Trispirocyclic Bis(dimethylaluminum)bis(amido)cyclodiphosph(V)azanes

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The synthesis of the 2,4-bis(amino)cyclodiphosph(V)azane *cis*-[^{t}Bu(H)N(O=PN^{t}Bu)$_2$N(H)^{t}Bu] (**3**) and the syntheses and solid-state structures of *cis*-[Ph(H)N(E=PN^{t}Bu)$_2$N(H)Ph] (E = S (**6**), Se (**7**)) are reported. When **6** was treated with ^{n}BuLi, the dilithio salt {[(2THF·LiPhN)(S=PN^{t}Bu)$_2$(NPhLi·2THF)]·THF} (**10**) was isolated. The reactions of *cis*-[^{t}Bu(H)N(E=PN^{t}Bu)$_2$N(H)^{t}Bu (E = O (**3**), S (**4**), Se (**5**)) and *cis*-[R(H)N(Ar=PN^{t}Bu)$_2$N(H)R] (R = ^{t}Bu, Ar = Ph (**8**), Ar = *p*-Tol (**9**)) with 2 equiv of trimethylaluminum afforded the bis(dimethylaluminum) complexes {(Me$_2$Al)[RN(E=PN^{t}Bu)$_2$NR](AlMe$_2$)} (R = ^{t}Bu, E = O (**11**), E = S (**12**), E = Se (**13**); R = Ph, E = S (**14**), Se (**15**), and R = ^{t}Bu, E = N-*p*-Tol (**16**), E = N−Ph (**17**)). Compounds **11**, **12**, and **16** were characterized by single-crystal X-ray studies and shown to be trispirocyclic complexes in which the ligands coordinate both dimethylaluminum moieties in an η^2-fashion, as dimeric aminophosphoranates.

Introduction

Homoleptic and heteroleptic aluminumalkyls are important industrial chemicals. Triethylaluminum, for example, is an activator in the Z−N polymerization of olefins,[1] while methylaluminoxane (MAO) is used as a cocatalyst for the homogeneous polymerization of olefins.[2] In the past alkylaluminum reagents had been relegated to a role of cocatalysts, because in the absence of additional reagents they merely oligomerize ethylene.[3] Recently, however, it was shown that cationic aluminum compounds,[4] particularly aluminum amidinates and -guanidinates,[5] can produce high molecular weight polyethylene.

We are investigating *cis*-[^{t}Bu(H)N(^{t}BuNP)$_2$N(H)^{t}Bu] (**1**) and *cis*-[Ph(H)N(^{t}BuNP)$_2$N(H)Ph] (**2**)[6] (Chart 1) as chelating bis(amido) ligands for homogeneous polyolefin catalysts.[7] Their phosphorus lone-pair electrons make these ligands too Lewis-basic, resulting in ring opening and subsequent catalyst deactivation.[8] Bis(1°-amino)cyclodiphosph(V)azanes (e.g., **9**), the oxidation products of **1** and **2**, lack phosphorus lone-pair electrons and are less susceptible to the destructive cycloreversion of the ligands. These phosphorus(V) species, however, no longer coordinate metals as bis(amido) ligands, but side-on, as aminophosphoranates (e.g., **A**).[9]

Chart 1

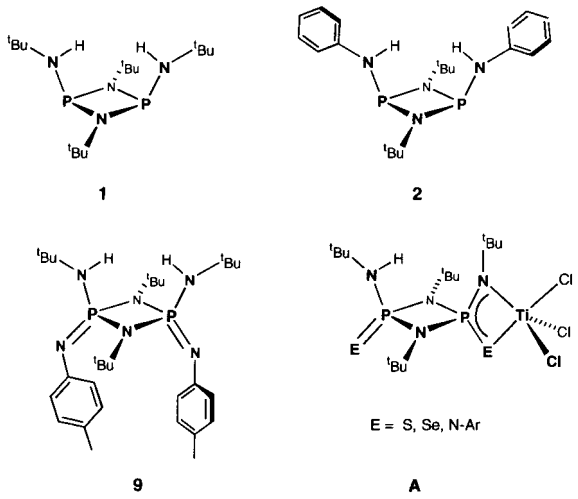

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Table 1. Crystal Data for 6, 7, 11, 12, and 16

	6	7	11	12	16
formula	$C_{20}H_{30}N_4P_2S_2$	$C_{20}H_{30}N_4P_2Se_2$	$C_{20}H_{48}Al_2N_4P_2O_2$	$C_{20}H_{48}Al_2N_4P_2S_2$	$C_{34}H_{62}Al_2N_6P_2$
fw	452.54	546.34	492.51	524.64	670.80
space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	*C*2/*c* (no. 15)	*Pbcn* (no. 60)	$P\bar{1}$ (no. 2)
T, K	298	213	293	213	213
a, Å	15.5166(15)	20.772(1)	18.560(2)	10.1296(5)	10.052(7)
b, Å	17.1999(16)	14.1984(8)	7.9179(7)	15.5105(7)	13.187(8)
c, Å	18.1167(17)	17.2051(9)	20.518(2)	19.7311(9)	15.711(5)
α, deg					89.074(2)
β, deg		107.402(1)	99.57(1)		81.087(8)
γ, deg					76.752(4)
V, Å^3	4835.1(8)	4842.0(4)	2973.2(6)	3100.1(3)	2002(2)
Z	8	8	4	4	2
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ(calc), g cm^{-3}	1.243	1.499	1.100	1.124	1.113
μ, mm^{-1}	0.366	3.200	0.226	0.346	0.182
$R(F)^a$ [$I > 2\sigma(I)$]	0.0444	0.0416	0.0394	0.0780	0.0516
$wR2(F^2)^b$ [all data]	0.1213	0.1005	0.1179	0.2357	0.1617

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$.

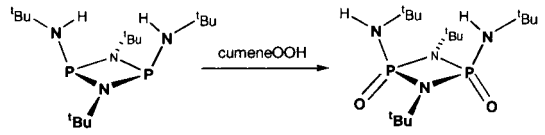
Aminophosphoranes,[10] especially aminoiminophosphoranes, are structurally similar to amidines[11] and guanidines,[12] and this caused us to investigate the suitability of these P(V) molecules as ancillary ligands for alkylaluminum catalysts.

Below we report the syntheses and structural characterizations of novel 2,4-dichalcogeno- and 2,4-bis(arylimino)-substituted bis(1°-amino)cyclodiphosph(V)azanes and their dimethylaluminum complexes.

Results and Discussion

Despite the ubiquity of cyclodiphoph(V)azanes, bis(1°-amino)-substituted versions of these heterocycles are scarce. Norman et al. had shown that the oxidation of *cis*-[^{t}Bu(H)N(PN^{t}Bu)$_2$N(H)^{t}Bu] with sulfur is stereospecific, furnishing exclusively *cis*-[^{t}Bu(H)N(S=PN^{t}Bu)$_2$N(H)^{t}Bu] (**4**).[13] More recently the diselenium analogue **5** was reported.[14] With *cis*-[^{t}Bu(H)N(O=PN^{t}Bu)$_2$N(H)^{t}Bu] (**3**) (Scheme 1) and *cis*-[Ph(H)N(E=PN^{t}Bu)$_2$N(H)Ph] (E = S (**6**), Se (**7**)) (Scheme 2) we have now synthesized three new 2,4-dichalcogen-substituted bis(1°-amino)-cyclodiphosph(V)azanes.

Scheme 1



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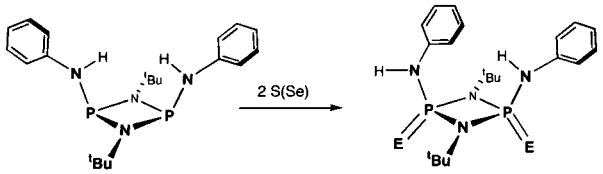
Scheme 2



2 E = S (**6**), Se (**7**)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6 and 7^a

	6	7
P(1)−N(1)	1.687(2)	1.689(2)
P(1)−N(2)	1.691(2)	1.687(3)
P(2)−N(1)	1.681(2)	1.693(2)
P(2)−N(2)	1.683(2)	1.685(2)
P(1)−N(3)	1.644(2)	1.652(2)
P(2)−N(4)	1.651(3)	1.655(3)
P(1)−S(1)Se(1)	1.9216(11)	2.0826(8)
P(2)−S(2)Se(2)	1.9264(9)	2.0815(8)
N(1)−P(2)−N(2)	83.39(11)	83.40(11)
P(1)−N(1)−P(2)	83.80(11)	83.37(11)
N(1)−P(1)−N(2)	96.10(12)	96.45(12)
P(1)−N(2)−P(2)	95.87(12)	96.08(12)

^{a} The values for **7** are the averaged metric parameters for the two independent molecules.

X-ray structural data on **3** and **5** are not available, but it may be assumed, based on the structures of their metal complexes (vide infra), that both have *cis*-configurations. The *cis* geometry of the bis(anilino)-cyclodiphosph(V)azanes **6** and **7**, whose crystal data and selected bond parameters are summarized in Tables 1 and 2, respectively, however, was unambiguously established by single-crystal X-ray studies. These compounds crystallize in orthorhombic and monoclinic systems, respectively, the latter with two independent molecules in the unit cell. All three molecules, however, have almost identical conformations.

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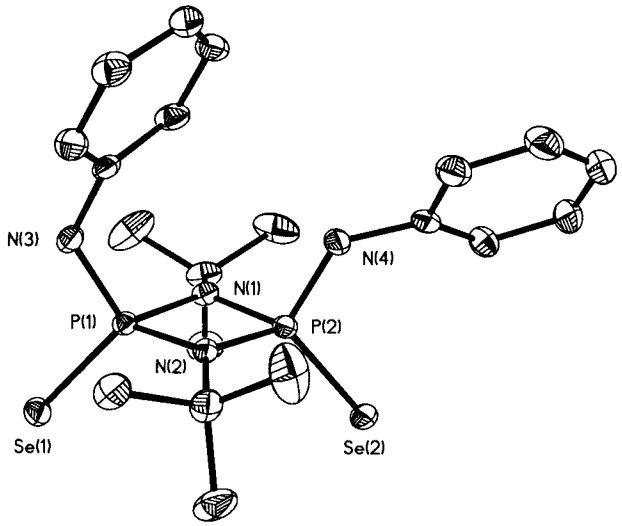


Figure 1. Solid-state structure of one of the independent molecules of **7**. The second molecule of **7** and the unique molecule of **6** have almost identical conformations to the one shown.

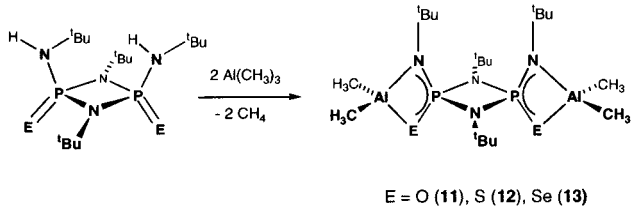
The thermal ellipsoid plot of **7** (Figure 1) shows that, like **2**, it has a *cis* configuration. In contrast to the slightly puckered cyclodiphosphazane moiety in **2**, the $(P-N)_2$ rings of these P(V) species are planar, the sums of the internal angles being 358.4° and 359.2°, respectively. The peculiar exo/endo orientation of the amino groups of **6** and **7** must be due to the chalcogen atoms, rather than the amino-nitrogen substituents, because it is found in 2,4-dichalcogenocyclodiphosph(V)azanes only.

A direct comparison of the bond parameters of **6** and **7** is given in Table 2. Only the P═S and P═Se bonds, which are unremarkable and similar to those in related compounds,[15] have significantly different lengths. Both the endocyclic and the exocyclic P−N bonds are ca. 0.04−0.05 Å shorter than those in **2**, while the endocyclic N−P−N angles are about 4° larger. This increase in bond angles with simultaneous bond shortening is caused by the removal of the sterically demanding lone-pair electrons and the greater inductive effect of the P(V) atoms.

While chalcogen oxidations are the most obvious and easiest P(III) to P(V) transformations, 2,4-bis(chalcogeno)cyclodiphosph(V)azanes suffer from at least two problems. Their monatomic substituents do not allow catalyst-tuning, and their odor compromises applications in polyolefin catalysis, because much polyethylene is used for food packaging.[16]

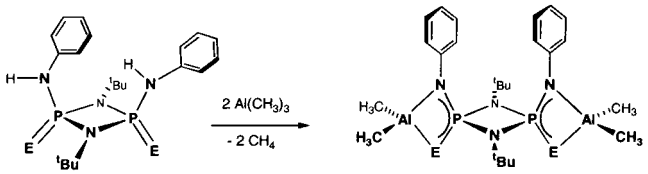
Aryl azides are more desirable oxidants, since they furnish ligands whose aromatic rings can be substituted with a variety of functional groups for improved catalyst activity and polymer microstructure. By treating *cis*-[^{t}Bu(H)N(PN^tBu)$_2$N(H)^{t}Bu] with *p*-tolyl and phenyl azides, we had previously obtained *cis*-[^{t}Bu(H)N(ArN═PN^tBu)$_2$N(H)^{t}Bu] (Ar = phenyl (**8**), *p*-tolyl (**9**)) and used them successfully as ligands for monotitanium complexes.[9]

Scheme 3



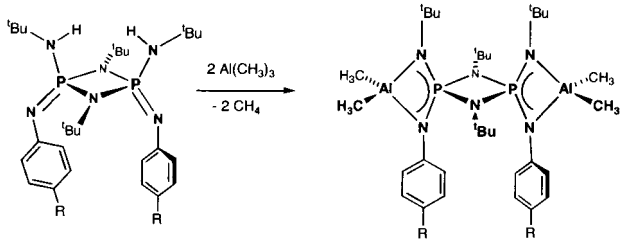
E = O (**11**), S (**12**), Se (**13**)

Scheme 4



E = S (**6**), Se (**7**) E = S (**14**), Se (**15**)

Scheme 5



R = CH_3 (**16**), R = H (**17**)

Bis(1°-amino)cyclodiphosph(V)azanes are much more acidic than their phosphorus(III) counterparts and react readily with a variety of metal alkyls. Treatment of **6** with ^{n}BuLi, for example, produced the dilithio salt {[(2THF·LiPhN)(S═PN^tBu)$_2$(NPhLi·2THF)]·THF} (**10**). A conclusive structure assignment—both a heterocube and a trispirocycle were consistent with the data—was not possible. A recent X-ray structural characterization of the *tert*-butyl analogue of **10**, viz., {[(2THF·Li^{t}BuN)-(S═PN^tBu)$_2$(N^{t}BuLi·2THF)]·THF}, by Chivers et al. showed it to be a trispirocycle,[17] however, suggesting that **10** also has a trispirocyclic structure.

Because of the role of aluminum alkyls in polyolefin catalysis, we were particularly interested in synthesizing dimethylaluminum complexes of these ligands. In contrast to titanium tetrachloride, which produced only mononuclear complexes (**A**),[9] 2 equiv of trimethylaluminum reacted with **3**−**9** (Schemes 3−5) to afford air-sensitive colorless, crystalline solids. The very simple NMR spectra (^{1}H, ^{13}C, ^{31}P) of these compounds (**11**−**17**) were consistent with symmetrically substituted bimetallic species. A spectroscopic feature common to their ^{31}P NMR spectra is the upfield shift of the lone ligand signal. Of these products, three (**11**, **12**, and **16**) were subjected to single-crystal diffraction studies.

Crystal data and refinement parameters for these bis(dimethylaluminum) complexes are collected in Table

(15) Keat, R.; Muir, K. W.; Thompson, D. G. *Tetrahedron Lett.* **1977**, 3087. (b) Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1980**, 928. (c) Keat, R.; Keith, A. N.; Macphee, A.; Muir, K. W.; Thompson, D. G. *J. Chem. Soc., Chem. Commun.* **1978**, 372. (f) Bulloch, G.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1974**, 2010.

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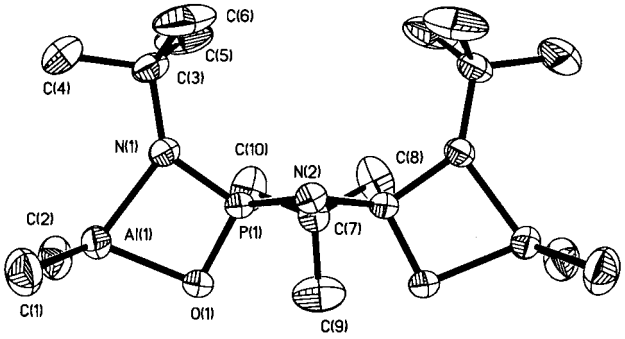

Figure 2. Solid-state structure of the dialuminum complex **11**. Hydrogen atoms and the proximal *tert*-butyl group of the phosph(V)azane ring have been omitted to enhance clarity.

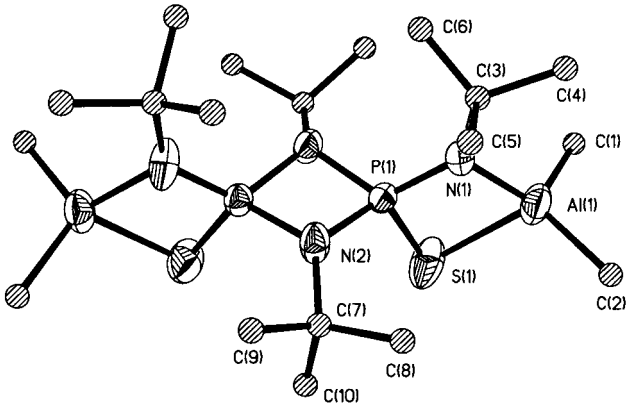

Figure 3. Solid-state structure and partial labeling scheme of **12**. To enhance clarity, the carbon atoms are drawn as isotropic spheres and the hydrogen atoms have been omitted.

1. The 2,4-dichalcogeno compounds **11** and **12** crystallize as molecular solids in space groups *C*2/*c* and *Pbcn*, respectively, the isolated molecules residing on 2-fold rotation axes that are perpendicular to the central $(P-N)_2$ ring. Thermal ellipsoid plots of **11** and **12** appear in Figures 2 and 3, respectively. These trispirocyclic molecules consist of a central $(P-N)_2$ rhombus, which is flanked by two distorted, kite-shaped (E−P−N−Al) heterocycles. The symmetrical P−N heterocycles of these dichalcogeno complexes are highly puckered along both the P···P and the N···N vectors and have short P···P contacts of 2.47 and 2.50 Å, respectively.

Despite their obvious structural similarities, the complexes differ in the disposition of the dimethylaluminum groups. Due to its much shorter P═E bonds (P−O = 1.5924(13) Å vs P−S = 2.0019(16) Å), the $AlMe_2$ moieties of **11** are tipped downward and lie below the $(P-N)_2$ plane, while those of **12** are almost parallel to the ring. The aluminum atoms are tetrahedrally coordinated by the chelating ligand and both methyl groups, the latter substituents having identical bond lengths of 1.946(3)−1.956(5) Å and enclosing angles of 116.61(13)° (**11**) and 117.1(3)° (**12**), respectively. The aluminum−methyl bonds are shorter than the terminal bonds of Al_2Me_6 (1.96−1.98 Å),[18] but comparable to the Al−Me bonds in amidinate complexes.[5c] The comparatively short aluminum bonds to nitrogen (1.939(2) and 1.919(4) Å) and to oxygen (1.884(2) Å) and the comparatively long aluminum−sulfur bond (2.354(2) Å) can be rationalized in terms of hard−soft acid−base principles. They are almost identical to those in related complexes with N, O[19] and N, S ligands.[20]

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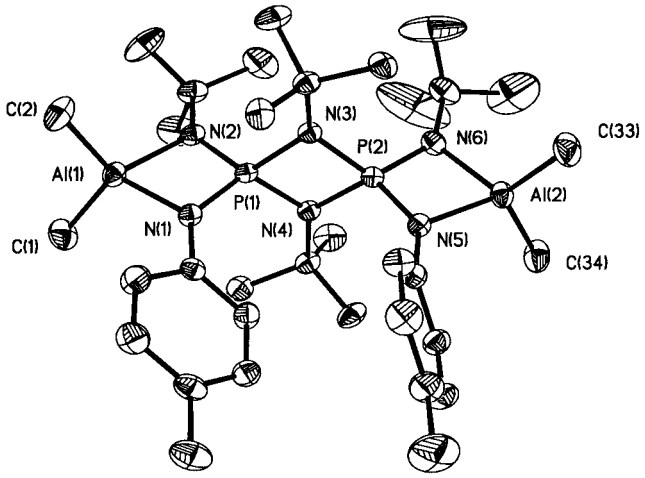

Figure 4. Solid-state structure and partial labeling scheme of **16**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 11 and 12

	11	**12**
Al(1)−C(1)	1.953(3)	1.953(6)
Al(1)−C(2)	1.946(3)	1.956(5)
Al(1)−N(1)	1.9389(17)	1.919(4)
Al(1)−O(S)	1.8843(15)	2.354(2)
P(1)−N(1)	1.5850(15)	1.589(4)
P(1)−O(S)	1.5294(13)	2.0019(16)
P(1)−N(2)	1.6823(15)	1.681(3)
P(1)−P(1)A	2.4716(9)	2.5003(18)
C(1)−Al(1)−C(2)	116.61(13)	117.1(3)
N(1)−Al(1)−O(S)	75.95(6)	80.11(12)
Al(1)−N(1)−P(1)	91.03(8)	102.1(2)
P(1)−O(S)−Al(1)	94.90(7)	77.38(6)
N(1)−P(1)−O(S)	98.11(8)	100.35(15)
N(2)−P(1)−N(2A)	84.59(8)	83.44(17)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 16

Al(1)−C(1)	1.950(3)	C(1)−Al(1)−C(2)	114.11(15)
Al(1)−C(2)	1.955(3)	C(33)−Al(2)−C(34)	116.26(14)
Al(2)−C(33)	1.927(3)	N(1)−Al(1)−N(2)	74.82(8)
Al(2)−C(34)	1.945(3)	N(5)−Al(2)−N(6)	75.56(9)
Al(1)−N(1)	1.913(2)	N(1)−P(1)−N(2)	93.39(10)
Al(1)−N(2)	2.003(2)	N(3)−P(1)−N(4)	81.18(10)
Al(2)−N(6)	1.931(2)	N(5)−P(2)−N(6)	94.70(11)
Al(2)−N(5)	1.986(2)		
P(1)−N(1)	1.668(2)		
P(1)−N(2)	1.603(2)		
P(1)−N(3)	1.697(2)		
P(1)−N(4)	1.701(2)		
P(2)−N(3)	1.702(2)		
P(2)−N(4)	1.702(2)		
P(2)−N(5)	1.601(2)		
P(2)−N(6)	1.661(2)		

The solid-state structure of **16** is depicted in Figure 4, and the data collection and bond parameters of this compound are summarized in Tables 1 and 4, respectively. Although this complex has no crystallographic symmetry, its tetradentate hexanitrogen ligand and the

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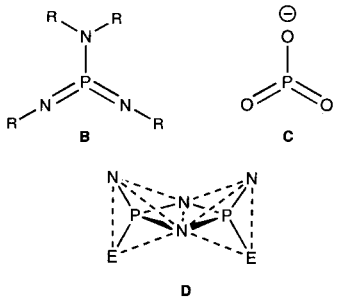
Chart 2



almost perfectly linear Al−P−P−Al arrangement give it a highly symmetrical appearance. The most glaring difference between this compound and the dichalcogen analogues are the large *p*-tolylimino groups, which provide more steric shielding for the metal atoms than either the sulfur or selenium atoms.

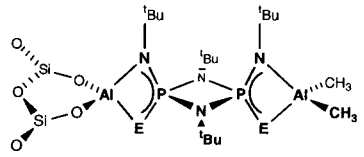
The overall symmetry of **16** belies a surprisingly high degree of variance in similar bonds. All aluminum−nitrogen bonds, for example, are decidedly unequal, spanning the relatively wide range of 1.913(2)−2.003(2) Å, as do the exocyclic P−N bonds, which range from 1.601(3) to 1.668(3) Å. The aluminum−methyl bonds have more uniform lengths (1.927(3)−1.955(3) Å) and are almost identical to the Al−C bonds of a dialkylaluminum troponiminate complex,[21] but slightly shorter than the aluminum−methyl bonds in a dinuclear guanidinate complex.[5b] The coordination environment of aluminum is distorted tetrahedral, the N−Al−N angle being much more acute (75.2(1)°) than the C−Al−C angle (115.2(2)°).

A comparison of the aluminum−imino bonds and the orientation of their nitrogen substituents suggests a possible cause for the asymmetry of the aluminum−nitrogen bonds. The Al−N1 bond is 0.075(2) Å shorter than its counterpart (Al2−N5), and this correlates well with the smaller dihedral angle between the metallacycle and its pendent *p*-tolyl groups, indicating that conjugation effects may be responsible for the bond shortening. (Steric constraints prevent a coplanar arrangement of both *p*-tolyl groups.) The competition between amido and imino nitrogen atoms for the aluminum atoms causes a short aluminum−imino bond to be accompanied by a long aluminum−amido bond, and hence the overall asymmetry.

Because O and O^- are isoelectronic with N−R and N−R_2, respectively, Scherer has compared aminobis(imino)phosphoranes (shown as **B** in Chart 2) to the metaphosphate ion (PO_3^-, **C**),[22] the formal monomer of oligo- and polyphosphates. Bis(amino)cyclodiphosph(V)azanes are dimeric aminobis(imino)phosphoranes and thus *quasi* diphosphates (**D**), albeit edge-sharing ones, rather than the ubiquitous corner-sharing $P_2O_7^{4-}$.[23] These dialuminum complexes can be considered hydrocarbon-soluble aluminum diphosphate analogues, with potential applications as polyphosphate precursors. The analogy to inorganic phosphates is particularly fitting for the dioxo species, and we are currently pursuing some aspects of the solid-state chemistry of these ligands.

A much more obvious and immediate use of the title compounds, however, is in polyolefin catalysis. It has been reported that amidinate and guanidinate complexes, of the general formulas [RC(NR′)$_2$]AlMe$_2$ and [R$_2$NC(NR′)$_2$]AlMe$_2$, when activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$], produce polyethylene of high molecular weight.[5a] The active species in these reactions are thought to be monomeric, three-coordinate, Lewis-acidic cations, which become inactive on dimerization. Steric bulk of the N−alkyl substituents appears to have a noticeable effect on the bite angle of the ligands and the degree of aggregation of their complexes.

Bis(amino)cyclodiphosph(V)azanes have a wider N···N gap than amidines[11h] (2.50 vs 2.31 Å) and allow a more complete chelation of the metal ions, which, in turn, may hinder dimerization. The phosphorus ligands are also easier to synthesize and to modify than amidines and guanidines, and this should facilitate the fine-tuning of the catalysts and the polymers they produce. Whether the dimethylaluminum complexes of bis(amido)cyclodiphosph(V)azanes have similar properties as the amidinate and guanidinate analogues remains to be seen. The title compounds appear to have at least one advantage over conventional monoaluminum catalysts in being ideally suited for heterogenization (**E**);[24] a property of great importance for industrial polyolefin catalysts.



E

Conclusion

Chalcogens (O, S, Se) and *p*-tolyl azide oxidize *cis*-bis(1°-amino)cyclodiphosph(III)azanes stereospecifically to the corresponding bis(1°-amino)cyclodiphosph(V)azanes. These P(V) molecules chelate dimethylaluminum in a manner similar to aminochalcogeno- and aminoiminophosphoranates, yielding trispirocyclic bimetallic complexes. The ligands and their complexes may have applications as hydrocarbon-soluble diphosphate analogues, but of more practical importance is their relationship to amidines and guanidines. Because of this similarity, bis(amino)cyclodiphosph(V)azanes should have an extensive coordination chemistry with applications in catalysis, particularly as ligands for supported polyolefin catalysts.

Experimental Section

All experiments were performed under an atmosphere of purified nitrogen or argon, using standard Schlenk techniques. Solvents were dried and freed of molecular oxygen by distil-

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lation under an atmosphere of nitrogen from sodium or potassium benzophenone ketyl immediately before use. NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced relative to C_6D_5H (7.15 ppm), C_6D_6 (128.0 ppm), and $P(OEt)_3$ (137.0 ppm), respectively. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed on well-developed macrocrystalline samples by E and R Microanalytical Services, Parsipanny, NJ, or Desert Analytics, Tucson, AZ. The samples were transferred in an all-glass apparatus and sealed in flame-dried capillaries, after ^{1}H NMR spectra on aliquot portions had revealed no extraneous peaks.

Trimethylaluminum (2.0 M heptanes solution), *n*-butyllithium (2.5 M hexanes solution), gray selenium, and cumene hydroperoxide were purchased from Aldrich and used as received. The cyclodiphosphazanes *cis*-[^{t}Bu(H)N(PN^{t}Bu)$_2$N(H)^{t}Bu] (**1**),[25] *cis*-[Ph(H)N(PN^{t}Bu)$_2$N(H)Ph] (**2**),[8b] *cis*-[^{t}Bu(H)N(E=PN^{t}Bu)$_2$N(H)^{t}Bu] (E = S(**4**),[13] Se (**5**))[14] *cis*-[^{t}Bu(H)N(PhN=PN^{t}Bu)$_2$N(H)^{t}Bu] (**8**), and *cis*-[^{t}Bu(H)N(*p*-tolylN=PN^{t}Bu)$_2$N(H)^{t}Bu] (**9**) were synthesized by published procedures.[9]

Syntheses. *cis*-[^{t}Bu(H)N(O=PN^{t}Bu)$_2$N(H)^{t}Bu] (3). In a two-necked round-bottomed flask, fitted with a dropping funnel and an inlet, **1** (3.92 g, 11.3 mmol) was dissolved in 35 mL of toluene. To this cooled (0 °C) solution was added dropwise 3.88 mL (22.5 mmol) of cumene hydroperoxide with vigorous stirring. After 0.5 h the solution was allowed to warm to room temperature, where it was kept for 4 h. It was then concentrated to 15 mL in vacuo and stored at −21 °C for 1 day. Several fractions of a colorless, crystalline solid were recovered, rinsed with cold hexanes, and dried in vacuo. Yield: 4.17 g (96.5%). Mp: 212−216 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 3.11 (br s, 2 H, NH^{t}Bu), 1.55 (s, 18 H, N^{t}Bu), 1.30 (s, 18 H, N^{t}Bu). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 55.17 (s), 52.73 (s), 31.70 (s), 30.77 (t, J_{PC} = 4.5 Hz). ^{31}P{H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ −3.38 (s). Anal. Calcd for $C_{16}H_{38}N_4P_2O_2$: C, 50.52; H, 10.07; N, 14.72. Found: C, 50.69; H, 10.08; N, 15.09.

***cis*-[Ph(H)N(S=PN^{t}Bu)$_2$N(H)Ph] (6).** A mixture of **2** (1.57 g, 4.05 mmol) and sulfur (0.267 g, 8.33 mmol) in 30 mL of toluene was refluxed for 16 h. The solution was allowed to cool, concentrated to 15 mL in vacuo, and stored at −21 °C. Several fractions of light yellow crystals yielded 3.05 g (75.3%) of product. Mp: 178−181 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.05 (d, 4 H, J = 9.6 Hz, *o*-Ph), 7.01 (t, 4 H, J = 7.5 Hz, *m*-Ph), 6.84 (t, 2 H, J = 7.3 Hz, *p*-Ph), 5.11 (s, 2 H, NH), 1.56 (s, 18 H, N^{t}Bu). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 139.80 (s, Ph), 129.36 (s, Ph), 124.56 (s, Ph), 122.60 (d, J_{PC} = 2.3 Hz, Ph), 57.08 (s, N^{t}Bu), 29.67 (t, J_{PC} = 4.5 Hz, N^{t}Bu). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 37.12 (s). Anal. Calcd for $C_{20}H_{30}N_4P_2S_2$: C, 53.08; H, 6.68; N, 12.38. Found: C, 53.14; H, 6.82; N, 12.47.

***cis*-[Ph(H)N(Se=PN^{t}Bu)$_2$N(H)Ph] (7).** In a manner identical to that used for the synthesis of **6**, 0.944 g (2.43 mmol) of **2** and 0.432 g (5.47 mmol) of gray selenium powder were allowed to react. The solution was concentrated in vacuo to ca. 7 mL and placed in a freezer (−21 °C). Several crops of light yellow crystals yielded 0.902 g (67.8%) of product. Mp: 201−204 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.06 (d, 4 H, J = 7.2 Hz), 6.99 (t, 4 H, J = 7.4 Hz), 6.83 (t, 2 H, J = 6.9 Hz), 5.34 (s, 2 H, NH), 1.62 (s, 18 H, N^{t}Bu). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 138.2 (s, Ph), 128.0 (s, Ph), 123.5 (s, Ph), 121.7 (t, J = 2.6 Hz, Ph), 56.55 (s, N^{t}Bu), 28.33 (t, J = 5.2 Hz). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 45.06 (s). Anal. Calcd for $C_{20}H_{30}N_4P_2Se_2$: C, 43.97; H, 5.54; N, 10.25. Found: C, 44.21; H, 5.94; N, 10.37.

{[(2THF·LiPhN)(S=PN^{t}Bu)$_2$(NPhLi·2THF)]·THF} (10). In a 100 mL two-necked flask, 2.46 g (5.43 mmol) of **6** was dissolved in 30 mL of THF, and the mixture was cooled to 0 °C. To this colorless solution was added dropwise 4.50 mL (11.3 mmol) of *n*-butyllithium, along with an additional 7 mL of THF. The resulting yellow solution was kept at 40 °C for 17 h and concentrated to 30 mL in vacuo. It was then stored at −21 °C to afford several crops of colorless needles (3.57 g, 79.6%). Mp: 218 °C dec. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 8.10 (d, 4 H, J = 7.1 Hz, *o*-Ph), 7.55 (t, 4 H, J = 6.9 Hz, *m*-Ph), 6.94, (m, 2 H, *p*-Ph), 3.62 (d, 16 H, THF), 1.83 (s, 18 H, N^{t}Bu), 1.39 (d, 16 H, THF). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 141.71 (s, Ph), 129.11 (s, Ph), 119.09 (s, Ph), 118.04 (s, Ph), 68.44 (d, J_{PC} = 17.1 Hz, THF), 55.79 (d, J_{PC} = 7.7 Hz, N^{t}Bu), 30.83 (t, J_{PC} = 30.3 Hz, N^{t}Bu), 25.79 (t, J_{PC} = 15.4 Hz, THF). ^{31}P{^{1}H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 24.80 (s). Anal. Calcd for $C_{40}H_{68}Li_2N_4O_5P_2S_2$: C, 58.24; H, 8.31; N, 6.79. Found: C, 58.32; H, 8.25; N, 6.87.

{(Me$_2$Al)[^{t}BuN(O=PN^{t}Bu)$_2$N^{t}Bu](AlMe$_2$)} (11). In a two-necked round-bottomed flask, equipped with dropping funnel and oil bubbler, 0.392 g (1.03 mmol) of **3** was dissolved in 20 mL of toluene. Trimethylaluminum (1.03 mL, 2.06 mmol) was then added dropwise to the cooled (0 °C) solution, which was allowed to stir at room temperature for an additional 14 h. It was then concentrated to 5.0 mL and stored at −21 °C for 20 h. Yield: 0.400 g (78.8%). Mp: 259−263 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 1.42 (s, 18 H, N^{t}Bu), 1.22 (s, 18 H, N^{t}Bu), −0.27 (s, 12 H, AlMe$_2$). ^{13}C{H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 57.95 (s, N^{t}Bu), 51.61 (t, J_{PC} = 4.4 Hz, N^{t}Bu), 33.22 (t, J_{PC} = 4.9 Hz, N^{t}Bu), 31.09 (t, J_{PC} = 4.4 Hz, N^{t}Bu), −7.42 (s, AlMe$_2$). ^{31}P{H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 1.79 (s). Anal. Calcd for $C_{20}H_{48}N_4P_2O_2Al_2$: C, 48.77; H, 9.82; N, 11.37. Found: C, 48.69; H, 9.91; N, 11.33.

{(Me$_2$Al)[^{t}BuN(S=PN^{t}Bu)$_2$N^{t}Bu](AlMe$_2$)} (12). In a manner identical to that used for the synthesis of **11**, 1.04 g (2.52 mmol) of **4** and AlMe$_3$ (2.52 mL, 5.04 mmol) were combined. Upon completion of the reaction (24 h), the solution was concentrated to 3 mL in vacuo and stored at −21 °C. Yield: 0.790 g (59.5%). Mp: 196−199 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 1.61 (s,18 H, N^{t}Bu), 1.28 (s, 18 H, N^{t}Bu), −0.18 (s, 12 H, AlMe$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 59.69 (s, N^{t}Bu), 56.25 (t, J_{PC} = 6.7 Hz, N^{t}Bu), 32.98 (t, J_{PC} = 6.9 Hz, N^{t}Bu), 30.52 (t, J_{PC} = 4.2 Hz, N^{t}Bu), −5.75 (s, AlMe$_2$). ^{31}P{^{1}H} (202.46 MHz, benzene-d_6, 26 °C): δ 22.30 (s). Anal. Calcd for $C_{20}H_{48}N_4P_2S_2Al_2$: C, 45.78; H, 9.22; N, 10.68. Found: C, 45.68; H, 9.68; N, 10.90.

{(Me$_2$Al)[^{t}BuN(Se=PN^{t}Bu)$_2$N^{t}Bu](AlMe$_2$)} (13). In a manner identical to that used for the synthesis of **12**, 0.534 g (1.05 mmol) of **5** and 1.15 mL (2.30 mmol) of AlMe$_3$ were allowed to react. Upon completion of the reaction, the solution was concentrated to 8 mL in vacuo and kept at −21 °C for 24 h. Yield: 0.481 g (74.1%) of colorless crystals. Mp: 194−197 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 1.66 (s, 18 H, N^{t}Bu), 1.28 (s, 18 H, N^{t}Bu), − 0.11 (s, 12 H, AlMe$_2$). ^{13}C{H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 60.79 (s, N^{t}Bu), 58.50 (t, J_{PC} = 7.8 Hz, N^{t}Bu), 33.42 (t, J_{PC} = 4.9 Hz, N^{t}Bu), 30.95 (t, J_{PC} = 4.0 Hz, N^{t}Bu), −4.54 (s, AlMe$_2$). ^{31}P{H} NMR (202.46 MHz, benzene-d_6, 26 °C): δ 3.91 (s). Anal. Calcd for $C_{20}H_{48}N_4P_2Se_2Al_2$: C, 38.84; H, 7.82; N, 9.06. Found: C, 39.07; H, 7.98; N, 9.20.

{(Me$_2$Al)[PhN(S=PN^{t}Bu)$_2$NPh](AlMe$_2$)·0.5toluene} (14). In a 100 mL round-bottomed flask, 0.502 g (1.11 mmol) of **6** was dissolved in 30 mL of toluene. To the cold (0 °C) solution was added dropwise 1.22 mL (2.44 mmol) of trimethylaluminum, resulting in the evolution of methane. The reaction mixture was stirred at room temperature for 16 h, concentrated to 8 mL in vacuo, and then stored at −21 °C for 24 h. Several fractions of colorless plates afforded 0.432 g (68.9%) of product. Mp: 161−164 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.07 (d, 4 H, J = 8.1 Hz, *o*-Ph), 6.92 (t, 4 H, J = 7.6 Hz, *m*-Ph), 6.84 (t, 2 H, J = 6.9 Hz), 1.48 (s, 18 H, N^{t}Bu), −0.17 (s, 12 H, AlMe$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 26 °C): δ 130.01 (s, Ph), 128.41 (s, Ph), 123.91 (s, Ph),

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122.91 (t, J_{PC} = 6.7 Hz, Ph), 58.79 (s, N^{t}Bu), 29.62 (t, J_{PC} = 4.4 Hz, N^{t}Bu), −7.59 (s, $AlMe_2$). $^{31}P\{H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): δ 22.79 (s). Anal. Calcd for $C_{27.5}H_{44}N_4P_2S_2Al_2$: C, 54.09; H, 7.26; N, 9.17. Found: C, 53.76; H, 7.62; N, 9.17.

{**(Me_2Al)[PhN(Se=P N^{t}Bu)$_2$NPh]($AlMe_2$)**} **(15).** In a manner identical to that used for the synthesis and isolation of **14**, 0.670 g (1.23 mmol) of **7** and 1.23 mL (2.46 mmol) of $AlMe_3$ were allowed to react. Yield: 0.600 g (74.1%). Mp: 150−154 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.07 (d, 4 H, J = 23.1 Hz, *o*-Ph), 6.88 (t, 4 H, J = 7.3 Hz, *m*-Ph), 6.83 (t, 2 H, J = 7.1 Hz, *p*-Ph), 1.52 (s, 18 H, N^{t}Bu), −0.12 (s, 12 H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): δ 129.79 (s, *m*-Ph), 128.34 (s, *o*-Ph), 123.84 (s, *p*-Ph), 122.86 (t, J_{PC} = 6.7 Hz, *ipso*-Ph), 59.13 (s, N^{t}Bu), 29.37 (t, J_{PC} = 4.0 Hz, N^{t}Bu), −7.28 (s, $AlMe_2$). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): δ 21.27 (s). Anal. Calcd for $C_{24}H_{40}Al_2N_4P_2Se_2$: C, 43.78; H, 6.12; N, 8.50. Found: C, 43.16; H, 6.44; N, 8.43.

{**(Me_2Al)[^{t}BuN(*p*-tolylN=P N^{t}Bu)$_2$N^{t}Bu]($AlMe_2$)**} **(16).** In a manner identical to that used for the synthesis of **15**, 0.95 g (1.7 mmol) of **9** and 1.7 mL (3.4 mmol) of $AlMe_3$ were allowed to react. The colorless solution was stirred overnight at room temperature, then concentrated in vacuo to about one-third of its volume and placed in a refrigerator (2 °C). After several days of cooling colorless crystals of **17** (0.70 g, 74%) formed. Mp: 258−263 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.01 (d, 4 H, J = 8.3 Hz), 6.64 (d, 4 H, J = 8.0 Hz), 2.092 (s, 6 H, *p*-tolyl), 1.496 (s, 18 H, N^{t}Bu), 1.458 (s, 18 H, N^{t}Bu), −0.242 (s, 12 H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (126.76 MHz, benzene-d_6, 26 °C): δ 140.59 (s), 130.65 (s), 130.38 (s), 124.83 (t, J = 5.3 Hz), 57.49 (s, N^{t}Bu), 53.10 (t, J = 8.0 Hz), 34.82 (t, J = 4.3 Hz), 31.86 (t, J = 4.1 Hz), 21.12 (s, Me), −7.40 (s, $AlMe_2$). $^{31}P\{^1H\}$ NMR (202.46 MHz, benzene-d_6, 26 °C): δ −16.18 (s). Anal. Calcd for $C_{34}H_{62}Al_2N_4P_6$: C, 60.88; H, 9.32; N, 12.52. Found: C, 60.82; H, 9.00; N, 12.53.

{**(Me_2Al)[^{t}BuN(PhN=P N^{t}Bu)$_2$N^{t}Bu]($AlMe_2$)**} **(17).** In a manner identical to that used for the synthesis of **15**, 1.08 g (2.04 mmol) of **8** and 2.1 mL (4.2 mmol) of $AlMe_3$ were allowed to react. The mixture was then concentrated in vacuo to ca. 5 mL and placed in a refrigerator (2 °C). Several crops of colorless crystals yielded 0.496 g (41.9%) of product. Mp: 168−176 °C. ^1H NMR (500.13 MHz, benzene-d_6, 26 °C): δ 7.097 (d, 4 H, J = 8.0 Hz, Ph), 6.841 (t, 4 H, J = 7.8 Hz, Ph), 6.793 (t, 2 H, J = 7.9 Hz, Ph), 1.463 (s, 18 H, N^{t}Bu), 1.443 (s, 18 H, N^{t}Bu), −0.264 (s, 12 H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, benzene-d_6, 26 °C): δ 53.91 (s), 52.15 (s), 50.27 (s), 31.75 (d, J_{PC} = 4.5 Hz), 30.23 (d, J_{PC} = 5.1 Hz), −7.42 (s, AlMe). ^{31}P NMR (202.46 MHz, benzene-d_6, 26 °C): δ −16.16 (s). Anal. Calcd for $C_{32}H_{58}Al_2N_6P_2$: C, 59.81; H, 9.03; N, 13.08. Found: C, 59.88; H, 8.92; N, 13.13.

X-ray Crystallography. Compounds 7, 12, and 16. Suitable, single crystals were coated with oil, attached to a glass capillary, and centered on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker SMART CCD diffractometer, equipped with an LT-2 low-temperature apparatus, operating at 213 K. Data were measured using ω scans of 0.3° per frame for 30 s until a complete hemisphere had been collected. The first 50 frames were re-collected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART[26] software and refined with SAINT[27] on all observed reflections. Data were reduced with SAINT, which corrects for *Lp* and decay. An empirical absorption correction was applied with SADABS.[28] The structures were solved by direct methods with the SHELXS-90[29] program and refined by full-matrix least-squares methods on F^2 with SHELXL-97,[30] incorporated in SHELXTL-PC, version 5.03.[31]

Compounds 6 and 11. The crystals were sealed inside argon-filled glass capillaries, and the intensity data were collected on a Bruker P4 diffractometer. Three check reflections were monitored after every 97 data, and the appropriate corrections were applied during data reduction. Intensity data were reduced with SHELXTL PC,[32]and the structures were solved by direct-methods, using SHELXL-NT, version 5.10.[33]

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Supporting Information Available: Five X-ray crystallographic files for structures **6**, **7**,**11**, **12**, and **16**, in CIF format, are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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