

Ligand Design for the Assembly of Polynuclear Complexes: Syntheses and Structures of Trinuclear and Tetranuclear Aluminum Alkyl Complexes Bearing Tripodal Diamidoselenophosphinito Ligands and a Comparison to Related Tripodal Triamidophosphine Complexes

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Reactions of the triaminophosphines $P(CH_2NAr^R)_3$ (**1a–c**, where $Ar^R = 3,5-(CF_3)_2C_6H_3$ for **a**; $Ar^R = Ph$ for **b**, $Ar^R = 3,5-Me_2C_6H_3$ for **c**) with selenium afford the triaminophosphine selenides $Se=P(CH_2NAr^R)_3$ (**2a–c**). The phosphine selenides **2a–c** react with 4 equiv of $AlMe_3$ at room temperature to generate the triangular trinuclear aluminum complexes $[P(CH_2NAr^R)_2Se](AlMe_2)_3$ (**3a–c**). The byproduct of the formation of **3a** was hydrolyzed and provided $CH_3CH_2N(H)-3,5-(CF_3)_2C_6H_3$. When **2a–c** are treated with excess $AlMe_3$, the corresponding tetranuclear Lewis acid–base adducts $Me_3Al \cdot [P(CH_2NAr^R)_2Se](AlMe_2)_3$ (**4b,c**) are isolated. The reaction of $P(CH_2NAr^R)_3$ (**1a–c**) with 2 equiv of $AlMe_3$ produces the dinuclear aluminum complexes $P(CH_2NAr^R)_3Al_2Me_3$ (**5a–c**). When **1b,c** are reacted with excess $AlMe_3$, the Lewis acid–base adducts $Me_3Al \cdot P(CH_2NAr^R)_3Al_2Me_3$ (**6b,c**) are isolated. Solid-state molecular structures were determined for complexes **2a**, **2b**, **2c**, **3a**, **3c**, **4b**, **5a**, and **6b** by X-ray crystallography.

Introduction

Triangular complexes are of current interest for both their potential in new stoichiometric and catalytic transformations, due to the ability of adjacent transition metals to cooperatively¹ activate substrates,² and their physical properties, which include luminescence³ and magnetic spin-frustration.⁴ A plethora of ligands are known to bridge metals and promote cluster formation;⁵ however, multidentate ancillary ligands that can assemble triangular complexes that contain adjacent metal centers bearing functionalizable sites with an array of different metals are uncommon. Our studies have utilized the trianionic triamidophosphine donors $P(CH_2NAr^R)_3$, where Ar^R represents an aryl substituent as an ancillary ligand for polynuclear complex assembly. Unlike other triamido and amidophosphine ligands, the $P(CH_2NAr^R)_3$ ligands cannot chelate all four of their donor atoms to a single metal.^{6,7} We have recently shown how

triangular trimetallic Mn(II) complexes are readily assembled using these ligands, along with their isostructural diamagnetic Mg(II) analogues;⁸ however, when used with trivalent or higher oxidation state metal centers with three labile ligand sites, these ligands have a tendency to chelate all three amido donors to a single metal,⁷ which does not allow for the assembly of complexes with multiple adjacent metal centers. This is shown as complex **A** in Figure 1.

The factors that led us to investigate selenium donors in polydentate ligand designs that favor polynuclear complex formation were both the increased polarizability of the heavier chalcogenides, which should encourage electronic communication between metal centers, and their propensity to bridge metal centers. In this article we report the synthesis of diamidoselenophosphinito ancillary ligands, which favor the formation of triangular complexes with aluminum, shown in Figure 1 as complex **B**. Anionic Se donors are much less common than their oxygen and sulfur analogues,⁹ and selenophosphinito donors (R_2PSe^-) have not previously been incorporated into multidentate donor ligands, to the best of our knowledge, although related ligands are known.^{10–12}

The similar ionic radius of Al(III) to the radii of the trivalent first-row transition metals and its diamagnetic nature make it a

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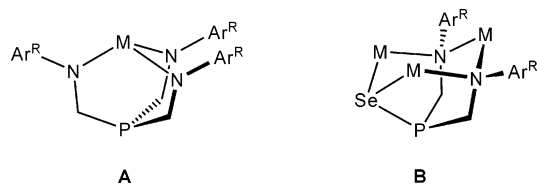
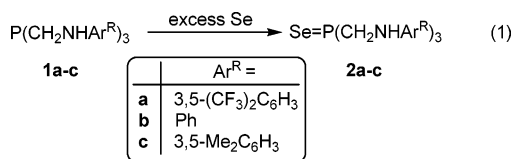


Figure 1. Potential bonding modes of the formally trianionic ligands $P[CH_2NAr^R]_3$ and $Se-P[CH_2NAr^R]_2$ with metal complexes labeled M.

convenient starting point for the study of this new ancillary ligand. Numerous amidophosphine^{13,14} as well as monodentate,^{15–17} bidentate,^{18–20} tridentate,²¹ and tripodal²² amido complexes of aluminum are known. These complexes have been studied largely as potential precursors for materials applications,²³ as well as to emulate the olefin polymerizations observed with related amidinate ligands.²⁴

Results and Discussion

Oxidation of $P(CH_2NAr^R)_3$ with Selenium. Treatment of the previously reported⁷ triamidophosphines $P(CH_2NAr^R)_3$, **1a–c** (where $Ar^R = 3,5-(CF_3)_2C_6H_3$, Ph, and $3,5-Me_2C_6H_3$ for **a**, **b**, and **c**, respectively), with excess elemental selenium in toluene afforded the phosphine selenides $SeP(CH_2NAr^R)_3$, as shown in eq 1. These white solids were isolated in yields ranging from 80 to 87% and are neither air- nor moisture-sensitive.



Colorless crystals of **2a–c** suitable for X-ray diffraction were grown by slow evaporation of solutions of equal amounts of ethanol and acetone. The solid-state molecular structure of **2c** is shown in Figure 2, and cell constants and refinement

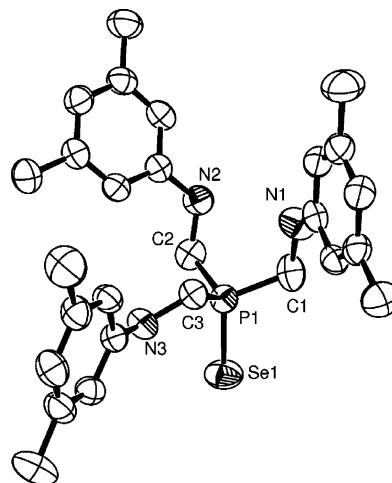


Figure 2. ORTEP depiction of the solid-state molecular structure of **2c** as determined by X-ray crystallography. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

parameters are provided in Table 1. The $C(1)-P(1)-C(2)$, $C(1)-P(1)-C(3)$, and $C(2)-P(1)-C(3)$ angles for the free ligand precursor **2c** are $105.84(13)^\circ$, $105.56(11)^\circ$, and $108.39(11)^\circ$, respectively, which are comparable to the tetrahedral angle of 109.5° . Comparison of the structure of phosphine selenide **2a** with that of the parent phosphine ligand **1a**⁷ reveals that the average $P-C$ bond length of **2a** is shorter by 0.017 \AA , and the sum of $C-P-C$ bond angles is wider by about 13.3° ($312.85(23)^\circ$ for **2a**, $299.51(20)^\circ$ for **1a**⁷). These differences correlate with the larger covalent radii of $P(III)$ compared to $P(V)$, as well as the larger repulsion of the lone pair of $P(III)$ versus the $P=Se$ bond. In **2a–c**, the $P-Se$ bond lengths are $2.0973(12)$, $2.1026(12)$, and $2.0960(7) \text{ \AA}$, respectively, which are similar to those observed in the selenides of substituted arylphosphines.²⁵ The $^{31}P\{^1H\}$ NMR spectra display singlets at δ 42.6, 46.3, and 44.5 and selenium satellites (^{77}Se , $I = 1/2$, 7.6%) with $^1J_{SeP}$ values of 742.8, 719.7, and 716.1 Hz for **2a–c**, respectively. These values are within the range expected for $R_3P=Se$ functional groups.^{26,27} The magnitude of $^1J_{SeP}$ has been used to characterize the lone-pair s-orbital character of phosphine donors and, thus, their σ -donor ability.²⁸ A larger value of $^1J_{SeP}$ corresponds to greater s-orbital character of the phosphorus lone pair and a weaker electron-donor ability of the phosphine ligand.²⁹ The donor abilities of the phosphines in precursors **1a–c** are affected by the nature of the aryl substituents, with the most electron-withdrawing aryl group providing the phosphine selenide with the largest $^1J_{SeP}$ value, 743.7 Hz. In comparison, $Se=PPh_3$ has a $^1J_{SeP}$ value of 733 Hz,^{28,30} which predicts that **1a–c** should have donor properties similar to triphenylphosphine. A similar conclusion regarding the donor ability of **1a–c** was reached via a study of the CO stretching frequencies³¹ of the complexes $trans-Rh(CO)Cl[P(CH_2NAr^R)_3]_2$, as previously reported.⁷

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Table 1. Crystallographic Data for Compounds 2a–c, 3a, 3c, 4b, 5a, and 6b

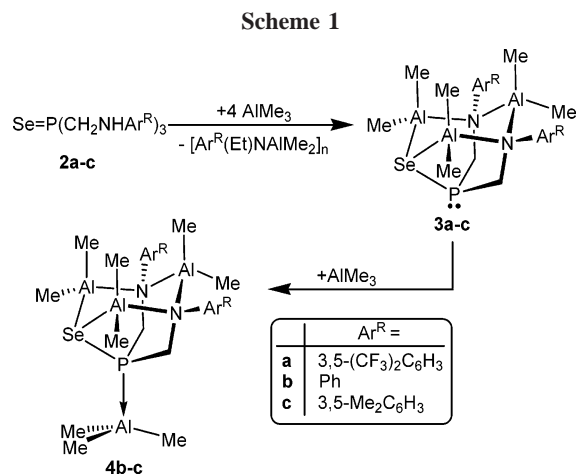
	2a	2b	2c	3a
empirical formula	C ₂₇ H ₁₈ F ₁₈ N ₃ PSe	C ₂₁ H ₂₄ N ₃ PSe	C ₂₇ H ₃₆ N ₃ PSe	C ₂₄ H ₂₈ Al ₃ F ₁₂ N ₂ PSe
fw	836.4	428.37	512.53	763.35
cryst syst	triclinic	triclinic	monoclinic	triclinic
<i>a</i> (Å)	14.832(2)	10.025(3)	8.1088(7)	9.0018(16)
<i>b</i> (Å)	15.494(2)	10.598(3)	11.4874(10)	13.892(3)
<i>c</i> (Å)	16.371(3)	10.605(3)	28.225(3)	13.947(3)
α (deg)	73.943(2)	65.584(3)	90.0	68.850(2)
β (deg)	65.716(2)	86.104(3)	94.317(2)	85.035(2)
γ (deg)	81.208(2)	75.794(3)	90.0	88.038(2)
<i>V</i> (Å ³)	3292.3(9)	993.9(5)	2621.6(4)	1620.5(5)
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i> value	4	1	4	2
<i>D</i> _{calc} (g/cm ³)	1.766	1.431	1.299	1.564
μ(Mo Kα) (mm ⁻¹)	1.320	1.979	1.512	1.377
temperature (K)	173	173	173	173
2θ _{max} (deg)	55.0	50.0	55.0	50.0
total no. of reflns	37705	11128	20415	18272
no. of unique reflns; <i>R</i> _{int}	14633; 0.072	4393; 0.063	4607; 0.034	7194; 0.022
transmn factors	0.89–0.91	0.89–0.96	0.89–0.99	0.89–0.96
no. with <i>I</i> ≥ 2σ(<i>I</i>)	8432	3497	3772	6346
no. of variables	988	247	307	412
no. of reflns/params	15.14	17.78	15.04	17.46
<i>R</i> ; <i>wR</i> ₂ (all data)	0.121, 0.151	0.077; 0.126	0.049; 0.112	0.042; 0.101
GOF	1.000	1.101	1.028	1.063
residual density (e ⁻ /Å ³)	0.721, -0.503	0.952, -0.492	0.570, -0.327	0.915, -0.507

	3c	4b	5a	6b
empirical formula	C ₂₄ H ₄₀ Al ₃ N ₂ PSe	C ₂₃ H ₄₁ Al ₄ N ₂ PSe	C ₃₀ H ₂₄ Al ₂ F ₁₈ N ₃ P	C ₂₇ H ₃₉ Al ₃ N ₃ P
fw	547.47	563.44	853.44	517.54
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic
<i>a</i> (Å)	13.118(2)	15.679(3)	11.2709(15)	11.8225(13)
<i>b</i> (Å)	8.3825(14)	10.954(2)	11.6947(15)	14.7615(16)
<i>c</i> (Å)	28.507(5)	8.5522(16)	15.652(2)	33.447(4)
α (deg)	90.0	90.0	68.4510(10)	90.0
β (deg)	90.187(2)	90.0	86.0640(10)	90.0
γ (deg)	90.0	90.0	78.9210(10)	90.0
<i>V</i> (Å ³)	3134.7(9)	1468.8(5)	1883.1(4)	5837.1(11)
space group	<i>P</i> 2(1)/ <i>n</i>	<i>Pmn</i> 2(1)	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>Z</i> value	4	2	2	8
<i>D</i> _{calc} (g/cm ³)	1.256	1.274	1.574	1.178
μ(Mo Kα) (mm ⁻¹)	1.351	1.466	0.239	0.204
temperature (K)	173	173	173	173
2θ _{max} (deg)	55.0	55.0	50.0	55.0
total no. of reflns	34 149	10 182	18 227	62 133
no. of unique reflns; <i>R</i> _{int}	7097; 0.038	3390; 0.052	6628; 0.024	6679; 0.043
transmn factors	0.89–0.99	0.89–0.91	0.89–0.99	0.89–0.96
no. with <i>I</i> ≥ 2σ(<i>I</i>)	5973	2761	5625	5618
no. of variables	311	151	527	313
no. of reflns/params	22.82	22.45	12.58	21.34
<i>R</i> ; <i>wR</i> ₂ (all data)	0.049; 0.115	0.064; 0.096	0.068; 0.175	0.055; 0.119
GOF	1.133	1.063	1.034	1.112
residual density (e ⁻ /Å ³)	0.852, -0.596	1.002, -0.398	0.750, -0.520	0.389, -0.241

Trinuclear Complexes via Reactions of Se=P(CH₂NHAr^R)₃ with AlMe₃. The phosphine selenides Se=P(CH₂NHAr^R)₃ (**2a–c**) react with 4 equiv of AlMe₃ in toluene at room temperature to give [P(CH₂NAr^R)₂Se](AlMe₂)₃ (**3a–c**), as shown in Scheme 1. The reactions proceed over the course of 24 h, with the putative and unisolable amine-trimethylaluminum adducts as the only intermediates observable by ¹H NMR spectroscopy; the observation of such adducts is not uncommon.^{19,32} The use of 4 equiv of AlMe₃ was necessary because the overall reaction involves the loss of one ligand –CH₂NHAr^R arm. This is a new synthetic route to selenophosphinito ligands, which are poorly studied and more commonly prepared by the insertion of 1 equiv of Se into a metal–phosphido bond.^{33,34} The byproducts are

much more soluble in pentane than the scarcely soluble **3a–c** and were easily rinsed from the crude product mixtures without significant loss of yield. The ¹H NMR spectra of these byproducts are complicated and exhibit a variety of triplet and quartet resonances, as would be expected for ethyl substituents bound to nitrogen. The byproducts are believed to be dimers of the type [CH₃CH₂N(Ar^R)AlMe₂]₂, and their complex ¹H NMR spectra are likely due to the presence of *cis* and *trans* isomers and perhaps also larger oligomers.^{16,32,35} Additional insight regarding the nature of the byproduct was obtained by the hydrolysis of the pentane fraction used to rinse the crude product mixture in the synthesis of **3a**. The hydrolysis product was identified as CH₃CH₂N(H)-3,5-(CF₃)₂C₆H₃ by ¹H and ¹³C{¹H} NMR spectroscopy. The exact mechanism by which the ligand arm

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loss occurs is not clear, and a mechanism with an imine intermediate ($\text{CH}_2=\text{NAr}^R$) cannot be distinguished from the direct reaction of the ligand precursors with AlMe_3 to liberate $\text{CH}_3\text{CH}_2\text{N}(\text{Ar}^R)\text{AlMe}_2$.

The solid-state molecular structures of **3a** and **3c** were determined by X-ray crystallography. Complex **3b** crystallized as thin needles that were unsuitable for crystallographic studies. An ORTEP depiction of the structure of **3c** is shown in Figure 3. Although there is no crystallographically imposed symmetry, these complexes have approximate C_s symmetry. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra of these complexes dissolved in C_6D_6 are consistent with an identical solution structure.

The tripodal ligand in **3c** binds three aluminum centers via one selenide and two amide donors, all of which act as bridging ligands. The three aluminum centers all have approximately tetrahedral geometries, and each retains two methyl groups. The lone pair of the phosphine donor is directed away from the aluminum centers. The donors and aluminum atoms form a six-membered $\text{Al}_3\text{N}_2\text{Se}$ ring, which adopts a chair conformation. The Al–N bond lengths in **3a** and **3c** vary from 1.977(2) to 2.0137(18) Å, and the Al–Se bond lengths range from 2.4760(8) to 2.4979(9) Å. These lengths, as well as the N–Al–N angles (**3a**, 102.85(8)°; **3c**, 102.65(7)°), are in the expected range.^{14,15,18,21,36} Both the P–Se bond lengths (e.g., **3a**: 2.2799(6) Å; **3c**, 2.2793(7) Å) and the $^1J_{\text{SeP}}$ values (**3a**, 176.2 Hz; **3b**, 179.0 Hz; **3c**, 181.3 Hz) are within the range expected for P–Se single bonds,³⁷ and thus the selenophosphinito donor in this case is best described by a resonance structure where the selenium atom bears a formal negative charge, rather than one where the phosphorus donor is formally anionic.¹⁰ As expected, complexes **3a–c** exhibit lower $^1J_{\text{SeP}}$ values than in related complexes, such as $\text{Me}_2\text{Al}[\text{PhP}(\text{Se})(\text{N}^t\text{Bu})(\text{NH}^t\text{Bu})]$,¹² where the anionic charge of the ligand can be delocalized between the nitrogen and selenium donors.

Chalcogenophosphinites (R_2PE^- , where E = O, S, Se, or Te) can be protonated at either the P or E sites to provide the tautomers $\text{R}_2\text{P}(\text{H})=\text{E}$ and $\text{R}_2\text{P}=\text{EH}$.^{10,38} The ratio of these products depends on the nature of R. Likewise, transition metals can bind to R_2PE^- ligands by a variety of bonding modes involving either the E or P centers, or both.¹⁰ Only a handful of examples of complexes containing R_2PSe^- donors have been reported,^{10,33,34,39–41} and few have been structurally character-

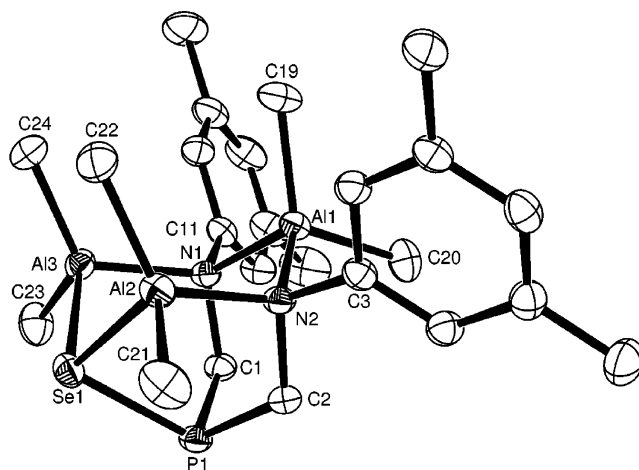


Figure 3. ORTEP depiction of the solid-state molecular structure of **3c** as determined by X-ray crystallography. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected distances (Å): Se(1)–P(1), 2.2793(7); Se(1)–Al(2), 2.4909(9); Se(1)–Al(3), 2.4979(9); P(1)–C(1), 1.852(3); P(1)–C(2), 1.846(3); N(2)–Al(2), 1.991(2); N(1)–Al(3), 1.977(2); N(1)–Al(1), 1.996(2); N(2)–Al(1), 2.005(2). Selected bond angles (deg): C(1)–P(1)–C(2), 99.06(11); C(1)–P(1)–Se(1), 101.23(8); C(2)–P(1)–Se(1), 100.65(8); Al(2)–Se(1)–P(1), 91.85(3); Al(3)–Se(1)–P(1), 90.37(3); Al(3)–Se(1)–Al(2), 104.00(3).

ized. The η^2 -binding mode has been observed in complexes of Mo³⁹ and Ru,⁴⁰ but for the more electropositive metals the only crystallographically characterized structure is that of the lithium salt, $[(\text{TMEDA})\text{Li}-\mu-\eta^1-\text{SePPh}_2]_2$;³³ however, it is reasonable to assume that the selenophosphinito complexes of the electropositive metals will be comparable to those of the thiophosphinito ligands, which prefer to coordinate metals via the chalcogenide,⁴² as is observed in complexes **3a–c**.

Trimethylaluminum Adducts of $[\text{P}(\text{CH}_2\text{NAr}^R)_2\text{Se}](\text{AlMe}_2)_3$. The reaction of **2b,c** with excess AlMe_3 provides the adducts $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{NAr}^R)_2\text{Se}(\text{AlMe}_2)_3$ (**4b,c**) at room temperature, which can also be obtained by the addition AlMe_3 to **3b,c**, as shown in Scheme 1. The trimethylaluminum adduct of **3a** is too thermally unstable to be isolated in the solid state. Both **4b** and **4c** were obtained as white crystalline solids at room temperature and in this state are stable with respect to decomposition for several days. Single crystals of **4b** suitable for X-ray diffraction were obtained from toluene at -30 °C. The solid-state molecular structure is shown in Figure 4, along with selected bond lengths and bond angles.

The solid-state molecular structure of **4b** has crystallographically imposed C_s symmetry. The connectivity is the same as that observed for **3b**, but with an additional AlMe_3 moiety bound to the phosphine lone pair. The Al–P distance of 2.553(2) Å is significantly elongated in comparison to the sum of the covalent radii (2.350 Å) of Al and P, but within the range observed for aluminum–phosphine adducts.^{43,44} In the solid-state structure of **4b** the sum of C–Al(3)–C angles is 353.24(39)°, which is close to that for a trigonal planar system. The C(12,13)–Al(3)

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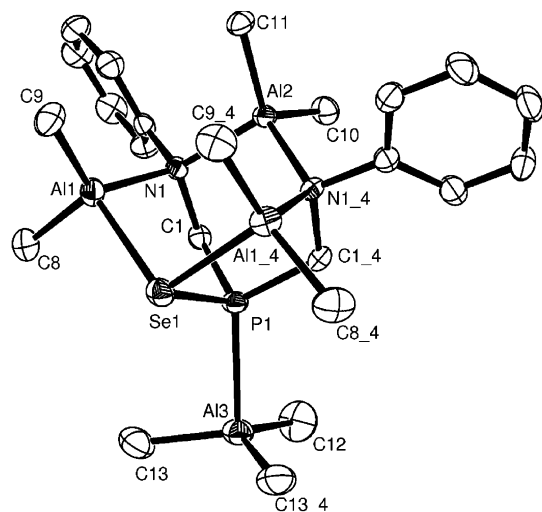


Figure 4. Solid-state molecular structure of **4b** as determined by X-ray crystallography. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected distances (Å): Al(3)–P(1), 2.553(2); Al(3)–C(13), 1.958(5); Al(3)–C(12), 1.951(7); Se(1)–P(1), 2.2388(16); Se(1)–Al(1), 2.5104(13); P(1)–C(1), 1.822(4); N(1)–Al(1), 1.990(3); N(1)–Al(2), 2.011(3). Selected bond angles (deg): C(1)–P(1)–C(1), 101.4(3); C(1)–P(1)–Se(1), 103.61(13); C(1)–P(1)–Al(3), 118.84(13); Al(1)–Se(1)–Al(1), 104.07(6); P(1)–Se(1)–Al(1), 89.86(4); N(1)–Al(1)–Se(1), 93.83(11); Al(1)–N(1)–Al(2), 122.26(17); C(1)–N(1)–Al(1), 104.1(2); C(1)–N(1)–Al(2), 108.2(2); C(12)–Al(3)–C(13), 119.12(18); C(13)–Al(3)–C(13), 115.0(3); C(13)–Al(3)–P(1), 97.45(16); C(12)–Al(3)–P(1), 101.1(3).

bond lengths range from 1.951(7) to 1.958(5) Å, which are almost identical to that of free AlMe_3 .⁴⁵ The change in $^{13}\text{C}\{-^1\text{H}\}$ NMR chemical shifts of the Al–Me₃ groups (**4b**, δ –8.0; **4c**, –7.8; free AlMe_3 , –8.1) are small, which also indicates only a slight distortion from planarity upon adduct formation.²⁶ All these factors are consistent with the poor σ -donor ability of the phosphine toward AlMe_3 in **4b** and **4c**.

The binding of trimethylaluminum to the phosphine donor in **4b** has an effect on the ancillary ligand bond lengths. In particular, the P–Se bond length of 2.2388(16) Å in **4b** is approximately 0.04 Å shorter than in either **3a** or **3c**. Additionally, the Se(1)–Al(1) bond length of 2.5104(13) Å in **4b** is slightly longer than the Se–Al bond lengths in **3a**, which are 2.4760(8) and 2.4866(8) Å, or in **3c**, where the bond lengths are 2.4909(9) and 2.4979(9) Å. These bond lengths can be interpreted in terms of a slight contribution from resonance structures where the phosphorus atom is formally an anionic P(V) donor,¹⁰ as shown in Scheme 2, though the structure is still best described by the resonance structure containing a P–Se single bond.

The ^1H NMR spectra of **4b,c** are consistent with the C_3 symmetry observed in the solid-state structure of **4b**. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **4b** and **4c** consist of singlets at δ –8.4

and –9.4 and display selenium satellites with $^1J_{\text{SeP}}$ values of 349.4 and 312.0 Hz, respectively. The change in the ^{31}P chemical shifts upon forming the adducts **4b,c** from **3b,c** to slightly higher field is fairly typical for phosphine donors with moderately large cone angles ($\Delta\delta$ = –4.3 for **b**; –6.0 for **c**).⁴⁴ The $^1J_{\text{SeP}}$ values are within the range expected for the P–Se single bonds,³⁷ but much greater than the values observed for **3b,c**. Moreover, the difference in these $^1J_{\text{SeP}}$ values of 37.4 Hz is much larger than in complexes **3b,c**, where the difference in $^1J_{\text{SeP}}$ is only 2.3 Hz. The vastly different $^1J_{\text{SeP}}$ values in **4b,c** indicate a large influence of the aryl substituents on the bonding in these complexes and their importance in determining the relative contributions of the resonance structures shown in Scheme 2.

Aluminum Complexes with the $\text{P}(\text{CH}_2\text{NAr}^{\text{R}})_3$ Ligands.

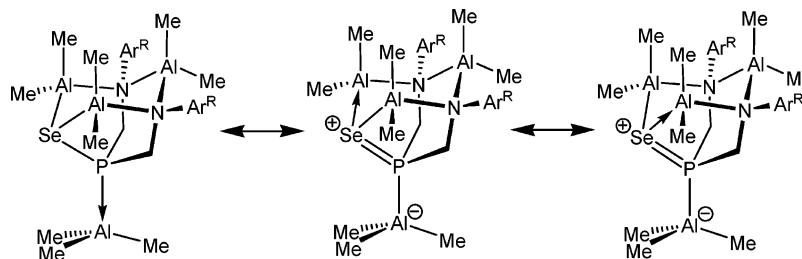
The tripodal diamidoselenophosphinito ligand in **3a–c** and **4b,c** promote the formation of triangular complexes, which is not typical of tripodal ligands,²² and a comparison to the parent $\text{P}(\text{CH}_2\text{NAr}^{\text{R}})_3$ ligands was desired to determine what factors might favor triangular trinuclear complex formation. The room-temperature reactions of **1a–c** with 2 equiv of AlMe_3 over 24 h cleanly provide the bimetallic aluminum amido complexes $[\text{P}(\text{CH}_2\text{NAr}^{\text{R}})_3]\text{Al}_2\text{Me}_3$ (**5a–c**) as white crystalline solids, as shown in Scheme 3. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra of these complexes in C_6D_6 are consistent with complexes of C_3 symmetry with the connectivity shown. For example, there are three Al–Me environments of equal intensities observed in the ^1H NMR of each of these complexes, and three PCH_2 environments are observed, in a 2:2:2 ratio, a pair of which are due to diastereotopic environments.

The solid-state structure of **5a** was determined by X-ray crystallography and is depicted in Figure 5. The triamidophosphine ligand binds to a central AlMe fragment with three nitrogen atoms, and two of these amido donors bridge to an AlMe_2 moiety. The phosphine donor is directed away from the central aluminum atom. Both geometries around the two aluminum centers are distorted tetrahedral.

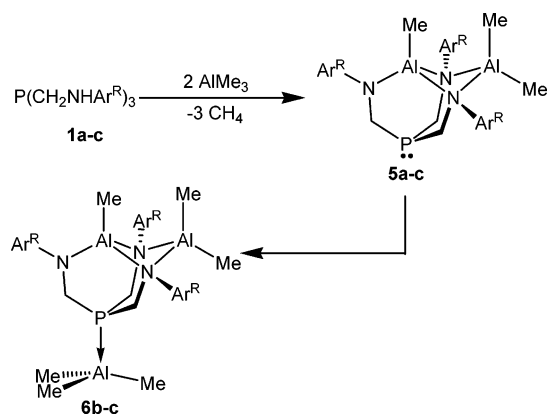
For example, the N(2)–Al(2)–N(3) angle of 81.40(9)° is more acute than the C(29)–Al(2)–C(30) angle of 117.77(17)°. The bond length of 1.964(2) Å for Al(1)–N(2) is about 0.032 Å shorter than that of 1.996(3) Å for Al(2)–N(2), but both distances are considerably longer than the terminal amido Al(1)–N(1) bond length of 1.829(3) Å. The aromatic substituent on the terminal amido donor is aligned such that its π -system has considerable overlap with the lone pair on the nitrogen, whereas the aromatic substituents associated with the bridging amido donors are aligned so that aromatic π -system is nearly orthogonal to the lone-pair p-orbital.

The reaction of the triamidophosphines (**1b,c**) with excess AlMe_3 at room temperature provides the Lewis acid–base adducts of **5b,c**, $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{NAr}^{\text{R}})_3\text{Al}_2\text{Me}_3$ (**6b,c**). These complexes could also be generated by the addition of AlMe_3 to **5b,c**, as shown in Scheme 3. Similar to **3a**, adducts of **5a** could

Scheme 2



Scheme 3



not be isolated. Single crystals of **6b** suitable for X-ray diffraction were obtained from toluene at $-30\text{ }^\circ\text{C}$. An ORTEP depiction is shown in Figure 6, along with selected bond lengths and bond angles.

The connectivity in **6b** is essentially the same as that observed for complexes **5a-c**, but with an additional $AlMe_3$ moiety bound to the phosphine lone pair. The sum of $C-Al(3)-C$ angles is $351.25(43)^\circ$, and $C-Al(3)$ bond lengths range from 1.946(3) to 1.966(3) Å. The small change in ^{13}C chemical shift of $Al-Me_3$ groups also indicates the slight distortion from planarity of aluminum.⁴⁴ The $^{31}P\{^1H\}$ NMR spectra of **6b** and **6c** contain resonances at $\delta -45.5$ and -44.5 , respectively, which are shifted to lower field by approximately +6 ppm compared to compounds **5b,c**. Adduct **6b** has slightly longer $Al-C$ bond distances and smaller $C-Al-C$ angles for the $AlMe_3$ moiety than in **4b**, which indicates that slightly stronger Lewis acid–base interactions occur in **6b**.³⁶ This is consistent with the shorter $Al-P$ distance of 2.5151(7) Å in **6b** than that of 2.553(2) Å in **4b**.

Ligand Design and Bonding Modes. Both the amido and selenophosphinito donors show a propensity to bridge, and so this cannot be the only factor that leads to the formation of triangular complexes for **3a-c**, but not for **5a-c**. To improve these ligand designs to assemble triangular complexes with a variety of metal precursors requires a better understanding of what factors promote polynuclear complex formation. The geometry of the ligand plays a role in the assembly of the trinuclear complexes in the case of **3a-c**. For the supporting diamidoselenophosphinito donor to chelate all its anionic donors to a central aluminum atom would require the formation of a [2.2.1] bicyclic. The resultant two five-membered rings and one six-membered ring seem ideal in terms of chelate ring sizes, but the fused nature of these rings leads to considerable strain and results in less than tetrahedral bond angles. For example, the analogous hydrocarbon norbornane possesses 71.8 kJ/mol of ring strain.⁴⁶

Conclusions

The reaction of the ligand precursors $Se=P(CH_2NHAr^R)_3$ (**2a-c**) with 4 equiv of $AlMe_3$ provides facile synthetic routes to triangular trinuclear complexes (**3a-c**) of the unanticipated diamidoselenophosphinito ligands, with concomitant loss of 1 equiv of $[Et(Ar^R)NAlMe_2]_n$. Tetranuclear complexes can be obtained by the formation of adducts with $AlMe_3$ at the phosphine donor. The large influence of adduct formation on

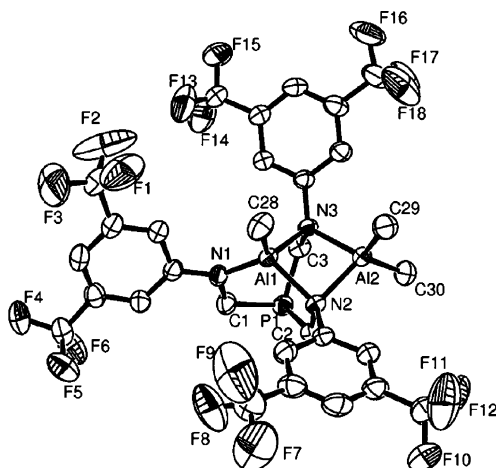


Figure 5. Solid-state molecular structure of **5a** as determined by X-ray crystallography. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected distances (Å): $P(1)-C(1)$, 1.844(3); $P(1)-C(2)$, 1.844(3); $P(1)-C(3)$, 1.856(3); $N(1)-Al(1)$, 1.829(3); $N(2)-Al(1)$, 1.964(2); $N(3)-Al(1)$, 1.958(2); $N(2)-Al(2)$, 1.996(3); $N(3)-Al(2)$, 1.997(2); $C(28)-Al(1)$, 1.930(3); $C(29)-Al(2)$, 1.948(4); $C(30)-Al(2)$, 1.947(4). Selected bond angles (deg): $C(1)-P(1)-C(2)$, 99.06(15); $C(1)-P(1)-C(3)$, 101.71(14); $C(2)-P(1)-C(3)$, 103.39(14); $N(1)-Al(1)-C(28)$, 119.30(14); $N(1)-Al(1)-N(2)$, 111.15(11); $N(1)-Al(1)-N(3)$, 107.67(11); $N(2)-Al(1)-N(3)$, 83.18(10); $C(29)-Al(2)-C(30)$, 117.77(17); $N(2)-Al(2)-C(29)$, 110.60(14); $N(3)-Al(2)-C(29)$, 114.06(13); $N(2)-Al(2)-N(3)$, 81.40(10).

the $^1J_{SeP}$ values as well the sensitivity of these values to the nature of Ar^R indicates that considerable delocalization of bonding occurs. These ligands may be an improvement to the $P(CH_2NHAr^R)_3$ ligands for the formation of polynuclear clusters of paramagnetic metals, where strong magnetic coupling between metal centers is desired, due to the increased polarizability of the selenophosphinito donor relative to amido donors.

The $P(CH_2NHAr^R)_3$ ligand precursors show no propensity to form triangular trinuclear structures, instead forming the dinuclear complexes $[P(CH_2NHAr^R)_3]Al_2Me_3$ and the adducts $Me_3Al \cdot [P(CH_2NHAr^R)_3]Al_2Me_3$. The preference of the diamidoselenophosphinito ligands in **3a-c** to form trinuclear structures, as opposed to adopting a $\kappa Se,N,N$ bonding mode similar to the $\kappa N,N,N$ bonding observed in complexes **5a-c**, can be ascribed to the ring strain associated with [2.2.1] bicyclic systems. We are currently investigating the coordination chemistry of these ligands with trivalent first-row transition metals in an attempt to generate paramagnetic analogues of these diamagnetic polynuclear aluminum complexes.

Experimental Section

General Procedures. All experiments were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane and toluene were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas. Deuterated benzene was dried by heating at reflux with sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled and freeze–pump–thaw degassed three times. NMR spectra were recorded on a Bruker AMX (300 MHz) or Bruker AMX (500 MHz) spectrometer. All chemical shifts are reported in ppm, and all coupling constants are in Hz. For ^{19}F NMR spectra, trifluoroacetic acid was used as the external reference at 0.00 ppm. 1H NMR spectra were referenced to residual protons (C_6D_5H , δ 7.15). $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3-

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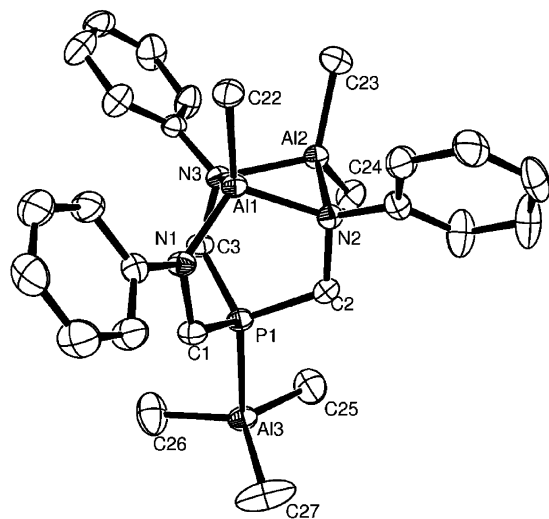


Figure 6. ORTEP depiction of the solid-state molecular structure of **6b** as determined by X-ray crystallography. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected distances (Å): P(1)–Al(3), 2.5151(7); P(1)–C(1), 1.8222(18); P(1)–C(2), 1.8328(19); P(1)–C(3), 1.8426(18); N(1)–Al(1), 1.8253(16); N(2)–Al(1), 1.9903(16); N(3)–Al(1), 1.9645(15); N(2)–Al(2), 1.9970(15); N(3)–Al(2), 1.9833(16); C(22)–Al(1), 1.9474(19); C(24)–Al(2), 1.945(2); C(23)–Al(2), 1.947(2); Al(3)–C(25), 1.960(2); Al(3)–C(26), 1.966(3); Al(3)–C(27), 1.946(3). Selected bond angles (deg): C(1)–P(1)–C(2), 101.96(9); C(1)–P(1)–C(3), 104.48(8); C(2)–P(1)–C(3), 105.72(8); C(2)–P(1)–Al(3), 114.35(6); C(3)–P(1)–Al(3), 112.73(6); N(1)–Al(1)–C(22), 118.28(8); N(1)–Al(1)–N(2), 110.19(7); N(1)–Al(1)–N(3), 107.88(7); N(2)–Al(1)–N(3), 82.66(6); C(23)–Al(2)–C(24), 117.82(9); N(2)–Al(2)–C(24), 113.97(8); N(3)–Al(2)–C(24), 115.08(8); N(2)–Al(2)–N(3), 82.02(6); C(26)–Al(3)–C(27), 116.59(16); C(25)–Al(3)–C(26), 117.39(12); C(25)–Al(3)–C(27), 117.27(15); C(27)–Al(3)–P(1), 101.32(9); C(26)–Al(3)–P(1), 99.28(8); C(25)–Al(3)–P(1), 99.23(7).

PO_4 at δ 0.0. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced relative to solvent resonances (C_6D_6 , δ 128.0). $^{77}\text{Se}\{^1\text{H}\}$ spectra were referenced relative to external Me_2Se in CDCl_3 . Elemental analyses were performed by the Centre for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. The ligand precursors $\text{P}(\text{CH}_2\text{NHAr}^R)_3$ (**1a–c**) were prepared as previously reported.⁷ Selenium powder and 2.0 M AlMe_3 in toluene were purchased from Aldrich and used as received.

Preparation of $\text{Se}=\text{P}[\text{CH}_2\text{NH-3,5-(CF}_3)_2\text{C}_6\text{H}_3]_3$ (2a**).** Selenium (789 mg, 10 mmol) was added to a solution of $\text{P}(\text{CH}_2\text{NH-3,5-(CF}_3)_2\text{C}_6\text{H}_3)_3$ (**1a**) (3.78 g, 5 mmol) in 50 mL of toluene. The solution was stirred 24 h and then filtered to remove the excess selenium. The solvent was removed under vacuum, and the remaining white solid was rinsed with a small portion of pentane and then dried under vacuum (3.55 g, 85%). Single crystals were grown from a mixture of ethanol (50%) and acetone (50%) at -30°C . ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 2.77 (dd, $^3J_{\text{HH}} = 5.8$ Hz, $^2J_{\text{PH}} = 5.2$ Hz, 6H, PCH_2), 3.94 (q, 3H, NH), 6.56 (s, 6H, Ph *o-H*), 7.28 (s, 3H, Ph *p-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ 40.3 (d, $J_{\text{PC}} = 49.4$ Hz, PCH_2), 113.3 and 122.4 (s, Ph *o-C* and *m-C*), 113.6 (s, Ph *p-C*), 133.4 (q, $J = 33.5$ Hz, PhC-F_3), 147.8 (d, $J = 8.8$ Hz, *ipso-C*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ 42.6 (s with satellites, $J_{\text{SeP}} = 742.8$ Hz.). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -463.8 (d, $J_{\text{SeP}} = 743.3$ Hz.). ^{19}F NMR (C_6D_6 , 282.1 MHz, 298 K): δ 14.68 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{F}_6\text{N}_3\text{SeP}$: C, 38.75; H, 2.17; N, 5.02. Found: C, 39.1; H, 2.46; N, 5.06.

Preparation of $\text{Se}=\text{P}(\text{CH}_2\text{NHPh})_3$ (2b**).** **2b** was prepared in an analogous manner to **2a** using $\text{P}(\text{CH}_2\text{NHPh})_3$ (**1b**) (1.75 g, 5 mmol) in lieu of **1a** with a yield of 1.92 g, 80%. Single crystals

were grown from a mixture of ethanol (50%) and acetone (50%) at -30°C . ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 3.30 (dd, $^3J_{\text{HH}} = 5.6$ Hz, $^2J_{\text{PH}} = 5.6$ Hz, 6H, PCH_2), 3.95 (b, 3H, NH), 6.36 (d, $^3J_{\text{HH}} = 8.5$ Hz, 6H, Ph *o-H*), 6.71 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H, Ph *p-H*), 7.03 (m, 6H, Ph *m-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ 42.1 (d, $J_{\text{PC}} = 47.8$ Hz, PCH_2), 114.5 and 119.9 (s, Ph *o-C* and *m-C*), 130.1 (s, Ph *p-C*), 147.6 (d, $J = 7.1$ Hz, *ipso-C*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ 46.3 (s with satellites, $J_{\text{SeP}} = 719.7$ Hz.). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 57.2 MHz, 298 K): δ -455.2 (d, $J_{\text{SeP}} = 720.8$ Hz.). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{PSe}$: C, 58.88; H, 5.65; N, 9.81. Found: C, 58.95; H, 5.47; N, 9.44.

Preparation of $\text{Se}=\text{P}(\text{CH}_2\text{NH-3,5-Me}_2\text{C}_6\text{H}_3)_3$ (2c**).** **2c** was prepared in an analogous manner to **2a** using $\text{P}(\text{CH}_2\text{NH-3,5-Me}_2\text{C}_6\text{H}_3)_3$ (**1c**) (1.75 g, 5 mmol) in lieu of **1a** with a yield of 2.22 g, 87%. Single crystals were grown from a mixture of ethanol (50%) and acetone (50%) at -30°C . ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 2.18 (s, 18H, PhCH_3), 3.51 (dd, $^3J_{\text{HH}} = 5.7$ Hz, $^2J_{\text{PH}} = 5.7$ Hz, 6H, PCH_2), 4.05 (b, 3H, NH), 6.16 (s, 6H, Ph *o-H*), 6.40 (s, 3H, Ph *p-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ 21.8 (s, PhCH_3), 42.1 (d, $J_{\text{PC}} = 47.2$ Hz, PCH_2), 112.5 and 121.9 (s, Ph *o-C* and *m-C*), 139.4 (s, Ph *p-C*), 147.6 (d, $J = 7.1$ Hz, *ipso-C*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ 44.46 (s with satellites, $J_{\text{SeP}} = 716.1$ Hz.). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 57.2 MHz, 298 K): δ -453.2 (d, $J_{\text{SeP}} = 716.9$ Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{N}_3\text{PSe}$: C, 63.27; H, 7.08; N, 8.20. Found: C, 63.51; H, 6.9; N, 7.93.

Preparation of $\text{P}[\text{CH}_2\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3]_2\text{Se}(\text{AlMe}_2)_3$ (3a**).** A 2.0 M solution of AlMe_3 in toluene (2.0 mL, 4.0 mmol) was added to a solution of **2a** (836.1 mg, 1 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane. The white solid was collected by filtration and dried (382 mg, 50%). X-ray-quality crystals were obtained from slow evaporation of a benzene solution. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ -1.71 and -0.28 (s, 3H each, $\text{N,N}'\text{-AlMe}_2$), -0.98 and 0.05 (s, 6H each, Se, N-AlMe_2), 2.93 (s, 2H, PCH_2), 2.95 (d, 2H, PCH_2), 7.44 (s, 2H, Ph *o-H*), 7.69 (s, 4H, Ph *p-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -9.4 , -7.9 , -3.9 , and -2.8 (s, AlMe_2), δ 46.4 (d, $J_{\text{PC}} = 41.2$ Hz, PCH_2), 118.3 and 123.5 (s, Ph *o-C* and *m-C*), 121.5 (s, Ph *p-C*), 133.6 (q, $J = 33.4$ Hz, PhC-F_3), 148.0 (s, *ipso-C*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -4.7 (s with satellites, $J_{\text{SeP}} = 176.2$ Hz). ^{19}F NMR (C_6D_6 , 282.1 MHz, 298 K): δ 14.81 (s). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -430.0 (d, $J_{\text{SeP}} = 176.6$ Hz). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{Al}_3\text{F}_6\text{N}_2\text{PSe}$: C, 37.76; H, 3.70; N, 3.67. Found: C, 38.20; H, 3.58; N, 3.76.

The pentane rinse was hydrolyzed with water, with the evolution of gas. The sample was extracted into C_6D_6 and passed through a short plug of alumina. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 0.62 (t, 3H, $^3J_{\text{HH}} = 7.3$ Hz, CH_2CH_3), 2.26 (qd, 2H, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 5.2$ Hz, NHCH_2CH_3), 5.2 (br, 1H, NH), 6.42 (s, 2H, Ph *o-H*), 7.21 (s, 1H, Ph *p-H*), consistent with $\text{EtN}(\text{H})\text{-3,5-(CF}_3)_2\text{C}_6\text{H}_3$.

Preparation of $\text{P}(\text{CH}_2\text{NPh})_2\text{Se}(\text{AlMe}_2)_3$ (3b**).** **3b** was prepared in an analogous manner to **3a** using **2b** (428.4 mg, 1.0 mmol) in lieu of **2a** with an isolated yield of 245.6 mg, 50%. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ -1.36 and -0.04 (s, 3H each, $\text{N,N}'\text{-AlMe}_2$), -0.81 , 0.23 (s, 6H each, Se, N-AlMe_2), 3.24 and 3.24 (m, 4H total, PCH_2), 6.81 (t, 2H, $J = 7.3$ Hz, Ph *p-H*), 7.0 (dd, 4H, Ph *m-H*), 7.17 (d, 4H, Ph *o-H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -15.1 , -8.6 , -5.8 , and -2.7 (s, AlMe_2), δ 46.7 (d, $J_{\text{PC}} = 36.5$ Hz, PCH_2), 122.05 and 125.5 (s, Ph *o-C* and *m-C*), 130.0 (s, Ph *p-C*), 145.9 (s, *ipso-C*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -4.1 (s with satellites, $J_{\text{SeP}} = 179.0$ Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -433.0 (d, $J_{\text{SeP}} = 179.9$ Hz.). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{Al}_3\text{N}_2\text{PSe}$: C, 48.89; H, 6.56; N, 5.70. Found: C, 48.48; H, 6.23; N, 5.89.

Preparation of $\text{P}(\text{CH}_2\text{N-3,5-Me}_2\text{C}_6\text{H}_3)_2\text{Se}(\text{AlMe}_2)_3$ (3c**).** **3c** was prepared in an analogous manner to **3a** using **2c** (512.5 mg, 1.0 mmol) in lieu of **2a** with an isolated yield of 328.5 mg, 60%. X-ray-

quality crystals were obtained from slow evaporation of a benzene solution. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ -1.24 and 0.03 (s, 3H each, $\text{N},\text{N}'\text{-AlMe}_2$), -0.74 and 0.30 (s, 6H each, Se, N-AlMe_2), 2.05 (s, 12H, PhCH_3), 3.30 (s, 2H, PCH_2), 3.32 (d, 2H, PCH_2), 6.51 (s, 2H, Ph *o*-H), 6.96 (s, 4H, Ph *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -14.8, -8.4, -5.6, and -2.3 (s, AlMe_2), 21.8 (s, PhCH_3), 46.7 (d, $J_{\text{PC}} = 37.3$ Hz, PCH_2), 120.1 and 127.4 (s, Ph *o*-C and *m*-C), 137.8 (s, Ph *p*-C), 146.1 (s, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -3.4 (s with satellites, $J_{\text{SeP}} = 181.3$ Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -434.9 (d, $J_{\text{SeP}} = 182.7$ Hz). Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{Al}_3\text{N}_2\text{PSe}$: C, 52.65; H, 7.36; N, 5.12. Found: C, 52.29; H, 6.99; N, 4.75.

Preparation of $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{NPh})_3\text{Se}(\text{AlMe}_2)_3$ (4b). A solution of AlMe_3 in toluene (3.0 mL, 2.0 M, 6.0 mmol) was added to a solution of **2b** (428.4 mg, 1.0 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane. The white solid was collected by filtration and dried (310 mg, 55%). X-ray-quality crystals were obtained from toluene solution at -30 °C. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ -1.04 and -0.69 (s, 3H each, $\text{N},\text{N}'\text{-AlMe}_2$), -0.80, 0.13, (s, 6H, Se, N-AlMe_2), -0.46 (s, 4H, P-AlMe_3), 3.54 (m, 4H, PCH_2), 2.83 (m, 2H, PCH_2), 6.81 (m, 9H, Ph *o*-H), 7.07 (m, 6H, Ph *p*-H and Ph *m*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -14.7, -8.5, -5.4, and -2.1 (s, AlMe_2), -8.0 (s, P-AlMe_3), 46.3 (d, $J_{\text{PC}} = 36.7$ Hz, PCH_2), 121.05 and 126.0 (s, Ph *o*-C and *m*-C), 130.0 (s, Ph *p*-C), 145.6 (s, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -8.4 (s with satellites, $J_{\text{SeP}} = 349.4$ Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -435.0 (d, $J_{\text{SeP}} = 349.7$ Hz). Anal. Calcd for $\text{C}_{23}\text{H}_{41}\text{Al}_4\text{N}_2\text{PSe}$: C, 49.03; H, 7.33; N, 4.91. Found: C, 49.43; H, 6.99; N, 4.87.

Preparation of $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{N-3,5-Me}_2\text{C}_6\text{H}_3)_2\text{Se}(\text{AlMe}_2)_3$ (4c). A solution of AlMe_3 in toluene (3 mL, 2.0 M, 6 mmol) was added to a solution of **2c** (512.5 mg, 1 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane. The white solid was collected by filtration and dried (403 mg, 65%). ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ -0.837 and -0.63 (s, 3H each, $\text{N},\text{N}'\text{-AlMe}_2$), -0.171 and 0.291 (s, 6H each, Se, N-AlMe_2), -0.447 (s, 9H, P-AlMe_3), 1.866, 1.994 (s, 6H each, PhCH_3), 2.56 (dd, 1H, PCH_2), 3.50 (m, 1H, PCH_2), 3.67 (m, 1H, PCH_2), 3.86 (dd, 1H, PCH_2), 6.5 (s, 2H, Ph *o*-H), 6.6 (s, 4H, Ph *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -14.1, -8.1, -2.25, and -1.63 (s, AlMe_2), -7.8 (s, P-AlMe_3), 21.8 (s, PhCH_3), δ 47.3 (m, PCH_2), 120.0 and 127.5 (s, Ph *o*-C and *m*-C), 142.7 (s, Ph *p*-C), 146.1 (d, $J = 19.5$ Hz, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -9.4 (s with satellites, $J_{\text{SeP}} = 312.0$ Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz, 298 K): δ -436.1 (d, $J_{\text{SeP}} = 312.9$ Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{49}\text{Al}_4\text{N}_2\text{PSe}$: C, 52.3; H, 7.97; N, 4.52. Found: C, 52.79; H, 7.68; N, 4.26.

Preparation of $\text{P}[\text{CH}_2\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3]_3\text{Al}_2\text{Me}_3$ (5a). A solution of AlMe_3 in toluene (3.09 mL, 2.0 M, 6.18 mmol) was added to a solution of **1a** (2.34 g, 3.09 mmol) in 15 mL of toluene. The solution was left for 12 h. The solution was evaporated to dryness, and the remaining solid was crystallized by cooling a saturated warm benzene solution to room temperature. The tan solid was collected by filtration and dried (1.5 g, 57%). A second crop was obtained by slow evaporation of the mother liquor. X-ray-quality crystals were obtained by slow evaporation of a benzene solution. ^1H NMR (C_6D_6 , 500 MHz, 298 K): δ -0.84 and -0.56 (s, 3H each, AlMe_2), -0.26 (s, 3H, AlMe), 2.70 (dd, 2H, $^2J_{\text{PH}} = 1.3$ Hz, $^2J_{\text{HH}} = 14.5$ Hz, PCH_2), 2.83 (d, 2H, $^2J_{\text{PH}} = 6.8$ Hz, PCH_2), 3.56 (dd, 2H, $^2J_{\text{PH}} = 16.9$ Hz, $^2J_{\text{HH}} = 14.4$ Hz, PCH_2), 7.30 (s, 2H, *p*-H), 7.38 (s, 1H, *p*-H), 7.45 (s, 4H, *o*-H), 7.50 (s, 2H, *o*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -14.5, -5.6, and -1.4 (s, AlMe), -5.16 (s, AlMe), 44.8 (d, $J_{\text{PC}} = 23.1$ Hz, PCH_2), 50.7 (d, $J_{\text{PC}} = 15.1$ Hz, PCH_2), 121.1 and 123.4 (s, Ph *o*-C and *m*-C),

124.6 (s, Ph *p*-C), 129.9 (m, PhC-F_3), 149.4 (s, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -54.2 (s). ^{19}F NMR (C_6D_6 , 282.1 MHz, 298 K): δ 14.67 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{-Al}_2\text{F}_{18}\text{N}_3\text{P}$: C, 42.22; H, 2.84; N, 4.92. Found: C, 41.77; H, 3.30; N, 4.89.

Preparation of $\text{P}(\text{CH}_2\text{NPh})_3\text{Al}_2\text{Me}_3$ (5b). A solution of AlMe_3 in toluene (1 mL, 2.0 M, 2 mmol) was added to a solution of **1b** (349.4 mg, 1 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane prior to crystallization from benzene. The white solid was collected by filtration and dried (328.5 mg, 60%). ^1H NMR (C_6D_6 , 500 MHz, 298 K): δ -0.6, 0.22, and -0.16 (s, 3H each, AlMe), 3.14 (d, 2H, $J = 14.2$ Hz, PCH_2), 3.53 (d, 2H, $J = 6.8$ Hz, PCH_2), 4.00 (dd, 2H, $^2J_{\text{HH}} = 14.2$ Hz, $^2J_{\text{PH}} = 16.6$ Hz, PCH_2), 6.86 and 6.88 (m, 3H total, *p*-H), 6.96 (dd, 4H, $J = 7.7$ Hz, *m*-H), 7.09 (d, 4H, $J = 7.7$ Hz, *o*-H), 7.22 (d, 2H, $J = 8.1$ Hz, *o*-H), 7.33 (dd, 2H, *m*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -11.1, -9.2, and -7.9 (s, AlMe_2), 49.7 (d, $J_{\text{PC}} = 12.9$ Hz, PCH_2), 55.5 (d, $J_{\text{PC}} = 27.0$ Hz, PCH_2), 116.8, 118.3, 125.8, 125.9, 129.5, and 130.1 (s, Ph *o*-C, *m*-C, and *p*-C), 150.6 and 154.6 (s, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -51.3 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{Al}_2\text{N}_3\text{P}$: C, 64.71; H, 6.79; N, 9.43. Found: C, 64.51; H, 6.93; N, 9.74.

Preparation of $\text{P}(\text{CH}_2\text{N-3,5-Me}_2\text{C}_6\text{H}_3)_3\text{Al}_2\text{Me}_3$ (5c). A solution of AlMe_3 in toluene (1 mL, 2.0 M, 2 mmol) was added to a solution of **1c** (433.6 mg, 1 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane prior to crystallization from benzene. The white solid was collected by filtration and dried (413.5 mg, 78%). ^1H NMR (C_6D_6 , 500 MHz, 298 K): δ -0.45, -0.1, and -0.02 (s, 3H each, AlMe), 2.0 (s, 12H, PhCH_3), 2.33 (s, 6H, PhCH_3), 3.30 (dd, 2H, $^2J_{\text{PH}} = 1.2$ Hz, $^2J_{\text{HH}} = 14.3$ Hz, PCH_2), 3.64 (d, 2H, $^2J_{\text{PH}} = 6.5$ Hz, PCH_2), 4.16 (dd, 2H, $^2J_{\text{HH}} = 14.3$ Hz, PCH_2), 6.56 (s, 1H, Ph *o*-H), 6.58 (s, 1H, Ph *o*-H), 6.95 (s, 6H, Ph *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -19.8, -7.3, and -5.8 (s, AlMe), 21.4 (s, PhCH_3), 22.3 (s, PhCH_3), 50.5 (d, PCH_2), 56.0 (d, PCH_2), 115.5, 120.5, 124.0, and 140.1 (s, Ph *o*-C and *p*-C), 151.1 and 155.1 (s, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -50.5 (s). $\text{C}_{30}\text{H}_{42}\text{-Al}_2\text{N}_3\text{P}$: C, 68.03; H, 7.99; N, 7.93. Found: C, 67.79; H, 7.95; N, 7.63.

Preparation of $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{NPh})_3\text{Al}_2\text{Me}_3$ (6b). A solution of AlMe_3 in toluene (5.0 mL, 2.0 M, 10.0 mmol) was added to a solution of **1b** (699 mg, 2.0 mmol) in 50 mL of toluene. The solution was left for 48 h. The colorless solution was evaporated to dryness, and the remaining solid was rinsed by pentane. The white solid was collected by filtration and dried (558 mg, 54%). X-ray-quality crystals were obtained from slow evaporation of a pentane solution at -30 °C. ^1H NMR (C_6D_6 , 500 MHz, 298 K): δ -0.68, -0.30, and -0.13 (s, 3H each, AlMe), -0.37 (s, 9H, P-AlMe_3), 3.22 (dd, 2H, $^2J_{\text{PH}} = 4.8$ Hz, $^2J_{\text{HH}} = 4.8$ Hz, PCH_2), 3.70 (s, 2H, PCH_2), 4.10 (dd, 2H, $^2J_{\text{PH}} = 8.6$ Hz, $^2J_{\text{HH}} = 5.6$ Hz, PCH_2), 6.9, 7.1, and 7.28 (m, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz, 298 K): δ -10.8, -9.0, and -8.5 (s, AlMe_2), -8.0 (s, P-AlMe_3), 47.3 (d, $J_{\text{PC}} = 10.3$ Hz, PCH_2), 52.7 (s, PCH_2), 117.7, 119.7, 126.0, 126.8, 130.0, and 130.6 (s, Ph *o*-C, *m*-C, and *p*-C), 149.8 (d, $J = 3.7$ Hz, *ipso*-C), 153.8 (d, $J = 6.2$ Hz, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz, 298 K): δ -45.5 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{39}\text{Al}_3\text{N}_3\text{P}$: C, 62.66; H, 7.60; N, 8.12. Found: C, 62.17; H, 6.95; N, 7.72.

Preparation of $\text{Me}_3\text{Al}\cdot\text{P}(\text{CH}_2\text{N-3,5-Me}_2\text{C}_6\text{H}_3)_3\text{Al}_2\text{Me}_3$ (6c). A solution of AlMe_3 in toluene (2.0 mL, 2.0 M, 4.0 mmol) was added to a solution of **1c** (433.6 mg, 1 mmol) in 25 mL of toluene. The solution was stirred at room temperature for 24 h. The solution was evaporated to dryness, and the remaining solid was rinsed by pentane. The white solid was collected by filtration and dried (367 mg, 60%). ^1H NMR (C_6D_6 , 500 MHz, 298 K): δ -0.57, -0.25,

and 0.01 (s, 3H each, AlMe), -0.38 (s, 9H, P-AlMe₃), 2.00 (s, 12H, PhCH₃), 2.27 (s, 6H, PhCH₃), 3.45 (dd, 2H, $^2J_{\text{PH}} = 9.5$ Hz, $^2J_{\text{HH}} = 5.1$ Hz, PCH₂), 3.87 (s, 2H, PCH₂), 4.29 (dd, 2H, $^2J_{\text{PH}} = 8.6$ Hz, $^2J_{\text{HH}} = 6.7$ Hz, PCH₂), 6.87 (s, 3H, Ph *o*-H), 7.00 (s, 6H, Ph *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 125.8 MHz, 298 K): δ -14.2 and -10.4 (s, AlMe₂), -8.8 (s, P-AlMe₃), -7.4 (s, AlMe), 21.5 (s, PhCH₃), 22.2 (s, PhCH₃), 47.7 (d, $J_{\text{PC}} = 12.7$ Hz, PCH₂), 52.8 (s, PCH₂), 116.3, 124.0, and 139.0 (s, Ph *o*-C, *m*-C, and *p*-C), 150.2 (d, $J = 6.3$ Hz, *ipso*-C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 202.5 MHz, 298 K): δ -44.5 (s). Anal. Calcd for C₃₃H₅₁Al₃N₃P: C, 65.87; H, 8.54; N, 6.98. Found: C, 65.52; H, 8.21; N, 7.34.

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Supporting Information Available: Tables of crystallographic data; crystallographic information in CIF format for **2a–c**, **2b**, **3a**, **3c**, **4b**, **5a**, and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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