An unusual trigonal-bipyramidal coordination of aluminum by an open-chain tetradentate amine. Synthesis and molecular structure of [Al(CH3)][C8H19N4][Al(CH3)2]

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in ~8% abundance and having the structure shown in Figure 1 and the major isomer being isostructural with II. The room-temperature ^{1}H NMR resonance at δ -10.4 is therefore a coalesence signal produced by interconversion of the two isomers. Variable-temperature ^{31}P and ^{11}B NMR spectra proved to be unhelpful in illustrating the presence of the minor isomer.[15]

The structurally characterized isomer of I exhibits two gold(I) phosphine units in positions which are probably sterically unacceptable to the AuPPh$_3$ fragments. Although the P···P distances in I and II are similar (5.401 and 5.307 Å, respectively) and thereby imply that substitution of phenyl for ethyl groups in I might well be sterically allowed with respect to *inter*-phosphine interactions, it is in fact difficult to find orientations of the Ph$_3$P substituents that allow the phenyl H atoms to be at reasonable distances *both* from the carbonyl O atoms of the Fe$_4$(CO)$_{12}$ framework and from the H atoms of the second triphenyl phosphine unit. Thus, in the case of II, the isomer equilibrium swings wholly in favor of the asymmetrical geometry in which one AuPPh$_3$ is forced down toward the iron framework and the endo-hydrogen atom migrates toward the boron atom (Chart I). It is significant, however, that in I, neither isomer exhibits a AuPEt$_3$ unit interacting completely with the tetrairon framework.[17] Thus, electronic factors[2] appear to drive the gold(I) phosphine units toward interaction with the boron atom, and steric factors then control the heavy metal atom assembly about the boron atom. These observations illustrate the limitations of applying the isolobal analogy to heterometallic- and mixed-metal–main group systems and underline the subtle balance existing between the steric and electronic effects that govern cluster geometry. For both isomers of Fe$_4$(CO)$_{12}$(AuPEt$_3$)$_2$BH to be observed by using NMR spectroscopy, the energy difference between the two must be small. It is likely, therefore, that crystal packing forces are important when it comes to determining which structure is preferred in the solid state.

Further evidence to support the above postulate comes from a study of the compound [Fe$_4$(CO)$_{12}${Au$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$}BH] which appears to exhibit the same solution equilibrium as I, but with the two isomers being approximately *equally* populated.[18] Work on this system is in progress, as are studies with other phosphine gold(I) substituents.

Registry No. I, 114465-57-5; Fe, 7439-89-6.

(15) Low-temperature ^{11}B NMR signals are broad,[16] and no new resonance could be detected on cooling. The ^{31}P NMR resonance (298 K) at δ 51.6 gave rise to signals (197 K) of roughly equal intensity (δ 52.9 and 51.5);[7] since the minor isomer possesses phosphorus atoms in an environment similar to one of the P atoms in the major isomer, we suggest that the resonance for the minor isomer coincides with one of those observed for the major isomer of I.

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An Unusual Trigonal-Bipyramidal Coordination of Aluminum by an Open-Chain Tetradentate Amine. Synthesis and Molecular Structure of [Al(CH₃)][C₈H₁₉N₄][Al(CH₃)₂]

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Summary: Reaction of trimethylaluminum with the tetradentate open-chain amine N,N'-bis(3-aminopropyl)-ethylenediamine affords the crystalline product [Al(CH$_3$)][C$_8$H$_{19}$N$_4$][Al(CH$_3$)$_2$]. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 8.193 (6) Å, b = 9.235 (7) Å, c = 12.094 (8) Å, α = 96.05 (6)°, β = 111.15 (5)°, γ = 107.18 (6)°, and D_{calcd} = 1.13 g cm^{-3} for Z = 2. Least-squares refinement based on 1739 observed reflections with intensities $I \geq 3\sigma(I)$ in the range $0.0° \leq 2\theta \leq 50.0°$ converged at R = 0.041 (R_w = 0.059). The title compound contains a pentacoordinate aluminum atom in a trigonal-bipyramidal environment.

Principally due to its ability to form stable complexes with such transition-metal ions as Ni(II),[1] Co(III),[2,3] and Rh(III),[3,4] the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane, [14]aneN$_4$ (commonly referred to as cyclam), has proven to be particularly useful in inorganic chemistry. Recently, we initiated an investigation into the main-group chemistry of [14]aneN$_4$ by exploring its interactions with organoaluminum species.[5-7] Although the tetradentate open-chain amine N,N'-bis(3-aminopropyl)ethylenediamine, C$_8$H$_{22}$N$_4$, has been employed in the Ni–template synthesis of [14]aneN$_4$,[8] its coordination chemistry has remained largely unexplored. Herein, we report the synthesis[9] and structure of [Al(CH$_3$)][C$_8$H$_{19}$N$_4$][Al(CH$_3$)$_2$] isolated from reaction of trimethylaluminum with N,N'-bis(3-aminopropyl)ethylenediamine. In addition to representing the first examination of the main-group organometallic coordination chemistry of this important open-chain amine, the title compound is unusual in that it contains a pentacoordinate aluminum atom in a trigonal-bipyramidal environment. The X-ray crystal structure of [Al(CH$_3$)][C$_8$H$_{19}$N$_4$][Al(CH$_3$)$_2$] is shown in Figure 1.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\theta$-scan technique with Mo Kα radiation (λ = 0.710 73 Å) at 26 °C. The title com-

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(9) A 50-mL reaction vessel was charged with N,N'-bis(3-aminopropyl)ethylenediamine (8.2 mmol) and trimethylaluminum (16.4 mmol) in a 2:1 pentane/methylene chloride solution in the drybox. Reaction was immediate; the evolution of gas was observed. The system was allowed to react at room temperature for several hours at which point a multitude of colorless extremely air-sensitive crystals were obtained. ^{1}H NMR (CDCl$_3$); δ -0.99 (s, 3 H, AlCH$_3$), -0.94 (s, 3 H, AlCH$_3$), -0.89 (s, 3 H, AlCH$_3$); The propano and ethano fragments of the amine consist of a pair of complex multiplets centered at δ 1.76 and 2.98.
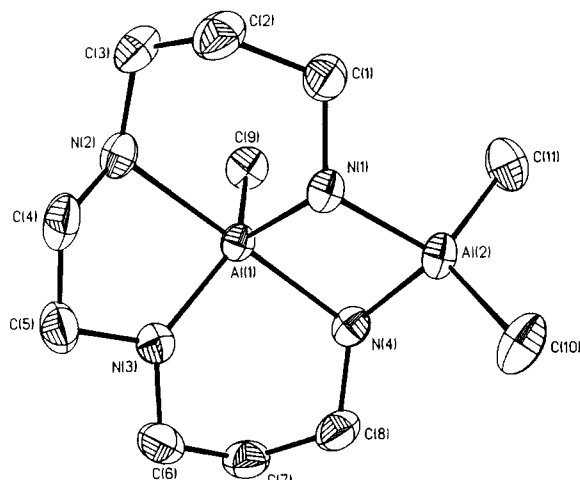
Figure 1. A view of the [Al(CH₃)][C₈H₁₉N₄][Al(CH₃)₂] molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted.

Figure 2. Reaction scheme for [Al(CH₃)][C₈H₁₉N₄][Al(CH₃)₂].

pound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 8.193 (6) Å, b = 9.235 (7) Å, c = 12.094 (8) Å, α = 96.05 (6)°, β = 111.15 (5)°, γ = 107.18 (6)°, and D_{calcd} = 1.13 g cm⁻³ for Z = 2. The structure was solved by direct methods and refined, based on 1739 observed reflections with intensities $I \geq 3\sigma(I)$, using SHELXTL.[10] Refinement converged at R = 0.041 (R_w = 0.059). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic temperature factors.

The interactions of organoaluminum species with monodentate primary and secondary amines have been previously studied by Smith and co-workers.[11-19] These studies pointed out that while at lower temperatures 1:1 addition compounds are formed, reaction at higher temperatures was shown to produce reaction products possessing Al₂N₂ fragments accompanied by alkane elimination. This laboratory has obtained similar results from reactions of organoaluminum species with macrocyclic amines.[5-7,20] Surprisingly, the literature reveals a paucity of structural data concerning organoaluminum compounds derived from multidentate open-chain amines. We have recently endeavored to address this area of organoaluminum chemistry.[21,22]

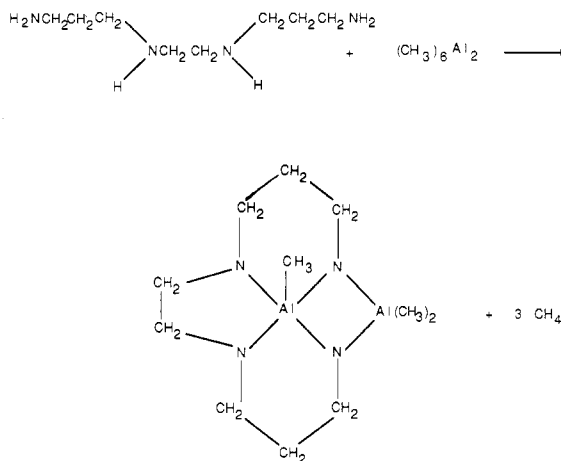The aza hydrogen atoms of the tetradentate open-chain amine proved to be quite reactive as N–H/Al–CH₃ con-

densation was shown to take place even at room temperature. The elimination of methane resulted from cleavage of N–H bonds (from N(1), N(3), and N(4)) and cleavage of Al–CH₃ fragments (two from Al(1) and one from Al(2)). The reaction scheme for [Al(CH₃)][C₈H₁₉N₄][Al(CH₃)₂] is given in Figure 2.

The four-coordinate tetrahedral coordination of the aluminum atom in the dimethylaluminum unit, Al(2), is generally unremarkable as this is the predominant coordination geometry of aluminum in organometallic chemistry. The remaining aluminum atom, Al(1), is clearly five-coordinate, being bonded to all four nitrogen atoms of the amine as well as one methyl carbon atom. The aluminum atom is coplanar with N(1), N(3), and C(9). The coordination sphere of Al(1) is completed by the remaining two nitrogen atoms of the amine situated in axial positions relative to the planar AlN₂C unit. The bond angle between the axial nitrogen atoms and the central aluminum atom, N(2)–Al(1)–N(4), is 169.2 (1)°. The coordination geometry of Al(1) may thus be described as trigonal bipyramidal. The Al–N distances from the central aluminum atom to the axial nitrogen atoms are 2.135 (2) and 2.055 (2) Å for Al(1)–N(2) and Al(1)–N(4), respectively. Notably, these values must be considered quite long.[23] These distances are placed in perspective when one considers that the remaining Al–N distances in the title compound are 1.826 (2) and 1.987 (3) Å, respectively, for Al(1)–N(3) and Al-(1)–N(1). Indeed, this rather substantial variation in bond distances may readily be viewed as a result of steric strain around the pentacoordinate aluminum atom in addition to the presence of aza hydrogen atoms associated with N(1), N(2), and N(4).

A comparison of other recently reported organometallic compounds containing pentacoordinate aluminum atoms is warranted. In the aluminum–nitrogen cage [Al(CH₃)]₂[C₈H₂₀N₆][Al(CH₃)₂]₂,[21] both of the pentacoordinate aluminum atoms are in square-pyramidal environments. This is contrasted with the trigonal-bipyramidal coordination of the aluminum atom in [Al(CH₃)₃][12]aneS₄[24] where two neutral sulfur macrocycles are bridged by a perfectly planar Al(CH₃)₃ unit. Thus, it appears that trigonal bipyramidal is the preferred coordination of pentacoordinate aluminum atoms in organo-main-group complexes. Only when the associated ligand(s) are sufficiently rigid will square-pyramidal coordination be favored.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (6 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Figure 1. $^{31}P\{^1H\}$ DNMR spectra of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(1,5\text{-}COD)$ (**2b**) in THF-d_8–pentane (1:2).

Unsaturated, PCy$_2$-Bridged Re–M Heterobimetallics (M = Rh, Ir, Pd; Cy = Cyclohexyl): Metal–Metal Bond Isomerism, Reversible P–H Bond Activation, and Cooperative Reactivity[†]

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Summary: The new d^4-d^8 heterobimetallics $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, Ir; COD = cyclooctadiene) are proposed, on the basis of ^{31}P DNMR, to exist in two isomeric forms: one with pseudotetrahedral (PT) coordination about M and an M=Re double bond and the other with square-planar (SP) coordination about M and an M→Re donor–acceptor bond. Structural models for this metal–metal bond isomerism are provided by $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(PMe_3)_2$ (PT, Re–Ir = 2.6573 (5) Å) and $[(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Rh(1,5\text{-}COD)]BF_4$ (SP, Re–Rh = 2.9361 (8) Å). Reversible P–H bond activation is observed for $(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$(*Pd=Re*) and $(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Pd(PPh_3)$(*Pd→Re*) and carbonylation of the Ir–COD complex occurs at both metal centers to give $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$ in which a PCy$_2$ ligand has been transferred to Ir.

One approach to the development of new selective transition-metal catalysts involves the use of heterobimetallic complexes in which each metal center performs a different function.[1] In most soluble heterobimetallic complexes one or both metal centers are electronically saturated,[2] and reactivity at both metal centers without fragmentation is rarely observed.[3] We have recently shown that reactions of groups 8–10 transition-metal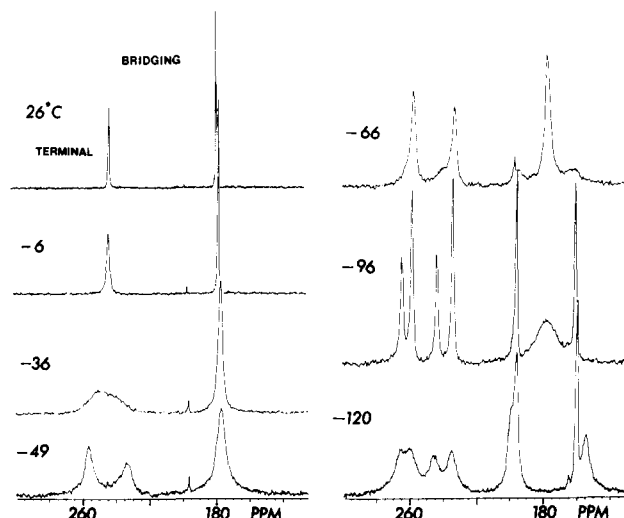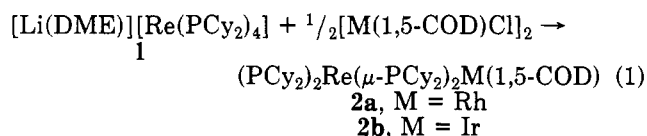 complexes with early transition-metal-containing phosphines that contain M≈P double bonds lead directly to heterobimetallics in which the early metal center is electronically unsaturated.[4] In this report we describe the synthesis and metal–metal bond isomerism of $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, Ir; COD = cyclooctadiene), the synthesis of $(PCy_2)(PCy_2H)(N_2)Re(\mu\text{-}PCy_2)_2Pd(PPh_3)$ and reversible P–H bond activation to give $(PCy_2)_2ReH(\mu\text{-}PCy_2)_2Pd(PPh_3)$, and the cooperative addition of CO to the M = Ir complex to give $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(CO)_2(PCy_2)$.

Displacement of chloride ion from $[M(1,5\text{-}COD)Cl]_2$[5] by the homoleptic $[Re(PCy_2)_4]^-$ anion[6] (1) gives the unsaturated heterobimetallics $(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD)$ (M = Rh, **2a**; M = Ir, **2b**) as dark purple and black microcrystalline solids in high yield.[7] Complexes **2a,b** have been characterized by IR and ^1H and ^{31}P NMR spectroscopy and by complete elemental analysis (Tables I–IV, supplementary material). The ^{31}P DNMR spectra of **2b** (Figure 1) indicate the presence of two isomers, each with four inequivalent PCy$_2$ ligands. Both isomers undergo two different dynamic processes, proposed to be inversion of the bent ReP$_2$Ir bridge ($\Delta G^{\ddagger}_{T_c}$ = 9.7 ± 0.2 [9.1 ± 0.2] kcal/mol for the major [minor] isomer)[8,9] and rotation

$$[Li(DME)][Re(PCy_2)_4] + 1/2[M(1,5\text{-}COD)Cl]_2 \rightarrow$$
$$1$$

$$(PCy_2)_2Re(\mu\text{-}PCy_2)_2M(1,5\text{-}COD) \quad (1)$$
$$\textbf{2a, M = Rh}$$
$$\textbf{2b, M = Ir}$$

[†]Contribution no. 4670.

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(8) $\Delta G^{\ddagger}_{T_c}$ was estimated by using the Eyring equation for two-site exchange. Cf. Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982.