$_3$)$_2$] (Ln = Ce,[2a] Nd,[2b] Y[2c]), where an additional interaction exists between the Ln metal and one Me substituent of the silyl group. A similar interaction also exists in [Cp*$_2$Sm(AsPh$_2$)],[9] where the missing electron density is provided by one phenyl ring bond.

Complexes **10** and **12** assume unsymmetrical dimer structures in the solid state. Since they are isomorphous, only the structure of **12** is represented in Figure 3.

Two different coordination modes exist in **10** and **12** for the heterocyclopentadienyl ring: one is coordinated to both samarium atoms in a μ:η^1,η^5- (σ−π) fashion (c.n. = 9), whereas the other is only η^1- (σ) bonded to one samarium (c.n. = 8). The P−Sm σ bond of the nonbridging phospholyl ligand in **10** is similar to that found in **9**, whereas the corresponding As−Sm σ bond in **12** is similar to that in [Cp*$_2$Sm(AsPh$_2$)]. The bonding of the η^1-heterocyclopentadienyl ligand is now completely symmetrical, as indicated by the similar values of the Cα−P−Sm and Cα′−P−Sm angles in **10** (116.8(1)° and 118.8(1)°, respectively) and those of the Cα−As−Sm and Cα′−As−Sm angles in **12** (114.6(1)° and 118.6(1)°, respectively). This is probably because the samarium atom that is bonded to two heteroatoms in **10** and **12** is less electrophilic than in **9** because of its optimum c.n. of 8. The bridging heterocyclopentadienyl group looks rather weakly π-bonded to samarium, as indicated by the long Sm−C distances (2.907(3)−3.059(4) Å for **10** and 2.938(4)−3.116(3) Å for **12**) that are greater than the longest bond distance in the overcrowded [Cp*$_3$Sm][3]. The P−Sm bonds of this ligand are not equal, the σ (donor) bond being the longest (**10**: Sm−P(σ) = 3.1032(8) Å, Sm−P(π) = 3.0132(8) Å; **12**: Sm−As(σ) = 3.1610(6) Å, Sm−As(π) = 3.0671(6) Å); lanthanide−phosphorus donor bonds are generally longer than lanthanide−phosphide bonds.[21] As expected, the nine-coordinated Sm atom displays the smallest centroid(Cp)*−Sm−centroid(Cp)* angle (126°) compared to 136° for the eight-coordinated Sm atom. The C(Cp*)−Sm bond lengths are unexceptional. When the structure of **10** was

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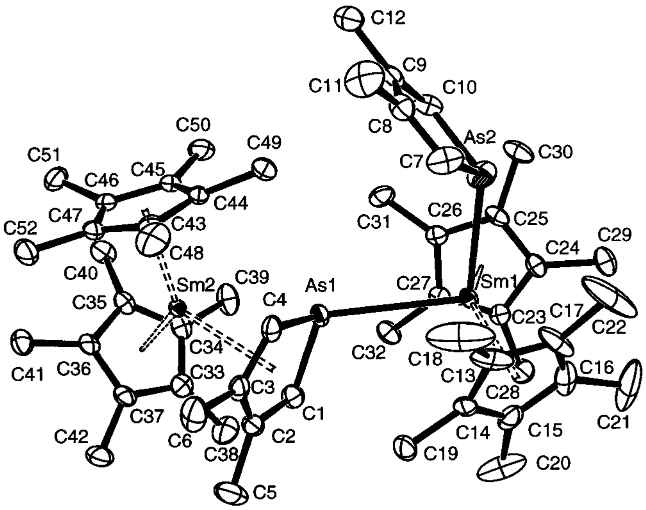

Figure 3. ORTEP plot of dimer **12** together with the numbering scheme used (50% ellipsoids, hydrogens omitted). Selected interatomic distances (Å) and angles (deg) for **12** [respectively, corresponding distances and angles found in **10**]: Sm(2)–C(1) 3.116(3) [Sm(1)–C(1) 3.037(3)], Sm(2)–C(2) 3.114(3) [Sm(1)–C(2) 3.059(4)], Sm(2)–C(3) 2.994(3) [Sm(1)–C(3) 2.960(3)], Sm(2)–C(4) 2.938(3) [Sm(1)–C(4) 2.907(3)], Sm(2)–As(1) 3.0671(6) [Sm(1)–P(1) 3.0132(8)], Sm(1)–As(1) 3.1610(6) [Sm(2)–P(1) 3.1032(8)], Sm(1)–As(2) 2.9776(8) [Sm(2)–P(2) 2.886(1)], Sm(2)–C(Cp*) (av) 2.755(15) [Sm(1)–C(Cp*) (av) 2.750(15)], Sm(1)–C(Cp*) (av) 2.73(1) [Sm(2)–C(Cp*) (av) 2.73(1)]; C(1)–As(1)–C(4) 85.4(1) [C(1)–P(1)–C(4) 88.8(2)], C(1)–As(1)–Sm(2) 73.5(1) [C(1)–P(1)–Sm(1) 73.8(1)], C(4)–As(1)–Sm(2) 67.9(1) [C(4)–P(1)–Sm(1) 69.3(1)], C(1)–As(1)–Sm(1) 114.6(1) [C(1)–P(1)–Sm(2) 116.8(1)], C(4)–As(1)–Sm(1) 118.6(1) [C(4)–P(1)–Sm(2) 118.8(1)], C(7)–As(2)–C(10) 85.3(1) [C(7)–P(2)–C(10) 89.7(2)], C(7)–As(2)–Sm(1) 121.3(1) [C(7)–P(2)–Sm(2) 122.9(1)], C(10)–As(2)–Sm(1) 120.1(1) [C(10)–P(2)–Sm(2) 124.2(1)].

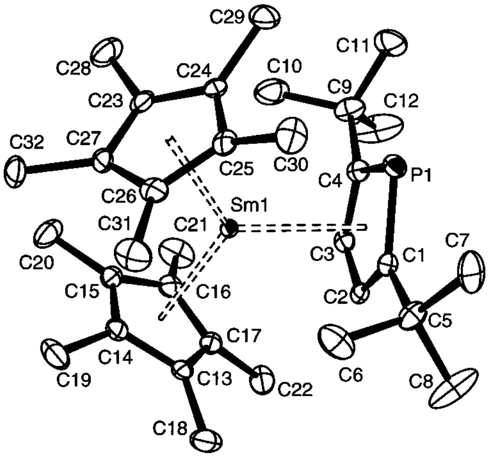

Figure 4. ORTEP plot of one molecule of **11** together with the numbering scheme used (50% ellipsoids, hydrogens omitted). Selected interatomic distances (Å) and angles (deg): Sm(1)–P(1) 3.153(1), Sm(1)–C(1) 2.913(3), Sm(1)–C(2) 2.762(3), Sm(1)–C(3) 2.758(3), Sm(1)–C(4) 2.917(3), Sm(1)–C(Cp*) (av) 2.85(2); C(1)–P(1)–C(4) 91.2(2), C(1)–P(1)–Sm(1) 65.8(1), C(4)–P(1)–Sm(1) 65.9(1).

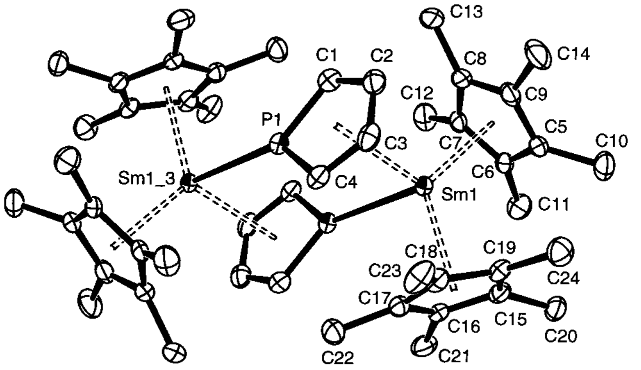

Figure 5. ORTEP plot of dimer **13** together with the numbering scheme used (50% ellipsoids, hydrogens omitted). Selected interatomic distances (Å) and angles (deg): Sm(1)–P(1) 3.274(1), Sm(1)–C(1) 3.095(4), Sm(1)–C(2) 2.884(4), Sm(1)–C(3) 2.772(4), Sm(1)–C(4) 2.893(3), P(1)–Sm(1)#3 3.101(2), Sm(1)–C(Cp*) (av) 2.814(6); C(1)–P(1)–C(4) 91.0(2), C(1)–P(1)–Sm(1) 68.5(1), C(4)–P(1)–Sm(1) 61.9(1), C(1)–P(1)–Sm(1)#3 129.4(2), C(4)–P(1)–Sm(1)#3 138.0(1).

compared to that of **12**, the replacement of phosphorus by arsenic has not altered the structure of this unusual dimer.

In **11**, all ligands are η^5-bonded to the samarium atom (Figure 4).

It seemed interesting to compare the steric crowding around Sm in **11** with those of [Cp*$_3$Sm][3] and [Cp*$_2$Sm(Cp)].[24] In **11**, [Cp*$_3$Sm], and [Cp*$_2$Sm(Cp)], the C(Cp*)–Sm bond lengths span ranges of 2.78–2.91 Å; 2.76–2.90 Å; and 2.73–2.81 Å, respectively. An additional indication of steric congestion around Sm is provided by the centroid(Cp)*–Sm– centroid(Cp)* angle, which is equal to 124° for **11**, 120° for [Cp*$_3$Sm], and 127° for [Cp*$_2$Sm(Cp)]. It can be seen that the steric crowding in **11** is intermediate between [Cp*$_3$Sm] and [Cp*$_2$Sm(Cp)], although in **11**, the C(Cp)*–Sm bonds show an elongation similar to that present in [Cp*$_3$Sm]. Steric crowding in **11** is also evidenced by the two long C–Sm bonds in the phospholyl ring (2.913(3) and 2.917(3) Å) and the long P–Sm bond (3.153(1) Å).

13 has a dimeric structure, in which the unsubstituted phospholyl ligands are σ–π-bonded to the two samarium atoms (Figure 5).

The overall structure of **13** is related to that of dimeric 10-coordinated [(C$_4$H$_2$Me$_2$P)$_6$Sm$_2$],[7] in which two C$_4$H$_2$Me$_2$P ligands are σ–π-bonded to Sm. There is one long C–Sm distance in the phospholyl ligand (3.095(4) Å), and, unlike in **10**, it is the P–Sm π bond (3.274(1) Å) that is much longer than the P–Sm σ bond (3.095(4) Å) in the σ–π phospholyl ligand. The centroid(Cp)*–Sm–centroid(Cp)* angle (123°) is also rather small.

Conclusion

We have prepared a series of [(Cp*)$_2$(phospholyl)] and [(Cp*)$_2$(arsolyl)] complexes with the new 3,4-dimethylarsolyl ligand. An alteration of the substitution pattern in the heterocyclic ring can dramatically change the solid state structure of the complexes. This study also stresses the difference between the phospholyl (and arsolyl) ligands and the cyclopentadienyl ligands: in the heterocyclopentadienyl group, there is more electron density at the heteroatom, and thus this atom is the preferred site of interaction with the electrophilic Sm. However, since σ-complexation with the metal just fills

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one coordination site, additional electron density from the ligand may interact with the metal in order to decrease the coordinative unsaturation. In **9**, this electron density comes from a C−C bond of the ligand, rather than from its π-bond system. Although tris-η^5-coordination in **9** should be possible on steric grounds, the actual structure of **9** is less sterically demanding and thus the compromise between electronic and steric factors is better. In **11**, because of the bulky *tert*-butyl substituents α to phosphorus, the sterically available electron density comes from the π bonds in the phospholyl ligand, and thus tris-η^5-coordination is observed. In **13**, both the phosphorus atom lone pair and the π-system of the ligand can be coordinated to the metal because of the small steric bulk of the unsubstituted phospholyl ligand. Stuctures **10** and **12** are more puzzling. Apparently, the two additional methyl groups do not sterically prevent π-complexation of one heterocyclopentadienyl group to one Cp*$_2$Sm residue, and the absence of substituents in the α-position causes the lone pair to be available for further complexation with a second Cp*$_2$Sm moiety; but after complexation with the heteroatom lone pair, the second Sm atom achieves the optimum c.n. of 8 by accommodating a σ-phospholyl ligand and thus does not need additional electron density. However, the dissymmetry in the structures of **9**, **10**, and **12** is broken up in solution, as implied by their NMR spectra.

Future developments of this research may include the study of the coordination of the ligands used with smaller lanthanides, especially the synthesis of analogues of **11**, which may display the sterically induced reductive chemistry developed by Evans.[25]

Experimental Section

General Procedures. All reactions were performed under inert atmosphere with dry, deoxygenated solvents by using vacuum line and drybox techniques. The following compounds were prepared according to known procedures: Cp*$_2$Sm(Et$_2$O),[26] 1-phenylphosphole,[27] 2,3,4,5,2′,3′,4′,5′-octamethylbi-1,1′-phospholyl,[11] 3,4,3′,4′-tetramethylbi-1,1′-phospholyl,[12] 2,5,2′,5′-tetra*tert*-butylbi-1,1′-phospholyl,[13] 1-chloro-2,5-di(trimethylsilyl)-3,4-dimethylarsole[14]; Cp*$_2$Sm was prepared from Cp*$_2$Sm(Et$_2$O) by desolvation and sublimation at 120 °C under vacuum (10^{-2} Torr).[28] All other reagents were commercial and used as received. NMR spectra were measured with Bruker instruments operating at 4.68, 7.02, or 9.36 T. Mass spectra were measured at 70 eV on a Hewlett-Packard spectrometer. Elemental analyses were performed by the Service Central d'Analyses du CNRS at Vernaison, France (for compounds **4**, **6**, **7**) and at the Service de Microanalyse de l'Université de Dijon, Dijon, France (for compounds **8**, **10**, **11**, **13**); despite several attempts, no meaningful analyses were obtained for compounds **9** and **12**.

2,5-Di(trimethylsilyl)-1,3,4-trimethylarsole, 6. To a cold (0 °C) solution of 1-chloro-2,5-di(trimethylsilyl)-3,4-dimethylarsole (6.69 g, 20 mmol) in Et$_2$O (50 mL) was added dropwise MeLi in Et$_2$O (14.5 mL of a 1.4 M solution, 20.3 mmol). After 1 h at room temperature, the reaction mixture was evaporated to dryness and the residue purified by column chromatography using hexane as eluent. 2,5-Di(trimethylsilyl)-1,3,4-trimethylarsole was obtained as a colorless oil (5.54 g, 17.6 mmol, 88%). ^{1}H NMR (CDCl$_3$): δ 0.21 (s, 18H,), 1.16 (s, 3H, CH_3-As), 2.10 (s, 6H, CH_3-C). ^{13}C NMR (CDCl$_3$): δ 0.73 (CH$_3$-Si), 8.75 (CH$_3$-As), 19.97 (CH$_3$-C), 153.50 (C2/5 or C3/4), 158.05 (C3/4 or C2/5). MS: *m*/*z* 314 (M$^+$, 18), 226 (100). Anal. Calcd for $C_{13}H_{27}AsSi_2$: C, 49.66; H, 8.65. Found: C, 49.80; H, 8.85.

1,3,4-Trimethylarsole, 7. To a solution of 2,5-di(trimethylsilyl)-1,3,4-trimethylarsole (3.14 g, 10 mmol) in acetonitrile (40 mL) was added tetrabutylammonium fluoride trihydrate (10 g, 31 mmol), and the reaction mixture was refluxed for 2 h, after which the reaction was finished as estimated by TLC monitoring. The dark red reaction mixture was then cooled to room temperature and partitioned into 200 mL of a 1:1 mixure of water and *n*-hexane. The hexane phase was dried with magnesium sulfate and evaporated to dryness, and the residue was purified by column chromatography using hexane as eluent. 1,3,4-Trimethylarsole was obtained as a colorless oil (0.98 g, 5.8 mmol, 58%). An analytical sample was short-path distilled at 80−90 °C/10 Torr. ^{1}H NMR (CDCl$_3$): δ 1.13 (s, 3H, CH_3-As), 2.03 (d, 6H, $J = 1$, CH_3-C), 6.63 (q, 2H, $J = 1$, CH). ^{13}C NMR (CDCl$_3$): δ 7.24 (CH$_3$-As), 19.04 (CH$_3$-C), 135.76 (C2 and C5), 149.68 (C3 and C4). MS: *m*/*z* 170 (M$^+$, 18), 91 (100). Anal. Calcd for $C_7H_{11}As$: C, 49.43; H, 6.52. Found: C, 49.42; H, 6.61.

3,4,3′,4′-Tetramethylbi-1,1′-arsolyl, 4. To a solution of 1,3,4-trimethylarsole (0.68 g, 4 mmol) in THF (10 mL) was added lithium metal (70 mg, 10 mmol), and the reaction mixture was stirred at room temperature for 2.5 h. Excess metal was removed from the solution, which was evaporated to dryness in a vacuum. The red residue was then stirred with 20 mL of a 1:1 mixture of toluene and diethyl ether, whereupon the reaction mixture became greenish-yellow and a precipitate appeared. The reaction mixture was then evaporated to dryness and the residue taken up in pentane (20 mL). The solution was allowed to settle and was decanted from a white precipitate, which was washed by decantation with two additional 20 mL portions of pentane and dried in a vacuum. This precipitate was dissolved in THF (20 mL), and solid PbCl$_2$ (1.2 g, 4.3 mmol) was added to the solution. The reaction mixture became immediately dark red, and the color faded to pale yellowish-green within 5 mn, while precipitation of lead metal was apparent. The reaction was then evaporated to dryness, and the residue extracted with pentane and filtered. The filtrate was evaporated to dryness, whereupon 3,4,3′,4′-tetramethylbi-1,1′-arsolyl precipitated as a pale yellow powder (0.46 g, 1.48 mmol, 74%), which was recrystallyzed in pentane. ^{1}H NMR (THF-d_8): δ 2.07 (s, 12H, CH_3-C), 6.73 (s, 4H, CH). ^{13}C NMR (THF-d_8): δ 19.04 (CH$_3$-C), 135.02 (C2 and C5), 151.69 (C3 and C4). MS: *m*/*z* 310 (M$^+$, 6), 190 (100). Anal. Calcd for $C_{12}H_{16}As_2$: C, 46.48; H, 5.20. Found: C, 46.38; H, 5.30.

Thallium Phospholide, 8. To a solution of 1-phenylphosphole (1.60 g, 10 mmol) in THF (20 mL) was added lithium metal (210 mg, 30 mmol). After 1 h at room temperature, excess lithium was removed from the dark purple-brown solution and 2-chloro-2-methylpropane (3 mL, 27 mmol) was added to the reaction mixture, which was then refluxed for 15 mn. The reaction mixture was allowed to cool to room temperature and chilled to 0 °C. Thallous ethoxide (2.5 g, 10 mmol) was then added, whereupon a yellow precipitate appeared. Water (60 mL) was then added, the reaction mixture was then filtered (in air), and the precipitate rinsed with acetone (20 mL) and dried in a vacuum. The yellow solid was transferred to a sublimation apparatus and sublimed at 80 °C/0.1 Torr. Thallium phospholide (1.77 g, 6.1 mmol, 61%) was obtained as an air-stable bright yellow crystalline powder.

^{1}H NMR (THF-d_8): (AA′BB′X spin system) δ 6.68 (m, 2H, H1, H1′, $J_{H1H1'} = 2.5$, $J_{H1H2} = 5.5$, $J_{H1H2'} = 1.4$, $J_{H1P} = 40$), 7.28 (m, 2H, H2, H2′, $J_{H2H2'} = 3.4$, $J_{H2H1} = 5.5$, $J_{H2H1'} = 1.4$, $J_{H2P} = 6.7$). ^{31}P NMR: 80.5. MS (^{205}Tl isotope): *m*/*z* 288 (M$^+$,

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26), 205 (100). Anal. Calcd for C_4H_4PTl: C, 16.71; H, 1.40. Found: C, 17.04; H, 1.48.

General Procedure for the Synthesis of the Bis(pentamethylcyclopentadienyl)phospholyl and Arsolyl Samarium Complexes. To a solution of Cp*$_2$Sm or Cp*$_2$Sm(Et$_2$O) in toluene (10 mL) at room temperature was added the biphospholyl or biarsolyl. The reaction mixture immediately turned dark reddish-brown. After 15 min of stirring at room temperature, the reaction mixture was evaporated to dryness and extracted in pentane. The resulting solution was concentrated, cooled at −20 °C, and filtered to afford the bis(pentamethylcyclopentadienyl)phospholyl and arsolyl samarium complexes as reddish-brown powders.

Bis(pentamethylcyclopentadienyl)(2,3,4,5-tetramethylphospholyl)samarium, 9. 9 was obtained from Cp*$_2$Sm(Et$_2$O) (495 mg, 1 mmol) and 2,3,4,5,2′,3′,4′,5′-tetramethylbi-1,1′-phospholyl (140 mg; 0.5 mmol) according to the general procedure (192 mg, 0.34 mmol, 34%). ^{1}H NMR (C$_6$D$_6$): δ −8.83 (s, 6H, C*H*$_3$-C(phospholyl)), 0.21 (s, 30H, C*H*$_3$-Cp*), 1.97 (s, 6H, C*H*$_3$-C(phospholyl)). ^{13}C NMR (C$_6$D$_6$): δ 7.42 (*C*H$_3$-(phospholyl)), 17.15 (*C*H$_3$-(phospholyl)), 21.01 (*C*H$_3$-Cp*), 120.72 (CH$_3$-*C*(Cp*)), 120.72 (*C*). One of the phospholyl carbons was not observed and is presumably obscured by the solvent.

Bis(pentamethylcyclopentadienyl)(3,4-dimethylphospholyl)samarium, 10. From Cp*$_2$Sm(Et$_2$O) (495 mg, 1 mmol) and 3,4,3′,4′-tetramethylbi-1,1′-phospholyl (110 mg; 0.5 mmol) according to the general procedure (320 mg, 0.60 mmol, 60%). ^{1}H NMR (C$_6$D$_6$): δ −0.39 (s, 6H, C*H*$_3$-C3/4) 0.15 (s, 30H, C*H*$_3$-Cp*) 10.85 (s, 2H). ^{13}C NMR (C$_6$D$_6$): δ 19.48 (*C*H$_3$-C3/4), 22.00 (*C*H$_3$-Cp*), 119.64 (CH$_3$-*C*(Cp*)), 126.18 (*C*), 137.43 (*C*H). Anal. Calcd for $C_{26}H_{38}PSm$: C, 58.71; H, 7.20. Found: C, 59.02; H, 7.36.

Bis(pentamethylcyclopentadienyl)(2,5-di-*tert*-butylphospholyl)samarium, 11. From Cp*$_2$Sm (420 mg, 1 mmol) and 2,5,2′,5′-tetra-*tert*-butylbi-1,1′-phospholyl (195 mg; 0.5 mmol) according to the general procedure (440 mg, 0.71 mmol, 71%). ^{1}H NMR (C$_6$D$_6$): δ −5.11 (s, 18H, C*H*$_3$(*t*-Bu)), −0.85 (s, 30H, C*H*$_3$-Cp*), 16.92 (s, 2H, C*H*(phospholyl)). ^{13}C NMR (C$_6$D$_6$): δ 28.16 (*C*H$_3$), 28.63 (*C*H$_3$), 37.05 (*C*(*t*-Bu)), 117.10 (CH$_3$-*C*(Cp*)), 117.64 (*C*H), 164.23 (C). Anal. Calcd for $C_{26}H_{38}PSm$: C, 62.39; H, 8.18. Found: C, 61.88; H, 8.02.

Bis(pentamethylcyclopentadienyl)(3,4-dimethylarsolyl)samarium, 12. 12 was obtained from Cp*$_2$Sm (420 mg, 1 mmol) and 3,4,3′,4′-tetramethylbi-1,1′-arsolyl (155 mg; 0.5 mmol) according to the general procedure (263 mg, 0.46 mmol, 46%). ^{1}H NMR (C$_6$D$_6$): δ −0.35 (s, 6H, C*H*$_3$-C3/4) 0.17 (s, 30H, C*H*$_3$-Cp*) 11.43 (s, 2H). ^{13}C NMR (C$_6$D$_6$): δ 20.78 (*C*H$_3$-C3/4), 21.29 (*C*H$_3$-Cp*), 119.57 (CH$_3$-*C*(Cp*)), 137.43 (*C*H), 141.49 (*C*).

Bis(pentamethylcyclopentadienyl)(phospholyl)samarium, 13. To a solution of Cp*$_2$Sm(Et$_2$O) (495 mg, 1 mmol) in toluene (10 mL) was added thallium phospholide (287 mg, 1 mmol). The reaction mixture progressively turned dark red, while precipitation of thallium metal was evident. The reaction mixture was stirred 15 mn and filtered and the filtrate evaporated to dryness, whereupon dark red crystals of bis(pentamethylcyclopentadienyl)(phospholyl)samarium precipitated. The precipitate was rinsed with cold pentane and dried under vacuum (280 mg, 0.56 mmol, 56%). ^{1}H NMR (C$_6$D$_6$): δ 0.81 (s, 30H, C*H*$_3$-Cp*), 8.97 (s, 2H), 18.78 (s, 2H). ^{13}C NMR (C$_6$D$_6$): δ 26.71 (*C*H$_3$-Cp*), 115.63 (CH$_3$-*C*(Cp*)) 123.26 (*C*H), 134.31 (*C*H). Anal. Calcd for $C_{24}H_{34}PSm$: C, 57.21; H, 6.80. Found: C, 58.45; H, 7.21.

X-ray Experimental Section. The following crystallization conditions were used: **8**, from hot THF (see text); **9**, from pentane at −30 °C; **10** and **12**, from toluene at −30 °C; **11**, from heptane at room temperature; **13**, from toluene at room temperature. X-ray intensities were measured with a Nonius KappaCCD diffractometer at 150(1) K using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. A summary of the crystal structure determinations is presented in Table 1. All structures were solved by direct methods using SIR97 and refined using SHELXL97. All atoms except hydrogens were refined anisotropically on F^2 using all data. A mixed model was used for the refinement of the hydrogen atoms. No absorption corrections were necessary.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacements, and hydrogen coordinates for compounds **8**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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