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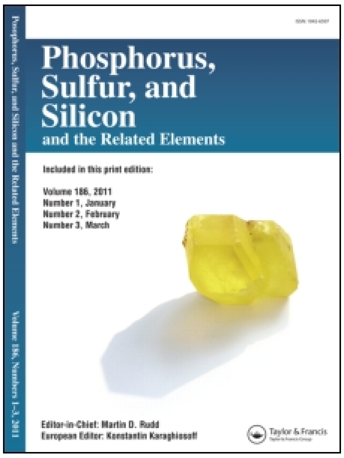

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Mono- and Bimetallic Cyclodiphosph(V)Azane Complexes

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The 2,4-bis(amino)cyclodiphosph(V)azanes *cis*-$\{R(H)N(E{=}PN^tBu)_2N(H)R]$ (R = Ph, E = S(**2**), Se(**3**); R = ^tBu, E = *p*-Tol (**4**)) were synthesized and X-ray structurally characterized. Treatment of **4** or *cis*-$[^tBu(H)N(E{=}PN^tBu)_2N(H)^tBu]$ with $TiCl_4$ afforded monometallic complexes of the type $\{[^tBu(H)N(E{=}PN^tBu)_2N^tBu]TiCl_3\}$ E = S(**5**), Se(**6**), NPh. Deprotonation of **2** and *cis*-$\{^tBu(H)N(E{=}PN^tBu)_2N(H)^tBu]$ with ^nBuLi, afforded dilithium complexes of the general formula $\{[(THF_2{\cdot}LiRN)(E{=}PN^tBu)_2(NRLi{\cdot}THF_2)]\}$ R = Ph(**7**), R = ^tBu(**8**). Treatment of $[^tBu(H)N(E{=}PN^tBu)_2N(H)^tBu]$ with trimethylaluminum produced $\{(Me_2Al)[(^tBuN)(E{=}PN^tBu)_2(N^tBu)](AlMe_2)\}$, E = O(**9**), S(**10**), *p*-Tol(**11**). Single-crystal X-ray analyses demonstrated that the monometallic **5** and **6** are bispirocyclic complexes, while the bimetallic **7–11** were shown to be trispirocyclic complexes.

Keywords: Cyclodiphosph(V)azanes; Aminobis(imino)phosphoranes; Amino(imino)(chalcogeno)phosphoranes; Dilithium; Dialuminum

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INTRODUCTION

We have been investigating bis(1°-amino)cyclodiphosph(III)azanes as chelating bis(amido) ligands for homogeneous polyolefin catalysts.[1] Unfortunately cyclodiphosph(III)azane complexes have unacceptably short lifetimes under realistic polymerization conditions. The isolation of ligand redistribution products and of 1,3-diaza-2-phosphaallylic species in a number of related reactions suggested that ring-opening of the heterocycle is the major cause of catalyst deactivation.[2]

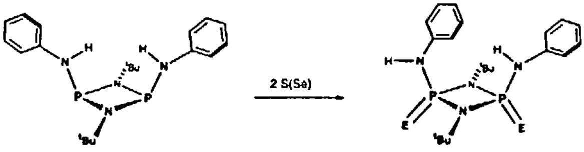
This cycloreversion of cyclodiphosph(III)azanes is likely due to both kinetic factors (facile attack of cocatalyst or cationic catalyst on the phosphorus lone-pair electrons) and thermodynamic factors (relatively weak P–N bonds).

To remove the lone pair electrons and to strengthen the P–N framework, we have oxidized the cyclodiphosph(III)azanes to cyclodiphosph(V)azanes. The superior bond strengths, greater Brønsted acidities and more variable coordination modes of cyclodiphosph(V)azanes has prompted us to investigate their ligand properties towards main group and transition metals.

RESULTS AND DISCUSSION

Norman *et al.* had shown that the oxidation of [^{t}Bu(H)N(PN^{t}Bu)$_2$N(H)^{t}Bu] with sulfur is stereospecific.[3] This suggested that oxidations of bis(amino)cyclodiphosphazanes should be a convenient way to transform these ligands to the corresponding P(V) species, because it leaves their chelating bis(amido) moieties intact. The selenium oxidation is equally facile and also furnishes the *cis*-isomer.[4]

Upon refluxing the bis(anilino)cyclodiphosph(III)azane *cis*-[Ph(H)N)(^{t}BuNP)$_2$N(H)Ph][2] (1) with sulfur or selenium (eq 1), off-white, crystalline *cis*-[Ph(H)N)(E=PN^{t}Bu)$_2$N(H)Ph], E = S (2) and Se (3), were obtained in good yields.



E = S (2), Se (3)

(1)

While chalcogen oxidations are the most facile P(III) to P(V) transformations, 2,4-bis(chalcogeno)cyclodiphosph(V)azanes — with the notable exception of dioxo species — are not good ligands for polyolefin catalysts. A major application of polymer films is in food packaging, and the malodorous byproducts of dichalcogeno ligands thus severely compromise their use in polyolefin catalysis. Moreover, the N–P–E coordination gap of these ligands is too open to provide the selectivity necessary for effective polymerization control.

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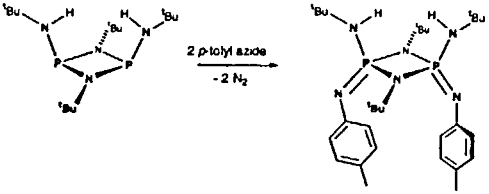
Aromatic azides are better oxidants, because they offer the possibility of both electronic and steric ligand tuning. Treatment of *cis*-[^{t}Bu(H)N(PN^{t}Bu)$_2$N(H)^{t}Bu] with two equivalents of *p*-tolyl azide (eq 2) afforded the 2,4-bis(*p*-tolylimino)cyclodiphosph(V)azane **4** in almost quantitative yields.

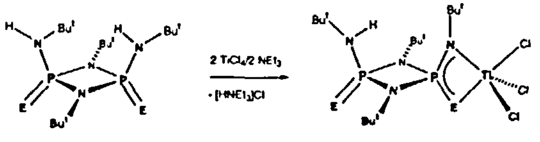


(4)

(2)

A single-crystal X-ray study of **4** confirmed the structure shown above, proving that azide oxidations, just like chalcogen oxidations, are stereospecific. The molecule has a planar central cyclodiphosphazane ring, bearing two *tert*-butylamino groups above and two *p*-tolylimino groups below the plane. In contrast to **2** and **3** both N–H groups are endo, just as in *cis*-[^{t}Bu(H)N(PN^{t}Bu)$_2$N(H)^{t}Bu].

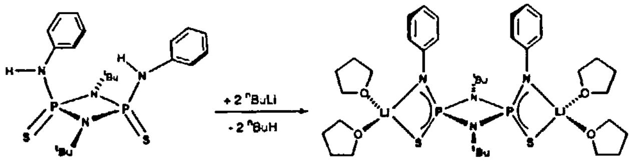
Titanium tetrachloride reacted with bis(1°-amino)cyclodiphosph(V)azanes (eq 3) to form only monometallic complexes of the type{[^{t}Bu(H)N(E=PN^{t}Bu)$_2$N^{t}Bu]TiCl$_3$} E = S(**5**), Se(**6**), NPh, despite a 2:1 metal to ligand stoichiometry.[5] We thought this to be due to solubility problems, and therefore attempted dimetallations with main-group metal alkyl species, because of their good leaving groups and the greater solubility of the ensuing products.



(3)

E = S (5), Se (6)

Treatment of **2** or *cis*-[^{t}Bu(H)N(S=PN^{t}Bu)$_2$N(H)^{t}Bu] with two equivalents of n-butyllithium (eq 4) afforded the colorless, crystalline {[(THF$_2$·LiRN)(S=PN^{t}Bu)$_2$(NRLi·THF$_2$)]·THF} R = Ph(**7**), ^{t}Bu(**8**), respectively.



(4)

(7)

When the ligands *cis*-[^{t}Bu(H)N(E=PN^{t}Bu)$_2$N(H)^{t}Bu] were allowed to interact with two equivalents of trimethylaluminum (eq 5) air-sensitive, colorless {(Me$_2$Al)[(^{t}BuN)(E=PN^{t}Bu)$_2$(N^{t}Bu)](AlMe$_2$)}, E = O(**9**), S(**10**), *p*-Tol(**11**) were isolated in almost quantitative yields. Single crystal analysis showed these dialuminum species to be trispirocyclic complexes, similar to the dilithio compounds **7** and **8**. They are composed of a central (P–N)$_2$ rhombus, which is flanked by two kite-shaped (Al–N–P–N) or (Al–N–P–E) metallacycles. The aluminum atoms are pseudo-tetrahedrally coordinated by the chelating ligands and two methyl groups.

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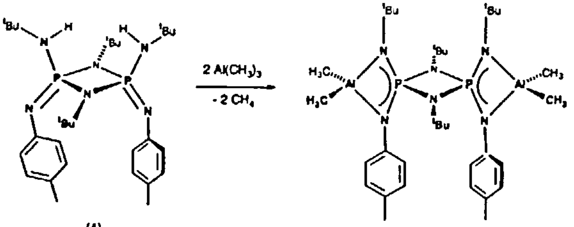

(4) (11) (5)

CONCLUSION

Chalcogens and aryl azides convert *cis*-bis(1°-amino)cyclodiphosph(III)azanes stereospecifically to the corresponding bis(1°-amino)cyclodiphosph(V)azanes. These phosphorus(V) species coordinate lithium and dimethylaluminum as dimeric phosphoranates, yielding trispirocyclic bimetallic complexes. Because of their close relationship to conventional phosphoranates and amidinates the bis(1°-amino)cyclodiphosph(V)azanes should have an extensive coordination chemistry.

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