5874 *Inorg. Chem.* **2009**, *48*, 5874–5883
DOI: 10.1021/ic900166u

Inorganic Chemistry
Article

# Coordination Diversity of Aluminum Centers Molded by Triazole Based Chalcogen Ligands

**Jocelyn Alcántara-García,[†] Vojtech Jancik,[†] Joaquín Barroso,[‡] Sandra Hidalgo-Bonilla,[†] Raymundo Cea-Olivares,[†] Rubén A. Toscano,[†] and Mónica Moya-Cabrera*[,†]**

[†]*Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, México D.F., México, and* [‡]*Centro de investigación en Polímeros, Grupo COMEX, Marcos Achar Lobatón 2, 55885 Tepexpan, México*

Received January 26, 2009

Equimolar and excess ratio reactions of $AlMe_3$ and $Al^iBu_3$ with the ligands 4,5-$(P(E)Ph_2)_2$tzH (tz = 1,2,3-triazole; E = O (**1**), S (**2**), Se(**3**)) were performed, showing a vast variety of coordination modes. The products obtained, $[AlR_2\{\kappa^2\text{-}O,O'\text{-}[4,5\text{-}(P(O)Ph_2)_2tz]\}]$ (R = Me (**4**), $^i$Bu (**5**)), $[AlR_2\{\kappa^3\text{-}N,N',S\text{-}[4,5\text{-}(P(S)Ph_2)_2tz]\}(\mu\text{-}tz)]_2$ (R = Me (**6**), R = $^i$Bu (**7**)), $[AlMe_2\{\kappa^2\text{-}N,Se\text{-}[4,5\text{-}(P(Se)Ph_2)_2tz]\}]$ (**8**), $[Al\{\kappa^2\text{-}N,Se\text{-}[4,5\text{-}(P(Se)Ph_2)_2tz]\}_3]$ (**9**), $[AlR_2\{\kappa^2\text{-}O,O'\text{-}[4,5\text{-}(P(O)\text{-}Ph_2)_2tz]\}\text{-}(N'\text{-}AlR_3)]$ (R = Me (**10**), $^i$Bu (**11**)), and $[AlR_2\{\kappa^2\text{-}N,S\text{-}[4,5\text{-}(P(S)Ph_2)_2tz]\}\text{-}(N'\text{-}AlR_3)]$ (R = Me (**12**), R = $^i$Bu (**13**)), were characterized by spectroscopic methods, and the structures of **1**, **4**, **6**, **7**, **9**, **10**, and **12** were obtained through X-ray diffraction studies. Theoretical calculations were performed on the deprotonated ligands and on selected compounds to obtain information regarding the coordination variety observed for these compounds.

## Introduction

The chemistry of the heavy elements of group 13, namely, gallium and indium, has been substantially explored through $N[P(E)R_2]_2^-$ (E = S, Se) ligands.[1] However, the corresponding aluminum complexes remain scarce and so far, are yet to be structurally characterized. This contrasts with the considerable number of structurally characterized aluminum compounds bearing ligands with P═NR and C═N units, that span from bis(diphenylphosphine)methane,[2,3] amidinate[4] to $\beta$-diketimidato compounds.[5,6] The high Lewis acid character of Al(III) and the hardness of the nitrogen donor atoms along with the highly delocalized charge on the backbone of these ligands are accountable for this behavior. In this regard, multidentate amido and imido ligands have been amply used in the preparation of aluminum complexes. Indeed, there is a fairly extensive literature on the interaction of $AlR_3$ with five-membered nitrogen heterocycles. In this regard, 1,2-azole rings react readily with aluminum alkyls forming compounds bearing $M_2N_4$ rings and their structural outcome depends on the steric bulk present on both the azole ring and the alkyl groups.[7−10]

We have recently reported on the preparation of indium compounds bearing 4,5-bis(diphenylphosphoranyl)-1,2,3-triazole ligands (4,5-$(P(E)Ph_2)_2$tzH).[11] These ligands were first introduced by Trofimenko and used selectively in

---

*To whom correspondence should be addressed. E-mail: monica.moya@correo.unam.mx. Phone: + 52 (55) 56 22 44 01. Fax: + 52 (55) 56 16 22 17.

(1) Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.* **2001**, *223*, 117–216.

(2) (a) Aparna, K.; McDonald, R.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 9314–9315. (b) Cavell, R. G.; Aparna, K.; Kamalesh, B. R. P.; Wang, Q. *J. Mol. Catal.* **2002**, *189*, 137–143. (c) Aparna, K.; McDonald, R.; Ferguson, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4241–4243.

(3) (a) Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197–4204. (b) Hill, M. S.; Hitchcock, P. B.; Karagouni, S. M. A. *J. Organomet. Chem.* **2004**, *689*, 722–730.

(4) (a) Aeitls, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. *Organometallics* **1998**, *17*, 3265–3270. (b) Coles, M. P; Swenson, D. C.; Jordan, R. F.; Young, V. G.Jr. *Organometallics* **1997**, *16*, 5183–5194. (c) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125–8126.

(5) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031–3065.

(6) (a) Roesky, H. W. *Inorg. Chem.* **2004**, *43*, 7284–7293. (b) Roesky, H. W.; Kumar, S. S. *Chem. Commun.* **2005**, 4027–4038. (c) Roesky, H. W.; Singh, S. S.; Jancik, V.; Chandrasekhar, V. *Acc. Chem. Res.* **2004**, *37*, 969–981.

(7) (a) Zheng, W.; Mösch-Zanetti, N. C.; Roesky, H. W.; Hewitt, M.; Cimpoesu, F.; Schneider, T. R.; Stasch, A.; Prust, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3099–3102. (b) Zheng, W.; Hohmeister, H.; Mösch-Zanetti, N.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2001**, *40*, 2363–2367.

(8) (a) Lewiński, J.; Zachara, J.; Gós, P.; Grabska, E.; Kopeć, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem.−Eur. J.* **2000**, *6*, 3215–3227. (b) Lewiński, J.; Zachara, J.; Gós, P.; Kopeć, T.; Madura, I.; Prowotorow, I. *Inorg. Chem. Commun.* **1999**, *2*, 131–134.

(9) Cortés-Llamas, S. A.; Hernández-Pérez, J. M.; Ho, M.; Muñoz-Hernández, M. A. *Organometallics* **2006**, *25*, 588–595.

(10) (a) Yu, Z.; Knox, J. E.; Korolev, A. V.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Eur. J. Inorg. Chem.* **2005**, 330–337. (b) Sirimanne, C. T.; Yu, Z.; Heeg, M. J.; Winter, C. H *J. Organomet. Chem.* **2006**, *691*, 2517–2527.

(11) Moya-Cabrera, M.; Jancik, V.; Castro, R. A.; Herbst-Irmer, R.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 5167–5171.

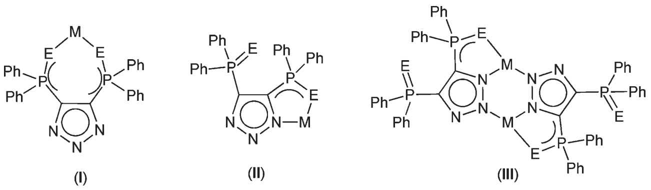


**Figure 1.** Coordination modes reported for ligands **1**− **3**.

the preparation of transitional (Pd, Ni, Rh, Co) and f-block (La, U) complexes, with Mg being the only main group metal explored.[12,13] The coordination patterns observed with these metals include the formation of a seven-membered ring (Figure 1, **I**) or the formation of a five-membered heterocycle (**II**), depending on either the metal or the chalcogen atom present on the ligand. However, in the case of the indium compounds only the formation of dinuclear species was observed (**III**).

The multifunctionality of the 4,5-bis(diphenylphosphoranyl)-1,2,3-triazoles, 4,5-(P(E)$Ph_2$)$_2$tzH [E = O (**1**), S (**2**), Se (**3**)], make them an interesting type of ligand for the preparation of aluminum complexes. This is due to their wide variety of coordination modes and the presence of both hard and soft donor atoms. In this regard, the coordination of a hard Lewis acid, such Al(III), to soft donor atoms (S, Se) can lead to a change in the acid properties of the metal center in the complexes obtained, and thus, to an overall modification of their chemical behavior. Indeed, there is a reduced number of examples of structurally characterized aluminum complexes that contain sulfur donor atoms in a chelating ancillary ligand.[14] Moreover, in the case of selenium, such types of aluminum compounds are extremely rare.[15,16] In this work, we describe the reaction of trialkylaluminum compounds ($AlR_3$, R=Me, $^i$Bu) in different molar ratios with 4,5-bis(diphenylphosphoranyl)-1,2,3-triazole ligands. The structures obtained include mono- and dinuclear aluminum compounds displaying a noticeable variety of coordination modes, with Al−E (E = O, S, Se) bonding as their most important feature. Additionally, theoretical calculations were performed on the deprotonated forms of the ligands, as well as on selected complexes.

## Experimental Section

**General Comments.** All reactions and handling of reagents were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and a glovebox. All glassware was oven-dried at 140 °C for at least 24 h, assembled hot under a stream of nitrogen prior to use. Toluene, hexanes, pentane, and tetrahydrofuran (Na/benzophenone ketyl) were dried and distilled prior to use. A 2.0 M solution of $AlMe_3$ in hexanes was purchased from Aldrich, and a 1.0 M solution of Al$^i$Bu$_3$ in toluene was prepared from neat Al$^i$Bu$_3$ (Aldrich). $^1$H (300 MHz), $^{31}$P (121.6 MHz), and $^{27}$Al (78.3 MHz) NMR spectra were recorded on a JEOL X300 spectrometer at 25 °C, unless otherwise stated. Chemical shifts are reported in ppm with reference to TMS (internal), $H_2PO_3$ 85% (external), or Al($H_2O$)$_6^{3+}$ (external). IR spectra were recorded on a Bruker Tensor 27 in the range 400−4000 cm$^{-1}$ as KBr discs. Mass spectra (EI) data were obtained on a JEOL JMS-AX505HA (70 eV) utility. Elemental analyses (C, H, N) were performed on a CE-440 Exeter Analytical Instrument. Melting points were measured in sealed glass tubes on a Melt Temp II apparatus and are not corrected. The ligands 4,5-(P(E)$Ph_2$)$_2$tzH [E = O (**1**), S(**2**), Se(**3**)] were prepared according to the literature procedures.[12,13,17,18]

**Preparation of [AlMe$_2${$\kappa^2$-*O*,*O′*-[4,5-(P(O)Ph$_2$)$_2$tz]}] (4).** To a suspension of **1** (0.41 g, 0.87 mmol) in 10 mL of toluene was added a 2.0 M solution of $AlMe_3$ in hexanes (0.44 mL, 0.88 mmol) at ambient temperature. Evolution of gas was observed, and within a few minutes a colorless solution resulted. After stirring for 2 h, the volatiles were removed under vacuum and the white solid was washed with 5 mL of hexanes. Yield (0.43 g, 82%). Mp 184−185 °C. IR (KBr, cm$^{-1}$): $\tilde{\nu}$ (P−O) 854. $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.60 [m, 8H, (*o*-$C_6H_5$)], 6.80 [m, 12H, (*m*, *p*-$C_6H_5$)], −0.41 [s, 6H, Al($CH_3$)$_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 35.5. No $^{27}$Al NMR signals were observed. EI-MS (70 eV): *m*/*z* 510 ($M^+$−Me). Anal. Calcd For $C_{28}H_{26}AlN_3P_2O_2$ (525.46) C, 64.0; H, 5.0; N, 8.0. Found: C, 64.1; H, 5.2; N, 7.8.

**Preparation of [Al$^i$Bu$_2${$\kappa^2$-*O*,*O′*-[4,5-(P(O)Ph$_2$)$_2$tz]}] (5).** A similar procedure as for **4** was used starting from **1** (0.30 g, 0.64 mmol) in 10 mL of toluene and a 1.0 M solution of Al$^i$Bu$_3$ (0.65 mL, 0.65 mmol) in toluene. After 2 h of vigorous stirring, all volatiles were removed under vacuum, and the white solid was washed with 5 mL of hexanes. Yield (0.27 g, 69%). Mp 198 °C. IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 832 (P−O). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.84 [m, 8H, (*o*-$C_6H_5$)], 6.85 [m, 12H, (*m*-, *p*-$C_6H_5$)$_2$], 2.05 [m, 2H, $CH_2CH(CH_3)_2$], 1.11 [d, $^3J$ = 6.3 Hz, 12H, $CH_2CH(CH_3)_2$], 0.31 [d, $^3J$ = 7.2 Hz, 4H, $CH_2CH(CH_3)_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 37.3. No $^{27}$Al NMR signals were observed. EI-MS (70 eV): *m*/*z* 552 ($M^+$ −$^i$Bu). Anal. Calcd for $C_{34}H_{38}AlN_3P_2O_2$ (609.62): C, 67.0; H, 6.3; N, 6.9. Found: C, 67.2; H, 6.2; N, 6.6.

**Preparation of [AlMe$_2${$\kappa^3$-*N*,*N′*,*S*-[4,5-(P(S)Ph$_2$)$_2$tz]}($\mu$-tz)]$_2$ (6).** To a suspension of **2** (0.49 g, 0.98 mmol) in 10 mL of toluene was added a 2.0 M solution of $AlMe_3$ in hexanes (0.49 mL, 0.98 mmol) at ambient temperature. Evolution of gas was observed and after stirring for 2 h, the volatiles were removed under vacuum, and the white solid was washed with 10 mL of hexanes. Yield (0.46 g, 84%). Mp 168−170 °C (dec). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 681(P=S), 654 (P−S). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.85 [m, 8H, (*o*-$C_6H_5$)], 6.95 [m, 12H, (*m*-,*p*-$C_6H_5$)], −0.12 [m, 6H, Al($CH_3$)$_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 28.3 (P=S), 37.0 (P−S(Al)). No $^{27}$Al NMR signals were observed. EI-MS (70 eV): *m*/*z* 1084 ($M^+$−2Me). Anal. Calcd for $C_{56}H_{52}Al_2N_6P_4S_4$ (1115.17): C, 60.3; H, 4.7; N, 7.5. Found: C, 60.1; H, 4.5; N, 7.2.

**Preparation of [Al$^i$Bu$_2${$\kappa^3$-*N*,*N′*,*S*-[4,5-(P(S)Ph$_2$)$_2$tz)}($\mu$-tz)]$_2$ (7).** A similar procedure as for **6** was used starting from **2** (0.56 g, 1.08 mmol) in 10 mL of toluene and a 1.0 M solution of Al$^i$Bu$_3$ (1.10 mL, 1.10 mmol) in toluene. After 2 h of stirring, all volatiles were removed under vacuum, and the white solid was washed with 10 mL of hexanes. Yield (0.51 g, 72%). Mp 198 °C. IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 668 (P=S), 640 (P−S). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.75 [m, 8H, (*o*-$C_6H_5$)], 6.85 [m, 12H, (*m*-,

---

(12) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3321–3324.

(13) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *Inorg. Chim. Acta* **2002**, *303*, 38–43.

(14) (a) Haagenson, D. C.; Moser, D. F.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **2002**, *41*, 1245–1253. (b) McMahon, C. N.; Francis, J. A.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1999**, 67–72. (c) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G.Jr. *Organometallics* **1998**, *17*, 4042–4048. (d) Kang, Y.; Yang, N.; Kang, S. O.; Ko, J.; Lee, C. -H.; Lee, Y.-H. *Organometallics* **1997**, *16*, 5522–5527.

(15) Han, H.; Johnson, S. A. *Organometallics* **2006**, *25*, 5594–5602.

(16) Briand, G. G.; Chivers, T.; Krahn, M.; Parvez, M. *Inorg. Chem.* **2002**, *41*, 6808–6815.

(17) Trofimenko, S.; Rheingold, A. L.; Incarvito, C. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 3506–3509.

(18) (a) Charrier, C.; Chadokiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 1002–1011. (b) Hartmann, V. H.; Beermann, C.; Czempik, H. *Z. Anorg. Allg. Chem.* **1956**, *46*, 261–272.

$p$-$C_6H_5$)], 2.09 [m, 2H, $CH_2CH(CH_3)_2$], 1.09 [d, $^3J = 6.6$ Hz, 12H, $CH_2CH(CH_3)_2$], 0.59 [d, $^3J = 6.9$ Hz, 4H, $CH_2CH(CH_3)_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 27.5 (P$=$S), 38.1 (P$-$S(Al)). $^{27}$Al NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 31 (s, $\omega_{1/2} = 130$ Hz). EI-MS (70 eV): 584 [(1/2$M^+$)$-^i$Bu]. Anal. Calcd for $C_{68}H_{76}Al_2N_6P_4S_4$ (1283.49): C, 63.6; H, 6.0; N, 6.5. Found: C, 63.9; H, 6.2; N, 6.8.

**Preparation of [AlMe$_2${$\kappa^2$-*N,Se*-[4,5-(P(Se)Ph$_2$)$_2$tz]}] (8).** To a suspension of **3** (0.42 g, 0.70 mmol) in 10 mL of toluene was added a 2.0 M solution of $AlMe_3$ in hexanes (0.36 mL, 0.72 mmol) at ambient temperature. After 2 h of vigorous stirring, all of the volatiles were removed under vacuum, and a white solid was precipitated with 10 mL of hexanes and then filtered and dried under vacuum. Yield (0.40 g, 87%). Mp 127−128 °C. IR (KBr/cm$^{-1}$): $\tilde{\nu}$ 601 (P$=$Se), 564 (P$-$Se). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.80 [m, 8H, ($o$-$C_6H_5$)], 6.77 [m, 12H, ($m$-, $p$-$C_6H_5$)], −0.18 [m, 6H, $Al(CH_3)_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 21.9 ($^1J_{P-Se} = -750$ Hz) (P$=$Se), 23.5 ($^1J_{P-Se} = -594$ Hz) (P$-$Se(Al)). $^{27}$Al NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 165 (br s, $\omega_{1/2} = 3130$ Hz). $^{77}$Se NMR ($C_6D_6$, 25 °C, ppm): $\delta$ −91.9 (d, $^1J_{Se-P} = -594$ Hz) (Se$-$Al), −244.9 (d, $^1J_{Se-P} = -750$ Hz) (P$-$Se(Al)). EI-MS (70 eV): $m/z$ 636 ($M^+ -$Me). Anal. Calcd for $C_{26}H_{26}AlN_3P_2Se_2$ (651.38): C, 51.6; H, 4.0; N, 6.4. Found: C, 51.4; H, 4.2; N, 6.3.

**Preparation of [Al{$\kappa^2$-*N,Se*-[4,5-(P(Se)Ph$_2$)$_2$tz]}$_3$] (9).** A similar procedure as for **8** was used starting from **3** (0.44 g, 0.74 mmol) in 10 mL of toluene and a 1.0 M solution of Al$^i$Bu$_3$ (0.75 mL, 0.75 mmol) in toluene. After stirring vigorously for 2 h, all volatiles were removed under vacuum, and the white solid was washed with 8 mL of hexanes. Yield (0.43 g, 98%). Mp 273−278 °C (dec). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 611 (P$=$Se), 537 (P$-$Se). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.8−8.1 [m, 60H, $o$-, $m$-, $p$-($C_6H_5$)]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 18.3 ($^1J_{P-Se} = -749$ Hz) (P$=$Se), 19.4 ($^1J_{P-Se} = -562$ Hz) (P$-$Se(Al)). $^{27}$Al NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 15 (s, $\omega_{1/2} = 45$ Hz). $^{77}$Se NMR ($C_6D_6$, 25 °C, ppm): $\delta$ −86.5 (d, $^1J_{Se-P} = -562$ Hz) (Se$-$Al), −243 (d, $^1J_{Se-P} = -749$ Hz) (Se$=$P). EI-MS (70 eV): $m/z$ 955 ($C_{40}H_{31}AlN_6P_3Se_3$). No elemental analysis data was obtained because of the highly sensitive nature of this compound and its extremely pungent odor.

**Preparation of [AlMe$_2${$\kappa^2$-*O,O′*-[4,5-(P(O)Ph$_2$)$_2$tz]}-(*N′*-AlMe$_3$)] (10).** To a suspension of **1** (0.33 g, 0.69 mmol) in 10 mL of toluene was added a 2.0 M solution of $AlMe_3$ in hexanes (0.70 mL, 1.40 mmol) at ambient temperature. Evolution of gas was observed, and after 2 h of vigorous stirring, all volatiles were removed under vacuum and the white solid obtained was washed with 5 mL of hexanes. Yield (0.34 g, 75%). Mp 184−185 °C. IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 810 (P$-$O). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.79 [m, 8H, ($o$-$C_6H_5$)], 6.88 [m, 12H, ($m$-, $p$-$C_6H_5$)], 0.27 [s, 9H, $Al(CH_3)_3$], 0.33 ppm [s, 6H, $Al(CH_3)_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 36.9. No $^{27}$Al NMR signals were observed; EI-MS (70 eV): $m/z$ 510, ($M^+ - AlMe_3 -$ Me). Anal. Calcd for $C_{31}H_{35}Al_2N_3O_2P_2$ (597.55): C, 62.3 H, 5.9; N, 7.0. Found: C, 61.9; H, 6.2; N, 6.9.

**Preparation of [Al$^i$Bu$_2${$\kappa^2$-*O,O′*-[4,5-(P(O)Ph$_2$)$_2$tz]}-(*N′*-Al$^i$Bu$_3$)] (11).** A similar procedure as for **10** was used starting from **1** (0.30 g, 0.64 mmol) and a 1.0 M solution of Al$^i$Bu$_3$ (1.30 mL, 1.30 mmol) in toluene. Evolution of gas was observed, and after stirring for 2 h, all volatiles were removed under vacuum and an oily product remained. Ten milliliters of pentane were added to the product, and it was stirred for 1 h, after which the solvent was decanted and the product was dried under vacuum leaving a yellow oil. Yield (0.28 g, 96%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 821 (P$-$O). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.74 [m, 8H, ($o$-$C_6H_5$)], 6.94 [m, 12H, ($m$-, $p$-$C_6H_5$)], 2.36 [m, 3H, $Al\{CH_2CH(CH_3)_2\}_3$], 2.00 [m, 2H, $Al\{CH_2CH(CH_3)_2\}_2$], 1.28 [d, $^3J = 6.3$ Hz, 18H, $Al\{CH_2CH(CH_3)_2\}_3$], 1.16 [d, $^3J = 6.6$ Hz, 12H, $Al\{CH_2CH(CH_3)_2\}_2$], 1.07 [d, $^3J = 6.9$ Hz 4H, $Al\{CH_2CH(CH_3)_2\}_2$], 0.77 [d, $^3J = 6.6$ Hz, 6H, $Al\{CH_2CH(CH_3)_2\}_3$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 36.3. No $^{27}$Al NMR signals were observed. EI-MS (70 eV): $m/z$ 552 ($M^+ -$ Al$^i$Bu$_3 - ^i$Bu). Anal. Calcd for $C_{46}H_{65}Al_2N_3O_2P_2$ (807.95): C, 68.4; H, 8.1; N, 5.2. Found: C, 68.3; H, 8.0; N, 4.8.

**Preparation of [AlMe$_2${$\kappa^2$-*N,S*-[4,5-(P(S)Ph$_2$)$_2$tz]}-(*N′*-AlMe$_3$)] (12).** To a suspension of **2** (0.42 g, 0.84 mmol) in 10 mL of toluene was added a 2.0 M solution of $AlMe_3$ in hexanes (0.84 mL, 1.68 mmol) at ambient temperature. Evolution of gas was observed, and after 2 h of stirring, all volatiles were removed under vacuum and the white solid obtained was washed with 10 mL of hexanes. Yield (0.36 g, 68%). Mp 303−305 °C (dec). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 683 (P$=$S), 642 (P$-$S). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.67, 7.50 [m, 8H, ($o$-$C_6H_5$)], 6.87, 6.68 [m, 12H, ($m$-,$p$-$C_6H_5$)], −0.20 [s, 6H, $Al(CH_3)_2$ ], −0.31 [s, 9H, $Al(CH_3)_3$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 27.5 (P$=$S), 36.5 (P$-$S (Al)). $^{27}$Al NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 154 (br s), 165 (br s). EI-MS (70 eV): $m/z$ 542 ($M^+ - AlMe_3 -$ Me). Anal. Calcd for $C_{31}H_{35}Al_2N_3P_2S_2$ (629.67): C, 59.1; H, 5.6; N, 6.7. Found: C, 59.2; H, 5.8; N, 6.5.

**Preparation of [Al$^i$Bu$_2${$\kappa^2$-*N,S*-[4,5-(P(S)Ph$_2$)$_2$tz]}-(*N′*-Al$^i$Bu$_3$)] (13).** A similar procedure as for **12** was used starting from **2** (0.35 g, 0.70 mmol) in 10 mL of toluene and a 1.0 M solution of Al$^i$Bu$_3$ (1.40 mL, 1.40 mmol) in toluene. After 2 h of vigorous stirring, volatiles were removed under vacuum, and the white solid was washed with 10 mL of hexanes. Yield (0.51 g, 86%). Mp 274−277 °C (dec). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 661(P$=$S), 634 (P$-$S). $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.67, 6.81 [m, 8H, ($o$-$C_6H_5$)], 7.07 [m, 12H, ($m$-,$p$-$C_6H_5$)], 3.11 [m br 3H, $Al\{CH_2CH(CH_3)_2\}_3$], 2.09 [m br 2H, $Al\{CH_2CH(CH_3)_2\}_2$], 0.99 [unresolved resonance signal, 30H, $Al\{CH_2CH(CH_3)_2\}_3$, $Al\{CH_2CH(CH_3)_2\}_2$, 0.18 [unresolved resonance signal, 10H, $Al\{CH_2CH(CH_3)_2\}_3$, $Al\{CH_2CH(CH_3)_2\}_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C): $\delta$ 30.8 (P$=$S), 31.2 (P$-$S(Al)). No $^{27}$Al NMR signals were observed. EI-MS (70 eV): 584 ($M^+ -$ Al$^i$Bu$_3$-$^i$Bu). Anal. Calcd for $C_{46}H_{65}Al_2N_3P_2S_2$ (840.0): C, 65.8 H, 7.8; N, 5.0. Found: C, 65.9; H, 7.6; N, 4.8.

**NMR Follow-up for the Formation of 9.** NMR samples were prepared according to the following procedure by duplicate. A 0.10 mL portion of a 1.0 M solution of Al$^i$Bu$_3$ (0.020 g, 0.100 mmol) in $C_6D_6$ was added to a 0.40 mL portion of a 0.25 M solution of **3** (0.60 g, 0.100 mmol) in $C_6D_6$ at 25 °C. The reaction mixture was followed for 10 h by $^1$H NMR and by $^{31}$P, $^{27}$Al, and $^{77}$Se NMR spectroscopy in a parallel experiment. $^1$H NMR measurements were taken every 10 min for the first 2 h, followed by one-hour intervals for the next 8 h. The $^{31}$P NMR experiments were taken every 30 min for the first 2 h followed by one-hour intervals for the next 8 h. The $^{27}$Al and $^{77}$Se NMR measurements were taken every 2 h for 10 h.

**Characterization of Transient [Al$^i$Bu$_2${$\kappa^2$-*N,Se*-[4,5-(P(Se)Ph$_2$)$_2$tz]}] in Solution.** $^1$H NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 7.77 (m, 8 H, $o$-$C_6H_5$), 7.31 (m, 4H, $p$-$C_6H_5$), 7.42 (m, 8H, $m$-$C_6H_5$), 1.98 [m, 2H, $Al\{CH_2CH(CH_3)_2\}_2$], 0.94 [d, $^3J = 6.2$ Hz, 12H, $Al\{CH_2CH(CH_3)_2\}_2$], 0.35 [d, $^3J = 6.4$ Hz, 4H, $Al\{CH_2CH(CH_3)_2\}_2$]. $^{31}$P NMR ($C_6D_6$, 25 °C, ppm): $\delta$ 18.1 ($^1J_{P-Se} = -766$ Hz) (P$=$Se), 19.6 ($^1J_{P-Se} = -634$ Hz) (P$-$Se(Al)). No $^{27}$Al NMR signals were observed. $^{77}$Se NMR ($C_6D_6$, 25 °C, ppm): $\delta$ −85.8 (d, $^1J_{Se-P} = -634$ Hz) (Se$-$Al), −253.8 (d, $^1J_{Se-P} = -766$ Hz) (Se$=$P).

**Computational Methods.** Ab initio calculations at RHF/3-21G** (for the deprotonated ligands [4,5-(P(O)Ph$_2$)$_2$tz]$^-$(**1a**), [4,5-(P(S)Ph$_2$)$_2$tz]$^-$(**2a**), and [4,5-(P(Se)Ph$_2$)$_2$tz]$^-$(**3a**)), RHF/6-31G**(**4** and **6**) and RHF/LANL2DZ (**9**) levels of theory were performed on the selected compounds. All calculations were carried out with the GAUSSIAN 03[19] suite of programs at the Hartree−Fock level of theory. Natural Bond Orbitals (NBO)[20]

---

(19) For a full description of the theoretical methods used and the full reference for GAUSSIAN 03 suite of programs please see the Supporting Information.

(20) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

**Table 1.** Crystal Data and Structure Refinement for Compounds **4a**, **6**, **7**, **9**, **10**, and **12**

| compound | **4a** | **6**·toluene | **7**·2 toluene | **9**·toluene | **10**[c] | **12** |
|---|---|---|---|---|---|---|
| formula | $C_{28}H_{26}AlN_3O_2P_2$ | $C_{63}H_{60}Al_2N_6P_4S_4$ | $C_{82}H_{92}Al_2N_6P_4S_4$ | $C_{85}H_{68}AlN_9P_6Se_6$ | $C_{60.81}H_{66.44}Al_4Cl_{1.19}N_6O_4P_4$ | $C_{31}H_{35}Al_2N_3P_2S_2$ |
| fw | 525.44 | 1207.25 | 1467.70 | 1902.04 | 1219.23 | 629.64 |
| crystal system | triclinic | orthorhombic | triclinic | triclinic | orthorhombic | triclinic |
| space group | $P\bar{1}$ | $Pca2_1$ | $P\bar{1}$ | $P\bar{1}$ | $Pca2_1$ | $P\bar{1}$ |
| temp, K | 173(2) | 173(2) | 173(2) | 173(2) | 100(2) | 173(2) |
| $\lambda$, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $a$, Å | 8.765(2) | 20.329(4) | 9.656(2) | 16.048(2) | 18.963(3) | 8.159(2) |
| $b$, Å | 11.598(2) | 17.450(3) | 14.175(2) | 16.886(2) | 18.529(2) | 12.158(3) |
| $c$, Å | 14.047(4) | 17.352(3) | 15.895(3) | 18.437(3) | 17.960(2) | 18.367(3) |
| $\alpha$, deg | 102.35(3) | 90 | 64.44(2) | 115.85(2) | 90 | 95.56(2) |
| $\beta$, deg | 100.14(3) | 90 | 85.80(3) | 90.51(2) | 90 | 96.66(3) |
| $\gamma$, deg | 104.43(2) | 90 | 88.35(3) | 112.88(2) | 90 | 104.70(3) |
| $V$, Å$^3$ | 1311(1) | 6156(2) | 1957.4(7) | 4045(2) | 6311(1) | 1735.2(7) |
| Z | 2 | 4 | 1 | 2 | 4 | 2 |
| $\rho_{calcld.}$, g·cm$^{-3}$ | 1.331 | 1.303 | 1.245 | 1.561 | 1.283 | 1.205 |
| $\mu$, mm$^{-3}$ | 0.231 | 0.332 | 0.273 | 2.894 | 0.276 | 0.320 |
| $F$(000) | 548 | 2520 | 776 | 1896 | 2550 | 660 |
| crystal size, mm$^3$ | 0.32 × 0.18 × 0.03 | 0.35 × 0.27 × 0.27 | 0.30 × 0.20 × 0.14 | 0.23 × 0.09 × 0.06 | 0.52 × 0.44 × 0.15 | 0.35 × 0.11 × 0.06 |
| $\theta$ range for data collection, deg | 1.53 to 25.51 | 1.17 to 25.37 | 1.59 to 25.03 | 1.68 to 25.39 | 1.54 to 25.36 | 1.13 to 25.05 |
| index ranges | $-10 \leq h \leq 10$<br>$-13 \leq k \leq 13$<br>$-16 \leq l \leq 16$ | $-24 \leq h \leq 24$<br>$-21 \leq k \leq 20$<br>$-20 \leq l \leq 20$ | $-11 \leq h \leq 11$<br>$-16 \leq k \leq 16$<br>$-18 \leq l \leq 18$ | $-19 \leq h \leq 19$<br>$-20 \leq k \leq 20$<br>$-22 \leq l \leq 22$ | $-22 \leq h \leq 22$<br>$-22 \leq k \leq 20$<br>$-21 \leq l \leq 16$ | $-9 \leq h \leq 9$<br>$-14 \leq k \leq 14$<br>$-21 \leq l \leq 21$ |
| no. of reflns collected | 13491 | 50062 | 20318 | 55802 | 24992 | 14139 |
| no. of indep. reflns ($R_{int}$) | 4827 (0.0372) | 11286 (0.0657) | 6887 (0.0564) | 14792 (0.0473) | 10366 (0.0631) | 6098 (0.0343) |
| no. of data/restraints/parameters | 4827/0 /327 | 11286/352/780 | 6887/381/548 | 14792/ 653/1074 | 10366/30/727 | 6098/0/366 |
| GoF on $F^2$ | 1.052 | 1.024 | 1.022 | 1.036 | 0.999 | 1.033 |
| $R_1$,[a] $wR_2$[b] ($I > 2\sigma(I)$) | 0.0490, 0.1102 | 0.0412, 0.0901 | 0.0480, 0.1094 | 0.0394, 0.0968 | 0.0534, 0.1082 | 0.0458, 0.1093 |
| $R_1$,[a] $wR_2$[b] (all data) | 0.0612, 0.1158 | 0.0468, 0.0932 | 0.0678, 0.1192 | 0.0543, 0.1044 | 0.0693, 0.1156 | 0.0614, 0.1172 |
| abs. struct. par. |  | −0.03(5) |  |  | 0.08(8) |  |
| largest diff. peak/hole, e·Å$^{-3}$ | 0.462/−0.249 | 0.409/−0.187 | 0.339/−0.255 | 1.440/−0.611 | 0.779/−0.375 | 0.380/−0.258 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$. [c] Although there are two independent molecules in the asymmetric unit, they have different content of chlorine (0.52 and 0.65, for details see the text), and thus, formula, fw, $Z$, and $F$(000) are reported for the sum of both molecules; thus the real $Z$ is 8.

analyses were performed on the optimized wave functions to assess the electronic density distribution in a localized manner over all the molecules considered. A frequencies analysis was carried out after every geometry optimization to assert the presence of a minimum on the potential energy surface. No imaginary frequencies were found for any of the compounds studied herein. All graphics were generated using the Molekul visualization package.[21]

**X-ray Crystallography.** Single crystals were removed from Schlenk flasks under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a nylon loop, and quickly placed in a low temperature stream of nitrogen. The diffraction data for all the compounds were collected on a Bruker-APEX three-circle diffractometer using MoKα radiation ($\lambda$ = 0.71073 Å) at 173 or 100 K. The structures were solved by direct methods (SHELXS-97)[22] and refined against all the data by full-matrix least-squares on $F^2$ using SHELXL-97.[23] The hydrogen atoms of C−H bonds were placed in idealized positions and refined isotropically with a riding model. The non-hydrogen atoms were refined anisotropically. The hydrogen atom attached to the nitrogen atom in **1** was located from the difference electron density map and refined with $U_{ij}$ tied to the parent atom. Crystallographic data and refinement details are summarized in Table 1 (**4a**, **6**, **7**, **9**, **10**, and **12**) and in Supporting Information, Table S1 (**1**, **4b**). Selected interatomic distances and angles for all the compounds are provided in Tables 2 (**4a**, **6**, **7**, **9**, **10**, and **12**) and Supporting Information, Tables S2−S4 (**1**, **4b**).

## Results and Discussion

**Equimolar Reactions.** Compounds **4**− **9** were synthesized in a straightforward manner by addition of trialkylaluminum compounds to the corresponding 4,5-(P(E)-$Ph_2)_2$tzH [E = O (**1**), S (**2**), Se (**3**); tz = 1,2,3-triazole] ligands at ambient temperature (Scheme 1). All compounds are air and moisture-sensitive and readily soluble at ambient temperature in most common organic solvents (toluene, benzene, $CH_2Cl_2$, diethylether, THF, etc.) but insoluble in pentane and hexanes.

Reaction of 4,5-(P(O)$Ph_2)_2$tzH (**1**) with $AlMe_3$ and $Al^iBu_3$ yielded compounds **4** and **5**, respectively; both compounds are highly soluble in toluene and were recrystallized from a mixture of toluene/hexane. The mass spectra for **4** and **5** reveal the peaks corresponding to the loss of one alkyl group [$M^+ - R$] (R = Me, $^i$Bu). The $^1$H NMR spectra for these compounds show the characteristic pattern owing to the deprotonated ligand along with the signals corresponding to the alkyl groups attached to the aluminum atoms. Examination of these compounds by $^{31}$P NMR shows single signals corresponding to a symmetric coordination, thus suggesting the formation of a seven-membered ring system (**I**). The

---

(21) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000.

(22) *SHELXS-97, Program for Structure Solution*; Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

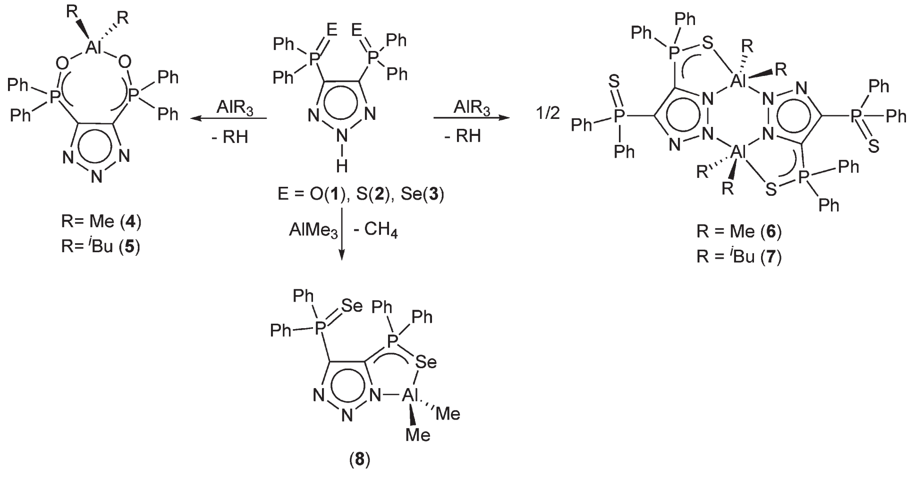
(23) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **4a**, **6**, **7**, **9**, **10**, and **12**

| | | | |
|---|---|---|---|
| | Compound **4a** (triclinic) | | |
| Al(1)−O(1) | 1.817(2) | Al(1)−O(2)−P(2) | 143.8(1) |
| Al(1)−O(2) | 1.808(2) | O(1)−Al(1)−O(2) | 99.0(1) |
| Al(1)−C(27) | 1.948(3) | O(1)−Al(1)−C(27) | 111.1(1) |
| Al(1)−C(28) | 1.946(3) | O(2)−Al(1)−C(27) | 106.6(1) |
| P(1)−O(1) | 1.522(2) | O(1)−Al(1)−C(28) | 108.5(1) |
| P(2)−O(2) | 1.514(2) | O(2)−Al(1)−C(28) | 110.5(1) |
| Al(1)−O(1)−P(1) | 143.2(1) | C(28)−Al(1)−C(27) | 119.3(1) |
| | Compound **6**·toluene | | |
| Al(1)−S(1) | 2.652(1) | Al(2)−S(3) | 2.736(1) |
| Al(1)−N(1) | 1.997(2) | Al(2)−N(4) | 1.988(2) |
| Al(1)−N(5) | 2.147(2) | Al(2)−N(2) | 2.101(2) |
| Al(1)−C(27) | 1.964(3) | Al(2)−C(55) | 1.946(3) |
| Al(1)−C(28) | 1.951(3) | Al(2)−C(56) | 1.970(3) |
| P(1)−S(1) | 1.972(1) | P(3)−S(3) | 1.966(1) |
| P(2)−S(2) | 1.938(1) | P(4)−S(4) | 1.940(1) |
| Al(1)−S(1)−P(1) | 94.5(1) | Al(2)−S(3)−P(3) | 93.4(1) |
| S(1)−Al(1)−N(1) | 82.4(1) | S(3)−Al(2)−N(4) | 80.8(1) |
| S(1)−Al(1)−N(5) | 168.4(1) | S(3)−Al(2)−N(2) | 166.6(1) |
| N(1)−Al(1)−N(5) | 88.3(1) | N(2)−Al(2)−N(4) | 89.7(1) |
| S(1)−Al(1)−C(27) | 88.1(1) | S(3)−Al(2)−C(55) | 93.4(1) |
| S(1)−Al(1)−C(28) | 92.8(1) | S(3)−Al(2)−C(56) | 85.4(1) |
| N(1)−Al(1)−C(27) | 117.3(1) | N(4)−Al(2)−C(55) | 111.9(1) |
| N(1)−Al(1)−C(28) | 112.4(1) | N(4)−Al(2)−C(56) | 120.6(1) |
| N(5)−Al(1)−C(27) | 90.0(1) | N(2)−Al(2)−C(55) | 99.0(1) |
| N(5)−Al(1)−C(28) | 97.2(1) | N(2)−Al(2)−C(56) | 91.4(1) |
| C(27)−Al(1)−C(28) | 130.0(2) | C(55)−Al(2)−C(56) | 126.4(2) |
| | Compound **7**·2toluene | | |
| Al(1)−S(1) | 2.739(1) | S(1)−Al(1)−N(2)$^{\#1}$ | 170.7(1) |
| Al(1)−N(1) | 1.996(2) | N(1)−Al(1)−N(2)$^{\#1}$ | 91.1(1) |
| Al(1)−N(2)$^{\#1}$ | 2.138(2) | S(1) -Al(1)−C(27) | 93.4(1) |
| Al(1)−C(27) | 1.968(3) | S(1)−Al(1)−C(31) | 87.0(3) |
| Al(1)−C(31) | 1.971(3) | N(1)−Al(1)−C(27) | 110.9(1) |
| P(1)−S(1) | 1.960(1) | N(1)−Al(1)−C(31) | 117.3(2) |
| P(2)−S(2) | 1.940(1) | N(2)$^{\#1}$−Al(1)−C(27) | 94.8(1) |
| Al(1)−S(1)−P(1) | 92.7(1) | N(2)$^{\#1}$−Al(1)−C(31) | 90.8(3) |
| S(1)−Al(1)−N(1) | 82.0(1) | C(27)−Al(1)−C(31) | 131.3(2) |
| | Compound **9**·toluene | | |
| Al(1)−Se(1) | 2.557(1) | Se(1)−Al(1)−Se(3) | 89.5(1) |
| Al(1)−Se(3) | 2.559(1) | Se(1)−Al(1)−Se(5) | 87.9(1) |
| Al(1)−Se(5) | 2.539(1) | Se(3)−Al(1)−Se(5) | 85.8(1) |
| P(1)−Se(1) | 2.150(1) | Se(1)−Al(1)−N(1) | 88.7(1) |
| P(2)−Se(2) | 2.096(1) | Se(1)−Al(1)−N(4) | 178.3(1) |
| P(3)−Se(3) | 2.161(1) | Se(1)−Al(1)−N(7) | 91.8(1) |
| P(4)−Se(4) | 2.100(1) | Se(3)−Al(1)−N(1) | 90.5(1) |
| P(5)−Se(5) | 2.157(1) | Se(3)−Al(1)−N(4) | 89.0(1) |
| P(6)−Se(6) | 2.100(1) | Se(3)−Al(1)−N(7) | 175.4(1) |
| Al(1)−N(1) | 1.981(3) | Se(5)−Al(1)−N(1) | 175.0(1) |
| Al(1)−N(4) | 1.978(3) | Se(5)−Al(1)−N(4) | 92.7(1) |
| Al(1)−N(7) | 1.966(3) | Se(5)−Al(1)−N(7) | 89.8(1) |
| Al(1)−Se(1)−P(1) | 95.0(1) | N(7)−Al(1)−N(4) | 89.8(1) |
| Al(1)−Se(3)−P(3) | 94.2(1) | N(1)−Al(1)−N(4) | 90.6(1) |
| | Compound **10** | | |
| molecule *a* | | molecule *b* | |
| Al(1)−O(1) | 1.830(3) | Al(3)−O(3) | 1.826(3) |
| Al(1)−O(2) | 1.850(3) | Al(3)−O(4) | 1.819(3) |
| Al(2)−N(2) | 1.964(3) | Al(4)−N(5) | 2.000(3) |
| Al(1)−C(27) | 1.931(5) | Al(3)−C(58) | 1.939(5) |
| Al(1)−C(28) | 1.938(4) | Al(3)−C(59) | 1.948(4) |
| Al(2)−C(29) | 1.937(4) | Al(4)−C(60) | 1.945(4) |
| Al(2)−C(30) | 1.991(4) | Al(4)−C(61) | 1.998(4) |
| Al(2)−C(31) | 1.975(4) | Al(4)−C(62) | 1.949(4) |
| Al(2)−Cl(1) | 2.129(2) | Al(4)−Cl(2) | 2.148(2) |
| P(1)−O(1) | 1.513(3) | P(3)−O(3) | 1.510(3) |
| P(2)−O(2) | 1.507(3) | P(4)−O(4) | 1.516(3) |
| Al(1)−O(1)−P(1) | 136.2(2) | Al(3)−O(3)−P(3) | 142.6(2) |
| Al(1)−O(2)−P(2) | 137.0(2) | Al(3)−O(4)−P(4) | 140.9(2) |
| O(1)−Al(1)−O(2) | 98.6(1) | O(3)−Al(3)−O(4) | 98.1(2) |
| O(1)−Al(1)−C(27) | 107.7(1) | O(3)−Al(3)−C(58) | 110.8(2) |
| O(1)−Al(1)−C(28) | 109.2(2) | O(3)−Al(3)−C(59) | 105.6(2) |
| O(2)−Al(1)−C(27) | 107.5(2) | O(4)−Al(3)−C(58) | 107.3(2) |
| O(2)−Al(1)−C(28) | 111.5(2) | O(4)−Al(3)−C(59) | 108.7(2) |
| C(27)−Al(1)−C(28) | 120.2(2) | C(58)−Al(3)−C(59) | 123.5(2) |
| N(2)−Al(2)−C(29) | 103.4(2) | N(5)−Al(4)−C(60) | 102.5(2) |
| N(2)−Al(2)−C(30) | 101.0(2) | N(5)−Al(4)−C(61) | 99.2(2) |
| N(2)−Al(2)−C(31) | 105.0(2) | N(5)−Al(4)−C(62) | 106.3(2) |
| Cl(1)−Al(2)−N(2) | 104.8(1) | Cl(2)−Al(4)−N(5) | 102.8(1) |
| Cl(1)−Al(2)−C(29) | 114.5(2) | Cl(2)−Al(4)−C(60) | 112.9(1) |
| Cl(1)−Al(2)−C(31) | 110.6(1) | Cl(2)−Al(4)−C(62) | 112.4(2) |
| C(29)−Al(2)−C(30) | 114.6(2) | C(60)−Al(4)−C(61) | 114.0(2) |
| C(29)−Al(2)−C(31) | 117.1(2) | C(60)−Al(4)−C(62) | 118.0(2) |
| C(30)−Al(2)−C(31) | 113.3(2) | C(61)−Al(4)−C(62) | 113.8(2) |
| | Compound **12** | | |
| Al(1)−S(1) | 2.382(1) | S(1)−Al(1)−C(27) | 109.1(1) |
| Al(1)−N(1) | 1.994(2) | S(1)−Al(1)−C(28) | 103.8(1) |
| Al(2)−N(2) | 2.055(2) | N(1)−Al(1)−C(27) | 110.3(1) |
| Al(1)−C(27) | 1.940(3) | N(1)−Al(1)−C(28) | 112.4(1) |
| Al(1)−C(28) | 1.938(3) | C(27)−Al(1)−C(28) | 125.5(2) |
| Al(2)−C(29) | 1.968(3) | N(2)−Al(2)−C(29) | 104.4(1) |
| Al(2)−C(30) | 1.960(3) | N(2)−Al(2)−C(30) | 103.2(1) |
| Al(2)−C(31) | 1.954(3) | N(2)−Al(2)−C(31) | 100.6(1) |
| P(1)−S(1) | 2.004(1) | C(29)−Al(2)−C(30) | 117.1(2) |
| P(2)−S(2) | 1.939(1) | C(29)−Al(2)−C(31) | 115.1(2) |
| P(1)−S(1)−Al(1) | 94.2(1) | C(30)−Al(2)−C(31) | 113.6(2) |
| S(1)−Al(1)−N(1) | 89.2(1) | | |

$^{\#1}$ $2 - x, 1 - y, -z$.

**Scheme 1.** Preparation of Compounds **4−8**



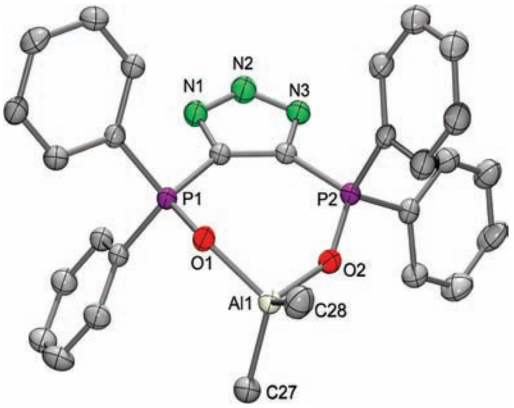
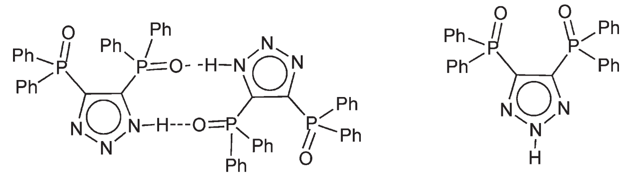


**Figure 2.** Perspective view of **4a** (triclinic) with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

signals of the $^{27}$Al NMR spectra appear to be too broad for observation. However, crystals of two polymorphic forms of **4**, suitable for X-ray diffraction studies, were obtained when allowing a saturated toluene solution to slowly cool from 80 °C to ambient temperature (**4a**, triclinic $P\bar{1}$) or crystallized at −30 °C, (**4b**, monoclinic $P2_1/c$). In both polymorphs there is one molecule in the asymmetric unit. The conformations of both seven membered-rings in these polymorphs are nearly identical (Supporting Information, Figure S1) and thus only the data for **4a** will be discussed, as they have better quality. The molecular structure of **4a** reveals a non-planar seven-membered ring (mean deviation from the plane = 0.16 Å) (Figure 2). The geometry around the metal center corresponds to a distorted tetrahedron; the Al−O bond distances (1.817(2) and 1.808(2) Å) are within the normal values for Al−O(P) bond lengths for tetracoordinate aluminum atoms.[24]

It is noteworthy that during the isolation of **4** and **5**, we obtained a polymorph form of the ligand **1** (Supporting Information, Figure S3). The crystal structure of **1** exhibits two molecules bounded by two intermolecular hydrogen interactions N−H···O (**IV**, Figure 3), as opposed to the molecular structure reported previously by Trofimenko (**V**).[12] The protropic behavior of **1** (**IV** and **V**) is also observed in solution and is strongly dependent on the solvent used. Thus, the $^{31}$P NMR spectrum of **1** shows two signals in CDCl$_3$, while in (CD$_3$)$_2$CO only one signal is observed.

Reaction of 4,5-(P(S)Ph$_2$)$_2$tzH (**2**) with AlMe$_3$ and Al$^i$Bu$_3$ gave the dimeric compounds **6** and **7**, respectively (Scheme 1). The $^1$H NMR spectra of **6** and **7** exhibit signals assigned to the PPh$_2$ moieties and to the aluminum alkyl groups. In addition, the $^{31}$P NMR spectra exhibit for **6** and **7** doublets signals for each compound. The $^{27}$Al NMR spectrum of **7** shows a broad signal at δ 31 ppm, corresponding to a pentacoordinate aluminum atom. However, in the case of **6**, the signal appears to be too broad for observation. The spectroscopic data suggest the existence of dimeric-like metallacycles comprising asymmetric coordination modes to the ligand (**III**).



(**IV**) (**V**)

**Figure 3.**

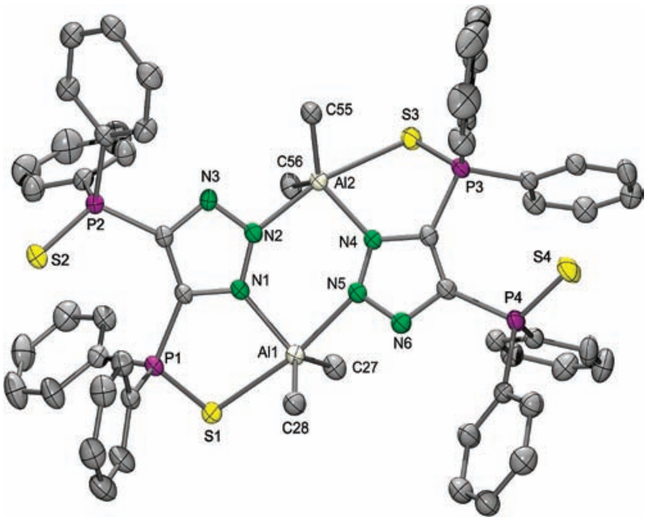


**Figure 4.** Perspective view of **6** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

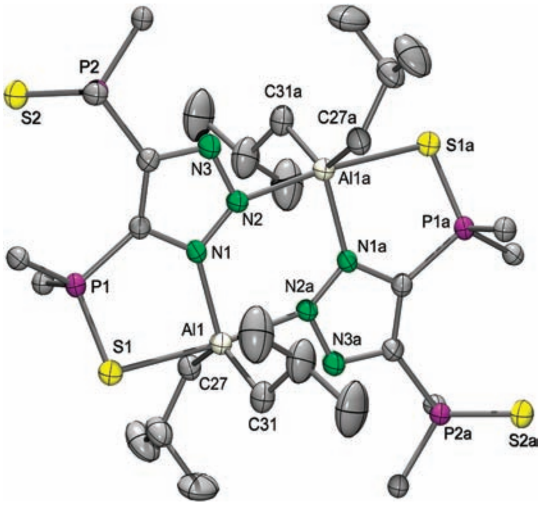


**Figure 5.** Perspective view of **7** with thermal ellipsoids at 50% probability. All hydrogen atoms, and carbon atoms from the phenyl groups, except the *ipso*, are omitted for clarity.

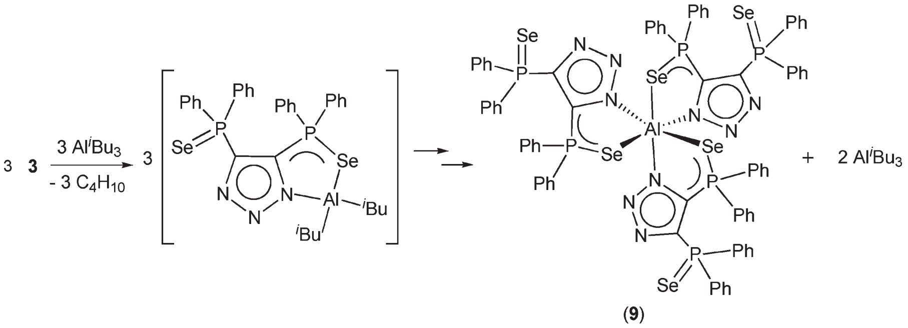
Furthermore, the composition of these compounds was unequivocally established by X-ray diffraction studies.

Single crystals of **6** and **7** were obtained from their saturated toluene solutions at ambient temperature. Compound **6** crystallizes in the orthorhombic system, space group $Pca2_1$ with one molecule of **6** and one molecule of toluene in the asymmetric unit, while **7** crystallizes in the triclinic system, space group $P\bar{1}$ with one-half of the molecule of **7** and one molecule of toluene in the asymmetric unit (Figures 4 and 5).

---

[24] For a full account of Al−O(P) bond lengths see the Al−O(P) bond length histogram for tetracoordinate Al atoms from CCDC in the Supporting Information, Figure S2.

**Scheme 2.** Formation of **9**



The molecular structures of **6** and **7** exhibit dimeric-like arrangements achieved through bridging triazole groups. The metal centers coordinate to the sulfur and nitrogen atoms of one ligand moiety, as well as to the central nitrogen atom of a second ligand moiety. This coordination mode results in the formation of five fused heterocycles with a central $Al_2N_4$ core. The $Al_2N_4$ core is nonplanar for **6** (mean deviation = 0.22 Å) and considered planar for **7** (mean deviation = 0.08 Å). Moreover, the $Al_2N_4$ six-membered ring in **6** shows a twisted conformation with an angle of 26.9° between the planes defined by Al(1)−N(1)−N(2) and Al(2)−N(4)−N(5). With the exception of the $Al_2N_4$ ring conformation, the structural traits in **6** and **7** are closely related. The aluminum centers in these two compounds are in distorted trigonal-bipyramid environments with the sulfur atom and the central nitrogen atoms from a second triazole moiety occupying the axial positions. The equatorial Al−N bond distances (1.988(2) and 1.997(2) Å for **6** and 1.996(2) Å for **7**) are comparable to the values observed in similar aluminum complexes bearing $Al_2N_4$ rings.[7−10] The axial Al−N bond distances with 2.101(2) and 2.147(2) Å for **6** and 2.138(2) Å for **7** are significantly longer than those of the above-mentioned $Al_2N_4$ compounds. The Al−S bond lengths, with 2.652(1) and 2.736(1) Å for **6** and 2.739(1) Å for **7**, are comparable with those observed in the pentacoordinate aluminum compounds:[25] [MeAl(xytbmp), (xytbmp = *o*-xylylenedithio-bis(6-$^t$Bu-4-methylphenol)] (2.621(1) Å),[26] [(MeAl)$_2$($\mu$-tbop), tbop = 2,2′-thiobis {4-(1,1,3,3-tetramethylbutyl)phenolato}] (2.675(2) Å)[27] and [R$_2$Al($\mu$-OC$_6$H$_4$-2-SMe)]$_2$ [R = Me (av. 2.738(5) Å), R = $^i$Bu (2.778(1))].[28]

The equimolar reactions of 4,5-(P(Se)Ph$_2$)$_2$tzH (**3**) with aluminum alkyls gave compounds with different coordination behavior (Scheme 2). The reaction of **3** with $AlMe_3$ yielded the monomeric compound **8**. The structural arrangement of **8** in solution was determined on the basis of its $^1$H, $^{31}$P, $^{27}$Al, and $^{77}$Se NMR data. The $^1$H NMR spectrum shows the pattern corresponding to the deprotonated ligand, along with the high-field signal owing to the $AlMe_2$ moiety. The $^{31}$P NMR spectrum displays two signals at $\delta$ 21.9 and 23.5, indicating two different phosphorus environments. While the $^{27}$Al NMR spectrum displays a broad signal at $\delta$ 165 ($\omega_{1/2}$ = 3130 Hz), which suggests a tetracoordinate aluminum atom in solution. Furthermore, the $^{77}$Se NMR spectrum exhibits two double signals at $\delta$ −91.9 ($^1J_{Se-P}$ = −594 Hz) and −244.9 ppm ($^1J_{Se-P}$ = −750 Hz). The difference between the chemical shifts and coupling constants of these signals clearly denotes the coordination of one selenium atom to the aluminum center. Finally, the mass spectra of **8** shows the peak with the highest *m*/*z* at 636, assigned to the fragment [M$^+$ −Me], which indicates a coordination mode corresponding to **II**.

On the other hand, the reaction of 4,5-(P(Se)Ph$_2$)$_2$tzH (**3**) with Al$^i$Bu$_3$ in a 1:1 ratio gave the trischelate **9** in a quantitative yield (98% on the basis of the mmol of **3** present). The reaction was repeated at ambient temperature in a 3:1 (ligand/metal) ratio, to examine if the formation of the trischelate could be optimized. However, only free ligand and an inseparable mixture of products containing **9** were observed. Accordingly, the formation of **9**, starting from **3** and Al$^i$Bu$_3$, was followed by NMR experiments ($^1$H, $^{31}$P and $^{27}$Al), and the aluminum monochelate [Al$^i$Bu$_2${$\kappa^2$-*N*, *Se*-[4,5-(P(Se)Ph$_2$)$_2$tz]}] was identified as a transient product. Indeed, upon gentle heating (50 °C) of the monochelate, a rapid conversion to **9** was observed along with the formation of Al$^i$Bu$_3$, thus confirming the mechanism proposed in Scheme 2. As mentioned earlier, aluminum compounds bearing multidentate ligands with selenium donor atoms are extremely scarce, to such a degree that **9** is to our knowledge the first example of a structurally characterized hexacoordinate aluminum compound bearing a Al−Se bond. Surprisingly, even pentacoordinate aluminum compounds bearing Al−Se bonds are unknown.

Compound **9** is highly soluble in toluene and extremely air- and moisture-sensitive with a strong pungent odor. Yellowish twinned crystals of **9** were obtained from a saturated toluene solution at ambient temperature. Compound **9** crystallizes in a triclinic, space group $P\bar{1}$ with one molecule of **9** and one molecule of toluene in the asymmetric unit (Figure 6).

The aluminum center in **9** displays an octahedral geometry with slightly distorted "trans" angles N−Al−Se (175.0(1), 175.4(1) and 178.3(1)°). The Al−N bond lengths in **9** (1.981(3), 1.978(3), 1.966(3) Å) are the shortest observed for the compounds in this study. Moreover, the relatively short Al−Se bond lengths (2.557(1), 2.559(1), 2.539(1) Å) present in this hexacoordinate

---

(25) For a full account of Al−S bond lengths see the Al−S bond length histogram for pentacoordinate Al atoms from CCDC in Supporting Information, Figure S4.

(26) Ma, H.; Melillo, G.; Oliva, L.; Spaniol, T. P.; Englert, U.; Okuda, J. *Dalton Trans.* **2005**, 721–727.

(27) Janas, Z.; Jerzykiewicz, L. B.; Sobota, P.; Szczegot, K.; Wioeniewska, D. *Organometallics* **2005**, *24*, 3987–3994.

(28) Hendershot, D. G.; Barber, M.; Kumar, R.; Oliver, J. P. *Organometallics* **1991**, *10*, 3302–3309.

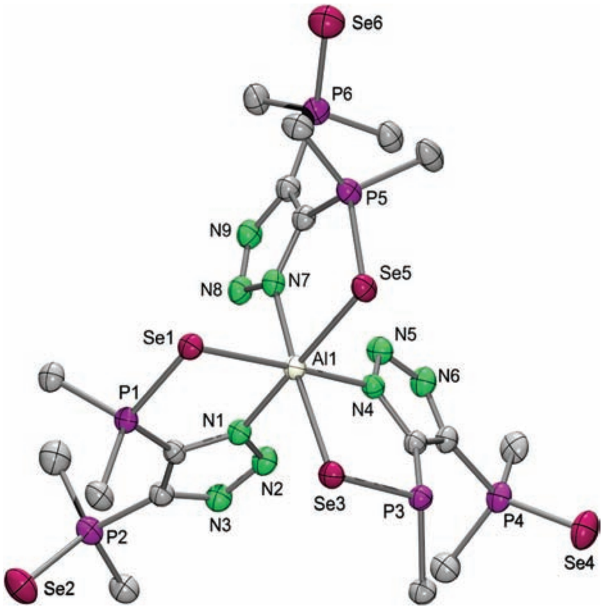


**Figure 6.** Perspective view of **9** with thermal ellipsoids at 50% probability. Carbon atoms from the phenyl groups, except the *ipso*, are omitted for clarity.

aluminum compound are comparable to those observed in the tetracoordinate aluminum complexes $Me_2Al[PhP(Se)(N^tBu)(NH^tBu)]$, (2.510(1) and 2.187(1) Å)[15] and $(Me_2Al)_3[P(CH_2NPh)_2Se]_2(AlMe_3)$ (2.510(1) and 2.239(2)Å).[16] Furthermore, the three five-membered C−P−Se−Al−N heterocycles display planar arrangements (mean deviation from the plane = 0.04 Å), with angles of 2.8, 11.0, and 11.1° between the planes defined by the C−P−Se−Al−N heterocycles and the triazole rings.

**Excess Ratio Reactions.** Reactions of $4,5\text{-}(P(O)Ph_2)_2tzH$ (**1**) and $4,5\text{-}(P(S)Ph_2)_2tzH$ (**2**) with 2 equiv of $AlR_3$ (R = Me, $^i$Bu) gave the organometallic adducts $[AlR_2\{\kappa^2\text{-}O,O'\text{-}[4,5\text{-}(P(O)Ph_2)_2tz]\}\text{-}(N'\text{-}AlR_3)]$ (R = Me (**10**), $^i$Bu (**11**)) and $[AlR_2\{\kappa^2\text{-}N,S\text{-}[4,5\text{-}(P(S)Ph_2)_2tz]\}\text{-}(N'\text{-}AlR_3)]$ (R = Me (**12**), $^i$Bu (**13**)), respectively, in good yields (Scheme 3). The reaction of $4,5\text{-}(P(Se)Ph_2)_2tzH$ (**3**) with 2 equiv of $AlMe_3$ gave the monometallic compound **8**, while reaction of the former with an excess of $Al^iBu_3$ produced an inseparable mixture of products.

Although X-ray quality crystals of **11** were not obtained, the spectroscopic evidence strongly supports the structure depicted in Scheme 3. The $^1$H NMR spectra of **10** and **11** show two sets of signals for the $AlR_2$ and $AlR_3$ groups and their $^{31}$P NMR spectra reveal single signals corresponding to symmetric coordination modes. Attempts to grow X-ray quality crystals from the recrystallized products were unsuccessful. However, single crystals of a lower quality of **10** were obtained when using a toluene/hexane mixture. Compound **10** crystallized as two independent molecules in the orthorhombic $Pca2_1$ space group (Figure 7). The crystal structure of **10** revealed positional disorder between the C(30) and Cl(1) atoms with the occupancy ratio of 48:52. The presence of the chlorine atom is most probably due to contamination of the ligand with its hydrochloride salt.[29] Compound **10** exhibits two tetracoordinate aluminum atoms with different coordination environments. The aluminum atom from the $AlMe_2$ moiety is coordinated to both oxygen atoms while the second aluminum atom from the $AlMe_3$ group coordinates through a dative bond to the central nitrogen atom from the triazole ring. The seven-membered ring displays a mean deviation from the plane = 0.32 Å, while the triazole ring remains planar. The Al−O bond lengths, with 1.830(3) and 1.850(3) Å, are similar to those observed in **4** (1.817(2) and 1.808(2) Å).

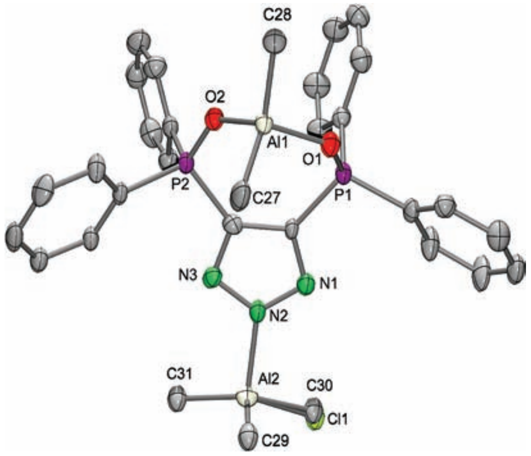
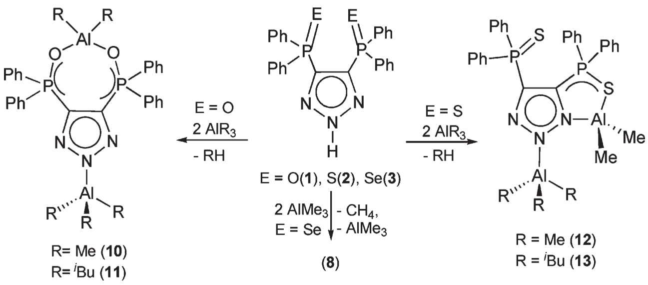


**Figure 7.** Perspective view of molecule *a* of **10** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

**Scheme 3.** Preparation of Compounds **10**−**13**



Furthermore, the reaction of $4,5\text{-}(P(S)Ph_2)_2tzH$ (**2**) with 2 equiv of $AlMe_3$ and $Al^iBu_3$ gave the dinuclear compounds **12** and **13**, respectively. The $^1$H NMR spectra of **12** and **13** show similar patterns for the corresponding $AlR_2$ and $AlR_3$ groups as those observed in **10** and **11**. However, the $^{31}$P NMR spectra of **12** and **13** display two different coordination environments for the two phosphorus atoms. The $^{27}$Al NMR spectrum of **12** was silent; however, that of **13** showed two broad signals that overlap, which is in agreement with the existence of two chemically different tetracoordinate aluminum atoms.

Suitable crystals for X-ray diffraction studies were obtained for **12** upon allowing its saturated toluene solution to slowly cool from 80 °C to ambient temperature. Compound **12** crystallizes in the triclinic system $P\overline{1}$ space group, with one molecule in the asymmetric unit (Figure 8).

Compound **12** exhibits two tetracoordinate aluminum atoms with different coordination environments. The aluminum atom from the $AlMe_2$ moiety is coordinated

---

[29] During the isolation of the free form of the ligand, the addition of a 10 M solution of HCl is required for precipitation, followed by thorough washing with distilled water.

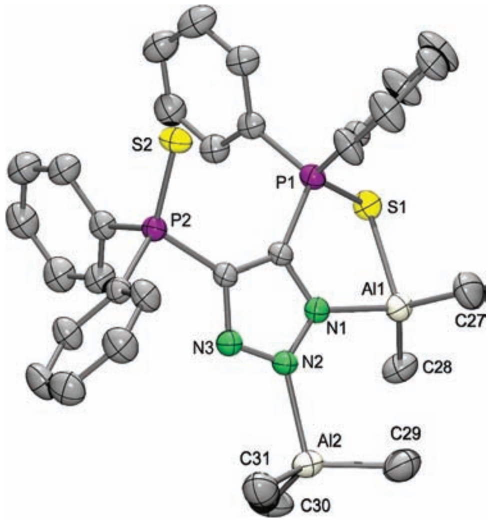


**Figure 8.** Perspective view of **12** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

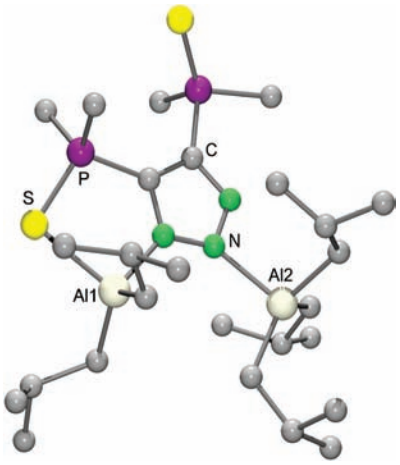


**Figure 9.** Molecular structure of compound **13**.

to sulfur and nitrogen atoms while the second aluminum atom from the $AlMe_3$ group coordinates through a dative bond to the central nitrogen atom from the triazole ring. Furthermore, the core of **12** can be viewed as two fused five-membered rings with a non-planar arrangement. However, the P(1) and Al(1) atoms are coplanar to the triazole ring, whereas, the S(1) atom lies 0.87 Å above the plane. The Al−S(P) bond length (2.382(1) Å) is longer than the mean value for Al−S bond lengths for tetracoordinate aluminum atoms (2.303 Å),[30] but significantly shorter than those observed for the dimeric compounds **6** (2.652(1) and 2.736(1) Å) and **7** (2.737(1) Å). The N(1)−Al(1)−S(1) angle is 89.2(1)°, more obtuse than those observed in **6** (82.4°(1)) and **7** (82.0°(1)). The Al(1)−N(1) bond length (1.994(2) Å) in **12** is closely related to those observed in **6** (1.997(2) and 1.988(2) Å) and **7** (1.996(2) Å) and comprehensively shorter than the Al(2)−N(2) dative bond (2.055(2) Å). The structure of **12** contrasts significantly with that of the adduct reported by Jordan and co-workers, $[AlMe_2[\kappa^2\text{-}N,S\text{-}\{S(NAd)CMe\}]\text{-}(S\text{-}AlMe_3)]$ (Ad = adamantyl).[14c] In the latter, the coordination of the $AlMe_3$ group occurs through the sulfur atom rather than through the nitrogen atom of the thioamidate ligand because of the steric bulk of the adamantyl group. While in **12**, the N(2) position is preferred over the N(3), in great part because of the steric bulk that the phenyl groups exerted over the N(3) atom.

Although the quality of the X-ray data for **13** did not allow a full structural characterization, a model of this compound was attained (Figure 9). Compound **13** shows the same coordination features as those observed in **12**, regardless of the difference in the steric bulk of the alkyl groups on the aluminum atom.

**Theoretical Calculations.** To gain insight into the coordination behavior of these ligands, theoretical calculations were carried out using the GAUSSIAN 03 suite of programs.[19] A plot of the frontier orbitals for the deprotonated ligands $[4,5\text{-}(P(E)Ph_2)_2tz]^-$(E = O(**1a**), S-(**2a**), Se(**3a**)) (Figure 10) shows the highest occupied molecular orbitals (HOMOs) distributed over the triazole ring (**1a**) and on both chalcogen atoms (**2a** and **3a**). This suggests that an orbital controlled process is not favored in the formation of their respective aluminum complexes.

Furthermore, NBO calculations show that the strongest negative electrostatic potentials for compounds **1a**−**3a** are located over the N−N−N fragments (Supporting Information, Figures S6−S8). However, in **1a** the natural charges for the oxygen atoms have values of −1.129 and −1.112, while those for the N(1), N(2), and N(3) atoms are −0.393, −0.137, and −0.285, respectively. This suggests that a charge control bonding process predominates over an orbital controlled bonding process in the formation of compounds **4** and **5**. On the other hand, the natural charges for the chalcogen atoms in **2a** and **3a** exhibit the strongest negative value in these molecules, −0.683 (S) and −0.605 (Se), respectively. While for the N(1) atom, the values of −0.351 and −0.318 are observed for **2a** and **3a**, respectively (Supporting Information, Figure S9). Therefore, the driving force in the formation of compounds **6**− **8**, where the bonding to the metal center occurs through the chalcogen and nitrogen atom, can be attributed to the formation of the five-membered chelate rings.

Furthermore, the electrostatic potential mapped onto the electronic density surfaces for **4** and one-half of **6** (Supporting Information, Figures S10 and S11) yield the most negative potentials on the nitrogen atoms in the triazole rings. This can account for the formation of the adduct-like compounds **10**−**13**, when **1** and **2** are treated with an excess of aluminum alkyls. Furthermore, the NBO analysis on one-half of **6** shows a highly electrostatic nature of the metal−ligand interaction, since the Wiberg bond indexes for Al are very small. The Wiberg bond index[31] for the Al−C bonds is 0.563, whereas for the Al−N(1) bond it is only about half (0.261) and for the Al−S bond the value is 0.441. This is unexpected from the point of view of the HSAB[32] theory by which the harder N(2) atom should be more strongly bound to the hard Al atom. This in turn may be explained by the fact that there is a

---

(30) For a full account of Al−S bond lengths see the Al−S bond length histogram for tetracoordinate Al atoms from CCDC in Supporting Information, Figure S5.

(31) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.

(32) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

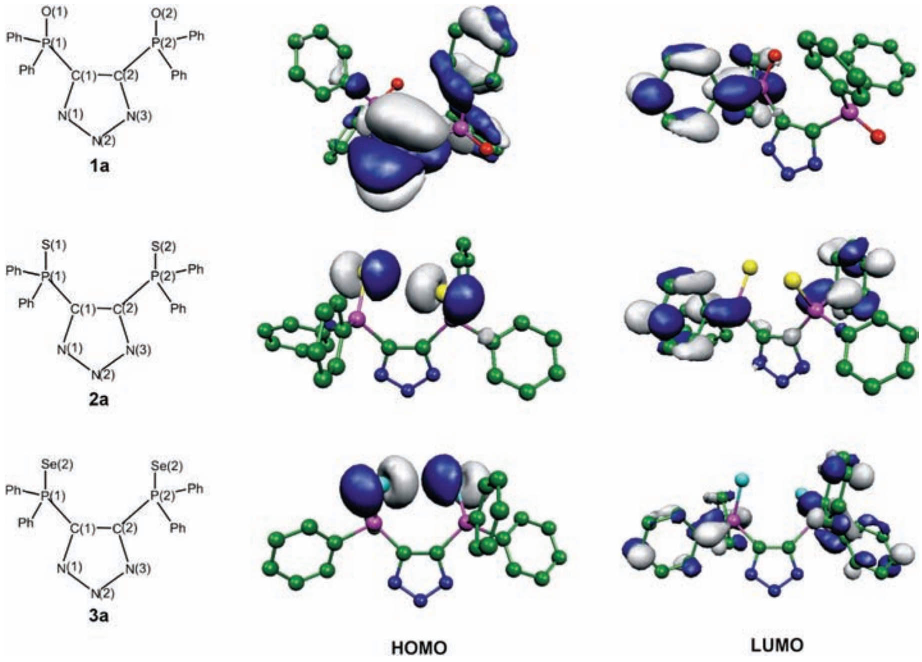


**Figure 10.** Frontier orbitals plot for the deprotonated ligands **1a**−**3a** calculated at the RHF/3-21G** level of theory (All hydrogen atoms omitted for clarity).

strong delocalization of the electron density over the triazole ring, making it less available for bond formation with the metal. Natural charges for compound **6** reflect this feature by exhibiting values of 1.83 for the Al atom, −0.624 for S(1), and −0.535 for N(1).

NBO analysis on compound **9** suggest that the Al−Se bonds have a higher covalent character than Al−N bonds, as reflected by their Wiberg bond indexes (0.49 vs 0.18). Moreover, the analysis of the natural charges of the N (−0.623, −0.623, and −0.618) and Se atoms (−0.390, −0.383, −0.387) bonded to the Al atom suggests the existence of essentially Al−N electrostatic interactions in this compound. Furthermore, there is little electron transfer from N to Al as observed by the second order perturbation theory analysis in which the delocalization energy is assessed. The energy for the electronic transfer from Se to Al is 134.04 kcal/mol, which is large when compared to regular delocalization energy in aromatic compounds.[33] The delocalization energy from N to Al in compound **9** is only 42.36 kcal/mol. This further supports the idea that covalent bonding is mainly carried out by Se atoms rather than by N atoms.

## Conclusions

The structural outcome of the compounds synthesized is essentially the result of the interaction of the hard Al(III) centers in different fashion, depending on the relative importance of the electrostatic ligand−metal interactions regarding the overlap of frontier orbitals. The reactivity and stability of these compounds are reflected in factors such as the nature of the donor atoms and the steric protection of the metal center. Compounds **4** and **5**, which bear a seven-membered ring system, are formed through the involvement of both oxygen atoms. The oxygen atoms are highly electronegative and exhibit the strongest negative charges in the deprotonated ligands. Therefore, the structural traits of these compounds can be viewed as a token of the high oxophility of aluminum(III) centers. On the other hand, **6**−**8** exhibit $\kappa^3$ coordination through a combination of hard and soft donor atoms, allowing the chelation of the aluminum centers by forming stable five- and six-membered ring systems, which provides sufficient electronic relief for the hard aluminum center. Furthermore, the highest negative potential in the N−N−N fragment of the triazole moieties calculated for **4** and **6** can account for the formation of adduct-like compounds **10**− **13**. Finally, the high covalent character of the Al−Se bonds combined with the essentially electrostatic nature of the Al−N bonds in **9** may explain the relative stability of this uncommon trischelate arrangement. The structural diversity observed in these compounds can be viewed as an example of charge control versus orbital control during the bond formation process.

**Acknowledgment.** We thank the UNAM-DGAPA (Grant IN205708) and CONACyT (Grant 058484) for financial support and M. N. Zavala-Segovia for her technical assistance. J.A.-G. acknowledges the CONACyT for her Ph.D. fellowship.

**Supporting Information Available:** Figures S1−S11, histograms from CCDC and X-ray data (CIF) for **1**, **4a**, **4b**, **6**, **7**, **9**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[33] The delocalization energy for the BD(C−C) bond to a BD*(C−C) one in a phenyl group is typically in the range 200 to 300 kcal/mol.