Inorganic Chemistry
Article
pubs.acs.org/IC

Synthesis and Calorimetric, Spectroscopic, and Structural Characterization of Isocyanide Complexes of Trialkylaluminum and Tri-*tert*-butylgallium

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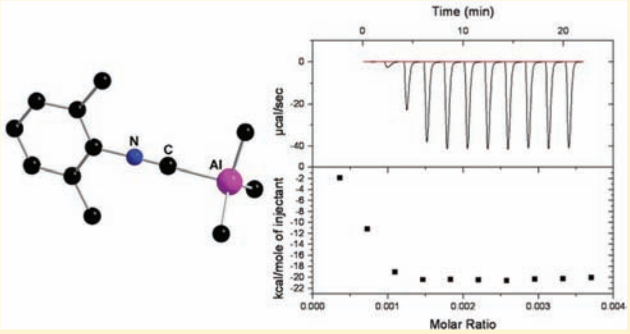
Supporting Information

ABSTRACT: Addition of *tert*-butylisocyanide or 2,6-dimethylphenylisocyanide to a solution of trialkylaluminum or trialkylgallium results in formation of complexes $R_3M{\cdot}C{\equiv}N^tBu$ (M = Al, R = Me (**1**), Et (**2**), ^{i}Bu (**3**), ^{t}Bu (**4**); M = Ga, R = ^{t}Bu (**9**)) or $R_3M{\cdot}C{\equiv}N(2,6\text{-}Me_2C_6H_3)$ (M = Al, R = Me (**5**), Et (**6**), ^{i}Bu (**7**), ^{t}Bu (**8**); M = Ga, R = ^{t}Bu (**10**)), respectively. Complexes **1**, **4**, **5**, and **8**−**10** are isolated as solids, whereas the triethylaluminum and triisobutylaluminum adducts **2**, **3**, **6**, and **7** are viscous oils. Complexes **1**−**10** were characterized by NMR (^{1}H, ^{13}C) and IR spectroscopies, and the molecular structures of **4**, **5**, and **8**−**10** were also determined by X-ray crystallography. The frequency of the C≡N stretch of the isocyanide increased by 58−91 cm^{-1} upon complexation, consistent with coordination of the isocyanide as a σ donor. Enthalpies of complex formation for **1**−**10** were determined by isothermal titration calorimetry. Enthalpy data suggest the following order of decreasing Lewis acidity: $^tBu_3Al \gg {}^iBu_3Al \geq Me_3Al \approx Et_3Al \gg {}^tBu_3Ga$. In the absence of oxygen and protic reagents, the reported complexes do not undergo insertion or elimination reactions upon heating their benzene-d_6 solutions to 80 °C.



INTRODUCTION

As part of our previous investigation into the chemistry of carbon monoxide with organoaluminum and organogallium reagents,[1,2] we initiated a parallel study of isocyanide coordination and insertion into Al−C and Ga−C bonds. Isocyanides have an isoelectronic relationship with CO, but there are important differences in the steric and electronic properties. Isocyanides are stronger sigma donors than CO, their insertion products have greater steric demand due to the substituents on nitrogen, and the N→M bond energies (M = Al, Ga) of the resulting insertion products are less than the O→M bond energies, an important driver in the CO insertion reactions of $^tBu_3Al$ and $^tBu_3Ga$.[1,2]

The coordination chemistry of isocyanides with aluminum and gallium alkyls has not been studied in great detail. The only reported isocyanide complexes of aluminum are $Ph_3Al{\cdot}C{\equiv}NCy$,[3] $Me_3Al{\cdot}C{\equiv}NMe$,[4] $Cp_3Al{\cdot}C{\equiv}N^tBu$,[5] and $\{Me_4C_2(C_5H_4)_2\}ClAl{\cdot}C{\equiv}N^tBu$.[6] Only the latter two complexes have been structurally characterized. There are no previously reported isocyanide complexes of gallium.

There are a few reports of isocyanide insertion into Al−Cl, Al−H, and Al−Al bonds, but these reactions have not been extensively studied. In 1970 Meller and Batka reported insertion of methylisocyanide into each of the Al−Cl bonds of aluminum trichloride to give a polymeric product of formula $[Al\{C(Cl){=}NMe\}_3]_n$ but of unknown structure.[4] Hoberg reported insertion of isocyanides into the Al−H bond of $^iBu_2AlH$ to give $[^iBu_2AlC(H){=}NR]_2$ (R = ^{t}Bu, Cy, CH_2Ph).[7] Spectroscopic and mass spectrometric data suggested a dimeric product with a six-membered $Al_2C_2N_2$ ring, analogous to the dimeric acyls $[^tBu_2MC(O)^tBu]_2$ with $M_2C_2O_2$ (M = Al, Ga) rings obtained upon reaction of $^tBu_3M$ with CO. Dimer formation contrasts with the results of DFT calculations by Schaefer and co-workers,[8] which predict that a cyclic iminoacyl monomer obtained from insertion of RN≡C into an Al−H bond of AlH_3 is energetically preferred, at least in the gas phase, over formation of a dimer. Dissociation of $[H_2AlC(H){=}NH]_2$ into cyclic monomers was calculated to be exothermic by −44 kJ mol^{-1}. A subsequent crystallographic analysis confirmed that $[^tBu_2AlC(H){=}N^tBu]_2$, formed by insertion of ^{t}BuN≡C into the Al−H bond of $^tBu_2AlH$, exists as a cyclic dimer in the solid state.[9] Insertion was also observed upon reaction of $(Mes^*AlH_2)_2$ with ^{t}BuNC to give $[Mes^*AlCH_2N^tBu]_2$.[10] Isocyanide insertion into the Al−H bonds of $H_3Al{\cdot}NMe_3$ results in fused carbaaminoalane formation.[11] Uhl found that isocyanides insert into the Al−Al and Ga−Ga bonds,

Received: November 11, 2011
Published: February 1, 2012

dx.doi.org/10.1021/ic202427z | *Inorg. Chem.* 2012, 51, 2494−2502

but not In−In bonds, of $\{(Me_3Si)_2CH\}_2M{-}M\{CH(SiMe_3)_2\}_2$ (M = Al, Ga, In).[12]

Shapiro and co-workers[13] reported the first of three examples of isocyanide insertion into an Al−C bond, that being double insertion upon reaction of $^tBuN{\equiv}C$ with $(C_5Me_4H)_3Al$. The steric bulk of the C_5Me_4H ligand is presumably a factor in the unique double-insertion reaction since reaction of $^tBuN{\equiv}C$ with Cp_3Al forms the simple adduct $Cp_3Al{\cdot}C{\equiv}N^tBu$. Cui[14] reported that isocyanides will also insert into a strained cyclopropene complex of aluminum to form an aluminacyclobutene. Insertion of the isocyanide is thought to be driven by relief of ring strain. There is also precedent for reactions of isocyanides with Al(I) species. Cui and co-workers[15] report that the β-diketiminato aluminum carbene analogue $HC[(C^tBu)(NAr)]_2Al$ reacts with 2 equiv of 2,6-diisopropylphenylisonitrile by isocyanide coordination and subsequent insertion of a second isocyanide into the Al−C bond that is formed by coordination. The nitrogen atom of the bound isocyanide then coordinates to the aluminum, creating a four-membered AlC_2N ring similar to that found in the double-insertion product reported by Shapiro.[13]

In addition to coordination and insertion reactions, isocyanides may potentially undergo cleavage of the $N{-}C_{substituent}$ bond upon reaction with aluminum and gallium reagents. *tert*-Butylisocyanide reacts with $\{(Me_3Si)_2CH\}_2Al{-}Al\{CH(SiMe_3)_2\}_2$ at room temperature over a period of 3 days to yield $[\{(Me_3Si)_2CH\}_2AlC{\equiv}N]_3$ in 26% yield.[16] Schaefer and co-workers calculated that hydride or alkyl transfer from aluminum or gallium to a coordinated isocyanide carbon in $R_3M{\cdot}C{\equiv}NR'$ (M = Al, Ga) complexes is exothermic and thermodynamically favorable.[8]

Herein we report the synthesis, characterization, and stability of isocyanide complexes **1**−**10**. The complexes have been characterized by IR and NMR spectroscopies as well as X-ray crystallography for **4**, **5**, and **8**−**10**. In addition, enthalpies of complex formation have been measured by isothermal titration calorimetry (ITC). If protected from protic reagents and oxygen, we find that these compounds are stable and not prone to insertion or elimination reactions up to 80 °C in benzene-d_6 solutions for more than 24 h.

$R_3Al{\cdot}C{\equiv}N^tBu$	$R_3Al{\cdot}C{\equiv}NAr$	$^tBu_3Ga{\cdot}C{\equiv}NR$
1,R=Me	**5**,R=Me	**9**,R=^{t}Bu
2,R=Et	**6**,R=Et	**10**,R=Ar
3,R=^{i}Bu	**7**,R=^{i}Bu	Ar=2,6-$Me_2C_6H_3$
4,R=^{t}Bu	**8**,R=^{t}Bu	

■ EXPERIMENTAL SECTION

General Procedures. All reactions were performed in an inert atmosphere of purified nitrogen using standard inert atmosphere techniques. Trimethylaluminum, triethylaluminum, and triisobutylaluminum were purchased from Strem Chemical, Inc. and used as received. Tri-*tert*-butylaluminum[17] and tri-*tert*-butylgallium[18] were prepared using published procedures. *tert*-Butylisocyanide and 2,6-dimethylphenylisocyanide were purchased from Aldrich. Toluene was distilled from sodium, and hexanes were distilled from calcium hydride prior to use. Benzene-d_6 and chloroform-*d* were dried by storage over activated molecular sieves and degassed with purified nitrogen. Solution NMR spectra were recorded on a Varian VXRS 400 MHz or Varian Unity Inova 600 MHz spectrometer using deuterated solvent. Chemical shifts are reported relative to TMS. ^{13}C NMR assignments for 2,6-dimethylphenylisocyanide resonances in complexes **5**−**8** and **10** were aided by spectral assignments for the free isocyanide as reported by Stephany, de Bie, and Drenth.[19] Infrared spectra were obtained on a Perkin-Elmer GX FT-IR infrared spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory and Galbraith Laboratories.

Preparation of $Me_3Al{\cdot}C{\equiv}N^tBu$ (1). *tert*-Butylisocyanide (0.25 mL, 2.21 mmol) was added via syringe to a solution of Me_3Al (1.0 mL, 2.0 M in toluene, 2.0 mmol) in 20 mL of hexanes, and the resulting colorless solution was stirred for 4 h. Volatiles were removed under vacuum, and the remaining solid was recrystallized by dissolution in a minimal amount of hexanes followed by cooling at −30 °C. The colorless microcrystalline solid was isolated by filtration and dried in vacuo. A second crop of product was similarly obtained by concentration and cooling of the filtrate. Crystals of **1** could also be obtained by sublimation at 20 °C/0.1 mmHg. Yield: 0.308 g, 99%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2224. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.56 (s, 9H, N^{t}Bu), −0.91 (s, 9H, $AlCH_3$). $^{13}C\{^1H\}$ ($CDCl_3$, 100.6 MHz): δ 133.41 (br s, *C*≡N), 58.02 (s, N*C*$(CH_3)_3$), 30.06 (s, NC$(CH_3)_3$), −9.32 (C, $AlCH_3$).

Preparation of $Et_3Al{\cdot}C{\equiv}N^tBu$ (2). *tert*-Butylisocyanide (0.30 mL, 2.65 mmol) was added via syringe to neat Et_3Al (0.300 g, 2.63 mmol), resulting in evolution of heat. This colorless solution was stirred for 2 h, and excess isocyanide was removed in vacuo to leave a colorless liquid. Yield: 0.50 g, 96%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2219. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.56 (s, 9H, N^{t}Bu), 1.00 (t, $^3J_{HH}$ = 8.0 Hz, 9H, $AlCH_2CH_3$)), −0.25 (q, $^3J_{HH}$ = 8.0 Hz, 6H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 57.41 (s, N*C*$(CH_3)_3$), 30.28 (s, NC$(CH_3)_3$), 10.44 (s, $AlCH_2CH_3$), −0.80 (br s, $AlCH_2CH_3$).

Preparation of $^iBu_3Al{\cdot}C{\equiv}N^tBu$ (3). *tert*-Butylisocyanide (0.300 mL, 2.65 mmol) was added via syringe to neat $^iBu_3Al$ (0.520 g, 2.63 mmol), resulting in evolution of heat. This colorless solution was stirred for 2 h, and excess isocyanide was removed in vacuo to leave a colorless liquid. Yield: 0.71 g, 96%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2218. ^1H NMR ($CDCl_3$, 600 MHz): δ 1.77 (m, 3H, $CH_2CH(CH_3)_2$), 1.55 (s, 9H, N^{t}Bu), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, 18H, $CH_2CH(CH_3)_2$), −0.11 (d, $^3J_{HH}$ = 7.2 Hz, 6H, $CH_2CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 57.67 (s, N*C*$(CH_3)_3$), 30.00 (s, NC$(CH_3)_3$), 28.42 (s, $AlCH_2CH(CH_3)_2$), 27.33 (s, $AlCH_2CH(CH_3)_2$), 22.18 (br s, $AlCH_2CH(CH_3)_2$).

Preparation of $^tBu_3Al{\cdot}C{\equiv}N^tBu$ (4). *tert*-Butylisocyanide (0.45 mL, 4.0 mmol) was added via syringe to a solution of $^tBu_3Al$ (0.750 g, 3.78 mmol) in 20 mL of hexanes, and the resulting colorless solution was stirred for 4 h. The solution was then concentrated in vacuo to one-half its original volume and stored at −30 °C for 12 h. Clear, colorless crystals were isolated by filtration and dried in vacuo. A second crop of product was similarly obtained by concentration and cooling of the filtrate. Yield: 1.05 g, 98%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2221. ^1H NMR ($CDCl_3$, 600 MHz): δ 1.59 (s, 9H, N^{t}Bu), 0.93 (s, 27H, Al^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150.8 MHz): δ 133.41 (br s, *C*≡N^{t}Bu), 58.33 (s, N*C*$(CH_3)_3$), 32.22 (s, AlC$(CH_3)_3$), 30.16 (s, NC$(CH_3)_3$), 16.42 (br s, Al*C*$(CH_3)_3$). Anal. Calcd for $C_{17}H_{36}NAl$: C, 72.55; H, 12.89; N, 4.98. Found: C, 67.19; H, 12.17; N, 4.37.

Preparation of $Me_3Al{\cdot}C{\equiv}N(2,6\text{-}Me_2C_6H_3)$ (5). A solution of 2,6-dimethylphenylisocyanide (0.25 g, 1.9 mmol) in 15 mL of toluene was added via syringe to a solution of Me_3Al (1.0 mL, 2.0 M in toluene, 2.0 mmol) in 20 mL of hexanes. The resulting colorless solution was stirred for 4 h, and then volatiles were removed in vacuo. The remaining solid was dissolved in a minimal amount of hexanes and stored at −30 °C. Clear, colorless crystals were isolated by filtration and dried in vacuo. A second crop of product was similarly obtained from the filtrate. Yield: 0.38 g, 97%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2203. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-CH)), 7.15 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-CH), 2.43 (s, 6H, CH_3), −0.38 (s, 9H, $AlCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 152.9 (t, $^1J_{CN}$ = 13.6 Hz, C≡N), 135.95 (s, *o*-C), 130.60 (s, *p*-CH), 128.39 (s, *m*-CH), 124.84 (t, $^1J_{CN}$ = 12.5 Hz, N−C), 18.81 (s, CH_3), −5.88 (s, $AlCH_3$).

Preparation of $Et_3Al{\cdot}C{\equiv}N(2,6\text{-}Me_2C_6H_3)$ (6). A solution of 2,6-dimethylphenylisocyanide (0.50 g, 3.8 mmol) in 15 mL of toluene was added via syringe to a solution of Et_3Al (0.440 g, 3.85 mmol) in 20 mL of hexanes. The colorless solution was stirred for 4 h, and volatiles were removed in vacuo to yield a light green liquid. Yield: 0.91 g, 97%.

IR (Nujol, $\nu_{C\equiv N}$, cm^{-1}): 2194. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.33 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-CH), 7.18 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-CH), 2.45 (s, 6H, CH$_3$), 1.07 (t, $^3J_{HH}$ = 7.8 Hz, 6H, AlCH$_2$*CH*$_3$), −0.11 (br, 9H, Al*CH*$_2$CH$_3$). ^{13}C{^{1}H} (CDCl$_3$, 150.8 MHz): δ 147.6 (br s, C≡N), 136.35 (s, *o*-C), 131.28 (s, *p*-CH), 128.60 (s, *m*-CH), 18.84 (s, CH$_3$), 10.61 (br s, AlCH$_2$CH$_3$), −0.50 (br s, AlCH$_2$CH$_3$).

Preparation of ^{i}Bu$_3$Al·C≡N(2,6-Me$_2$C$_6$H$_3$) (7). A solution of 2,6-dimethylphenylisocyanide (0.50 g, 3.8 mmol) in 15 mL of toluene was added via syringe to a solution of ^{i}Bu$_3$Al (0.755 g, 3.81 mmol) in 20 mL of hexanes. The red solution was stirred for 4 h, and volatiles were removed in vacuo to yield a red liquid. Yield: 1.2 g, 95%. IR (Nujol, $\nu_{C\equiv N}$, cm^{-1}): 2193. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-CH)), 7.17 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-CH), 2.44 (s, 6H, CH$_3$), 1.85 (m, 3H, AlCH$_2$*CH*(CH$_3$)$_2$), 0.94 (d, $^3J_{HH}$ = 5.4 Hz, 18H, AlCH$_2$CH(*CH*$_3$)$_2$), 0.02 (d, $^3J_{HH}$ = 7.2 Hz, 6H, Al*CH*$_2$CH(CH$_3$)$_2$). ^{13}C{^{1}H} (CDCl$_3$, 150.8 MHz): δ 136.40 (s, *o*-C), 131.20 (s, *p*-CH), 128.61 (s, *m*-CH), 28.53 (s, AlCH$_2$CH(CH$_3$)$_2$), 27.44 (s, AlCH$_2$CH(CH$_3$)$_2$), 22.57 (br, AlCH$_2$CH(CH$_3$)$_2$), 18.85 (s, CH$_3$).

Preparation of ^{t}Bu$_3$Al·C≡N(2,6-Me$_2$C$_6$H$_3$) (8). A solution of 2,6-dimethylphenylisocyanide (0.50 g, 3.8 mmol) in 15 mL of toluene was added via syringe to a solution of ^{t}Bu$_3$Al (0.750 g, 3.78 mmol) in 20 mL of hexanes. The colorless solution was stirred for 4 h, concentrated to one-half its original volume, and then stored at −30 °C for 12 h. The resulting colorless crystals were isolated by filtration and dried in vacuo. A second crop of product was similarly obtained from the filtrate. Yield: 1.2 g, 96%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2197. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.34 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *p*-CH), 7.20 (d, $^3J_{HH}$ = 7.2 Hz, 1H, *m*-CH), 2.49 (s, 6H, CH$_3$), 1.02 (s, 27H, Al^{t}Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 150.8 MHz): δ 147.7 (b, C≡N), 136.21 (s, *o*-C), 131.10 (s, *p*-CH), 128.46 (s, *m*-CH), 32.15 (s, AlC(CH$_3$)$_3$), 18.96 (s, CH$_3$), 16.64 (br s, AlC(CH$_3$)$_3$). Anal. Calcd for C$_{21}$H$_{36}$NAl: C, 76.54; H, 11.01; N, 4.25; Al, 8.19. Found: C, 73.15; H, 11.30; N, 4.30; Al, 8.77.

Preparation of ^{t}Bu$_3$Ga·C≡N^{t}Bu (9). *tert*-Butylisocyanide (0.45 mL, 4.0 mmol) was added via syringe to a solution of ^{t}Bu$_3$Ga (0.910 g, 3.77 mmol) in 20 mL of hexanes. The colorless solution was stirred for 4 h, concentrated to one-half its original volume, and then stored at −30 °C for 12 h. The resulting colorless crystals were isolated by filtration and dried in vacuo. A second crop of product was similarly obtained from the filtrate. Yield: 1.2 g, 98%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2205. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 1.56 (s, 9H, N^{t}Bu), 1.02 (s, 27H, Ga^{t}Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 150.8 MHz): δ 57.66 (s, NC(CH$_3$)$_3$), 32.90 (s, GaC(CH$_3$)$_3$), 30.3 (s, NC(CH$_3$)$_3$). Anal. Calcd for C$_{17}$H$_{36}$NGa: C, 62.98; H, 11.19; N, 4.32. Found: C, 61.70; H, 10.84; N, 4.38.

Preparation of ^{t}Bu$_3$Ga·C≡N(2,6-Me$_2$C$_6$H$_3$) (10). A solution of 2,6-dimethylphenylisocyanide (0.50 g, 3.8 mmol) in 15 mL of toluene was added via syringe to a solution of ^{t}Bu$_3$Ga (0.910 g, 3.77 mmol) in 20 mL of hexanes. The colorless solution was stirred for 4 h, concentrated to one-half its original volume, and then stored at −30 °C for 12 h. The resulting colorless crystals were isolated by filtration and dried in vacuo. A second crop of product was similarly obtained from the filtrate. Yield: 1.37 g, 98%. IR (KBr, $\nu_{C\equiv N}$, cm^{-1}): 2183. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.36 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-CH), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-CH), 2.50 (s, 6H, CH$_3$), 1.02 (s, 27H, Ga^{t}Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 150.8 MHz): δ 136.56 (s, *o*-C), 131.48 (s, *p*-CH), 128.73 (s, *m*-CH), 32.37 (s, GaC(CH$_3$)$_3$), 19.20 (s, CH$_3$), 16.82 (br, GaC(CH$_3$)$_3$). Anal. Calcd for C$_{21}$H$_{36}$NGa: C, 67.76; H, 9.75; N, 3.76; Ga, 18.73. Found: C, 65.71; H, 10.51; N, 3.60; Ga, 17.69.

Isothermal Titration Calorimetry. Solutions of the metal alkyls and isocyanides were prepared in distilled and dried hexanes. All samples were stored and loaded in an Innovative Technology, Inc. glovebox containing an argon atmosphere. A MicroCal Omega isothermal titration calorimeter was employed to determine the enthalpy of the interaction between the metal alkyls and the isocyanide derivatives at 25 °C. The instrument was modified with the appropriate inert seals and equipped with a small port capable of maintaining a static argon atmosphere over the sample. A solution of the metal alkyl (1.5 mL, 100 mM) was added to the ITC calorimetric cell under an inert atmosphere of argon. A solution of the isocyanide derivative (10 mM) was loaded into the 250 μL calorimetry syringe, and the temperature of the system was allowed to equilibrate for 60 min prior to injections. A 10 injection matrix was employed for each sample with each 5 μL injection lasting for 10 s. A 120 s interval was allotted between each injection of the isocyanide solution into the calorimetric cell. The enthalpy (ΔH) of the interaction was determined from the calorimetric data employing Origin data analysis software. The enthalpy values were determined from the average of 2−3 separate experiments from independently prepared solutions. The first 2−3 injections for each experiment were not included in the calculations due to premature leaching of isocyanide solution from the syringe. The remaining 7−8 injections were highly reproducible. Addition of isocyanide in hexane to a blank solution of hexane provided negligible heats of dilution.

X-ray Crystallography for 4, 5, and 8−10. Crystals of **4**, **5**, and **8**−**10** were grown from highly concentrated hexanes solutions at −20 °C. Single-crystal diffraction data were collected at 140 K with a Bruker platform diffractometer equipped with a Smart6000 CCD detector.[20] Data were integrated using SAINT 6.45.[21] Correction for absorption, decay, and inhomogeneity of the X-ray beam were applied using SADABS[22] (**4** and **8**−**10**) or TWINABS (**5**).[23]

Structures of **4**, **5**, **8**, and **10** were solved using direct methods. Remaining atoms were located with difference Fourier techniques. Hydrogen atoms were located and refined isotropically with the exception of several hydrogen atoms in the twinned structure of **5**, which were calculated on ideal positions and included in the refinement as restrained atoms. The crystal structure of **9** was solved by isomorphous methods refining all atoms with starting coordinates acquired from the structure of **4**. In all cases the non-hydrogen atoms were refined with anisotropic atomic displacement parameters, and calculations were performed using SHELXTL 6.12.[24]

Crystal structures of the analogous aluminum and gallium compounds **4**/**9** and **8**/**10** are isomorphous, respectively. The diffraction data of **4** and **9** revealed a superstructure with the strong diffraction data representing a smaller unit cell of 1/4 of the volume of the here described cell. These substructure data allowed a refinement of a disordered molecule which converged to R_1 (all 2060 data) = 6.56% for **4** and R_1 (all 2620 data) = 3.45% for **9**. The here presented model is a 4-fold superstructure obtained by including the weak superstructure reflections resulting in an ordered arrangement of the ^{t}Bu groups in the extended cells and final residual values of R_1 (all 7825 data) = 7.17% for **4** and R_1 (all 7891 data) = 5.74% for **9**.

Data collected from a crystal of **5** were identified as originated by a nonmerohedral twin using RLATT.[25] Two orientation matrices were assigned to the two different twin components (GEMINI 1.02[26]). Integration of the data using both orientation matrices deconvoluted the data set into overlapped reflections and reflections originated by only one of the twin components. Equivalent reflections were merged if they originated from the same twin component or if they originated simultaneously from both components. The number of crystallographically dependent data was subtracted when calculating the esds. The twinning law is a 180° rotation about the *a* axis. The ratio of the two twin components was refined to 0.75:0.25.

Details of data collection and refinement are provided in Table 1. Further details, including atomic coordinates and complete distances and angles, are found in the CIFs provided as Supporting Information.

■ RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. Complexes **1**−**10** were prepared by stirring the appropriate isocyanide with trialkylaluminum or tri-*tert*-butylgallium at room temperature, either neat (**2**, **3**) or in a solution of hexanes (eqs 1−3). Complexes **1**, **4**, **5**, and **8**−**10** were isolated as clear, colorless crystals by concentration of the reaction solution and cooling to −30 °C overnight. Crystalline samples of **1** were also obtained by sublimation at 20 °C/0.1 mmHg. Compounds **2**, **3**, and **6** were isolated as colorless or light yellow/green oils in

Table 1. Crystal Data and Structure Refinement Details

	${}^tBu_3Al{\cdot}C{\equiv}N^tBu$, **4**	$Me_3Al{\cdot}C{\equiv}NAr$, **5**	${}^tBu_3Al{\cdot}C{\equiv}NAr$, **8**	${}^tBu_3Ga{\cdot}C{\equiv}N^tBu$, **9**	${}^tBu_3Ga{\cdot}C{\equiv}NAr$, **10**
formula	$C_{17}H_{36}AlN$	$C_{12}H_{18}AlN$	$C_{21}H_{36}AlN$	$C_{17}H_{36}GaN$	$C_{21}H_{36}GaN$
fw	281.45	203.25	329.49	324.19	372.23
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a, Å	16.2302(11)	7.3740(8)	8.8875(2)	16.2533(4)	8.9135(2)
b, Å	12.2005(8)	10.6098(11)	11.8471(2)	12.2320(3)	11.8766(2)
c, Å	21.0379(15)	17.2788(19)	11.9501(2)	21.1259(5)	11.9732(3)
α, deg	90.00	92.014(4)	64.069(1)	90.00	64.192(1)
β, deg	106.540(2)	94.854(4)	87.109(1)	106.481(1)	87.174(1)
γ, deg	90.00	91.319(4)	72.330(1)	90.00	72.371(1)
V, Å^3	3993.5(5)	1345.7(3)	1073.19(4)	4027.48(17)	1082.45(4)
Z	8	4	2	8	2
D_{calcd}, g cm^{-3}	0.936	1.003	1.020	1.069	1.142
T, °C	−133(2)	−133(2)	−133(2)	−133(2)	−133(2)
μ, mm^{-1}	0.093	0.118	0.096	1.358	1.272
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
transm coeff	0.896−1.00	0.837−1.00	0.850−1.00	0.840−1.00	0.858−1.00
2θ limits, deg	2.6−52.0	2.4−52.0	3.8−66.6	3.9−52.0	3.8−56.6
total no. of data	26 764	11 880	19 702	50 383	15 412
no. of unique data	7825	11 880	7553	7891	5367
no. of obsd data^a/params	5050/631	10 581/338	6228/352	5632/631	5143/352
$R_1{}^b$ (F, $I > 2\sigma(I)$)	0.0404	0.0478	0.0496	0.0375	0.0231
w$R_2{}^c$ (F^2, all data)	0.1220	0.1198	0.1168	0.0812	0.0602
max, min peaks, e/Å^3	0.324, −0.191	0.280, −0.208	0.536, −0.190	0.377, −0.225	0.511, −0.297
special information	superstructure	nonmerohedral twin		superstructure	

$^a I > 2\sigma(I)$. $^b R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. $^c wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

essentially quantitative yields. Compound **7** was isolated as a red oil. We attribute the red color of **7** to a highly colored impurity resulting from isocyanide insertion into the Al−H bond of DIBAL,[7] a known impurity in commercially available ${}^iBu_3Al$. Compounds **2**, **3**, **6**, and **7** did not distill under vacuum, thus thwarting purification attempts. Elemental analyses were obtained for crystalline samples, but carbon and nitrogen analyses were often lower than calculated. Shapiro and coworkers[5] similarly reported low carbon analyses for $Cp_3Al{\cdot}C{\equiv}N^tBu$ and attributed this discrepancy to formation of aluminum carbides in the combustion analyses.

$$R_3Al + C{\equiv}N^tBu \xrightarrow[25\,^\circ C]{\text{hexanes}} R_3Al{\cdot}C{\equiv}N^tBu \quad \begin{matrix}\mathbf{1}, R=Me\\ \mathbf{2}, R=Et(\text{neat})\\ \mathbf{3}, R={}^iBu(\text{neat})\\ \mathbf{4}, R={}^tBu\end{matrix} \qquad (1)$$

$$R_3Al + C{\equiv}NAr \xrightarrow[25\,^\circ C]{\text{hexanes}} R_3Al{\cdot}C{\equiv}NAr \quad \begin{matrix}\mathbf{5}, R=Me; Ar=2,6\text{-}Me_2C_6H_3\\ \mathbf{6}, R=Et; Ar=2,6\text{-}Me_2C_6H_3\\ \mathbf{7}, R={}^iBu; Ar=2,6\text{-}Me_2C_6H_3\\ \mathbf{8}, R={}^tBu; Ar=2,6\text{-}Me_2C_6H_3\end{matrix} \qquad (2)$$

$${}^tBu_3Ga + C{\equiv}NR \xrightarrow[25\,^\circ C]{\text{hexanes}} {}^tBu_3Ga{\cdot}C{\equiv}NR \quad \begin{matrix}\mathbf{9}, R={}^tBu\\ \mathbf{10}, R=2,6\text{-}Me_2C_6H_3\end{matrix} \qquad (3)$$

Integration of ^1H NMR resonances ($CDCl_3$) for **1**−**10** confirms the presence of one isocyanide per metal. Proton resonances for ${}^tBuN{\equiv}C$ in complexes **1**−**4** and **9** appear as singlets in the range 1.55−1.59 ppm, downfield from the resonance of the free ligand at 1.45 ppm. The xylyl resonances for complexes **5**−**8** and **10** appear as a doublet and a triplet for the meta and para protons of the aryl as well as a singlet for the ortho methyl substituents in the range 2.43−2.50 ppm. The aryl and methyl resonances are only slightly shifted from those in the free ligand. Metal alkyl resonances are unexceptional and typical of group 13 alkyl complexes.

^{13}C NMR spectra for **1**−**10** are consistent with the proposed structures, although the C≡N resonance for the coordinated isocyanide is observed only for complexes **1**, **4**−**6**, and **8**. When observed, the C≡N resonance is shifted upfield by approximately 20 ppm relative to those for uncoordinated ${}^tBuN{\equiv}C$ (154.5; 152.4 ppm)[19,27] and $(2,6\text{-}Me_2C_6H_3)N{\equiv}C$ (169.5; 167.7 ppm),[19,27] and is broad and poorly resolved from the baseline due to interaction with adjacent quadrupolar aluminum and nitrogen atoms. The exception is the N≡C ^{13}C resonance for **5** which appears as three equally intense lines due to coupling with ^{14}N ($I = 1$; $^1J_{C\equiv N} = 13.6$ Hz). The C≡N ^{13}C resonance for uncoordinated ${}^tBuN{\equiv}C$ and $(2,6\text{-}Me_2C_6H_3)N{\equiv}C$ appear as equal intensity "triplets" with $^1J_{C\equiv N}$ values of 3.7−4.5 and 5.0−6.2 Hz, respectively.[19,27]

The isocyanides in **1**−**10** are labile in solution. In the presence of excess isocyanide, the ^1H NMR spectra for **1**−**10** exhibit only a single set of isocyanide resonances, indicating rapid exchange on the NMR time scale. The chemical shifts for the resulting isocyanide resonances are weighted averages of the bound and unbound isocyanide resonances. The exchange remains rapid by ^1H NMR spectroscopy even at −60 °C.

The C≡N stretches observed in the infrared spectra of the new complexes, as well as those of the complexes previously reported, are tabulated in Table 2. Values for $\nu_{C\equiv N}$ are shifted

Table 2. Isocyanide Complexes of Aluminum and Gallium Trialkyls

	$\nu_{\mathrm{C\equiv N}}$ (cm^{-1})	$\Delta(\nu_{\mathrm{C\equiv N}})$ (cm^{-1})	ref
complex			
$\mathrm{Ph_3Al\cdot C\equiv NCy}$	2215	+90	3
$\mathrm{Me_3Al\cdot C\equiv NMe}$	2240	+83	4
$\mathrm{Cp_3Al\cdot C\equiv N^tBu}$	2218	+85	5
$\mathrm{\{Me_4C_2(C_5H_4)_2\}ClAl\cdot C\equiv N^tBu}$	2258	+125	6
$\mathrm{Me_3Al\cdot C\equiv N^tBu}$ (**1**)	2224	+91	this work
$\mathrm{Et_3Al\cdot C\equiv N^tBu}$ (**2**)	2219	+86	this work
$\mathrm{^iBu_3Al\cdot C\equiv N^tBu}$ (**3**)	2218	+85	this work
$\mathrm{^tBu_3Al\cdot C\equiv N^tBu}$ (**4**)	2221	+88	this work
$\mathrm{Me_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**5**)	2203	+78	this work
$\mathrm{Et_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**6**)	2194	+69	this work
$\mathrm{^iBu_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**7**)	2193	+68	this work
$\mathrm{^tBu_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**8**)	2197	+72	this work
$\mathrm{^tBu_3Ga\cdot C\equiv N^tBu}$ (**9**)	2205	+72	this work
$\mathrm{^tBu_3Ga\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**10**)	2183	+58	this work
ligands			
$\mathrm{C\equiv N^tBu}$	2133		this work
$\mathrm{C\equiv N(2,6\text{-}Me_2C_6H_3)}$	2125		this work
$\mathrm{C\equiv NMe}$	2157		4
$\mathrm{C\equiv NCy}$	2125		3

to higher frequency than for the free ligand (see $\Delta(\nu_{\mathrm{C\equiv N}})$, Table 1) as expected for isocyanides coordinated as σ donors in the absence of π-backbonding. These shifts are in the range 85−90 cm^{-1} for the $\mathrm{^tBuN\equiv C}$ complexes of aluminum and 69−78 cm^{-1} for the $\mathrm{(2,6\text{-}Me_2C_6H_3)N\equiv C}$ complexes of aluminum. Data for **1**−**8** agree well with those reported previously for $\mathrm{Ph_3Al\cdot C\equiv NCy}$,[3] $\mathrm{Me_3Al\cdot C\equiv NMe}$,[4] and $\mathrm{Cp_3Al\cdot C\equiv N^tBu}$.[5] The $\Delta(\nu_{\mathrm{C\equiv N}})$ values for aluminum complexes **1**−**8** are less than those observed for borane complexes $\mathrm{(C_6F_5)_3B\cdot C\equiv N^tBu}$ (170 cm^{-1}),[28] $\mathrm{(C_6F_5)_3B\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (150 cm^{-1}),[28] $\mathrm{H_3B\cdot C\equiv NMe}$ (150 cm^{-1}),[29] and $\mathrm{Me_3B\cdot C\equiv N^tBu}$ (114 cm^{-1})[30] and greater than those observed for $\mathrm{^tBu_3Ga\cdot C\equiv N^tBu}$ (72 cm^{-1}) and $\mathrm{^tBu_3Ga\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (58 cm^{-1}), suggesting that increasing $\Delta(\nu_{\mathrm{C\equiv N}})$ correlates with increasing Lewis acidity of the group 13 compound.

X-ray Crystallography. The molecular structures of **4**, **5**, and **8**−**10** were further confirmed by X-ray crystallography. ORTEP diagrams are shown in Figure 1. Selected bond distances and angles are provided in Table 3. The molecular structures of **4**, **5**, and **8**−**10** are typical of Lewis acid−base complexes of aluminum and gallium alkyls. In each complex, the metal is ligated by three alkyl substituents and one isocyanide to give a four-coordinate metal with maximum molecular symmetry of C_{3v} and C_{2v} for the *tert*-butylisocyanide and 2,6-dimethylphenylisocyanide complexes, respectively. The isocyanides are nearly linear with M−C−N angles ranging from 170.77(19)° to 175.59(9)° and C−N−C angles ranging from 177.0(1)° to 178.7(2)°. The isocyanide C(1)−N(1) distances are relatively insensitive to changes in steric and electronic differences in the complexes and fall in a narrow range from 1.145(3) to 1.149(1) Å. There is a slight shortening of the C(1)−N(1) distance of the free 2,6-dimethylphenylisocyanide (1.160(3), 1.161(2) Å)[31] upon coordination (1.148(2)−1.149(1) Å), consistent with the calculations by Schaefer,[8] although less pronounced than in previously reported isocyanide complexes of gold.[31] The C(1)−N(1) distances for **4** and **9** are similar at 1.146(2)−1.145(3) Å, slightly

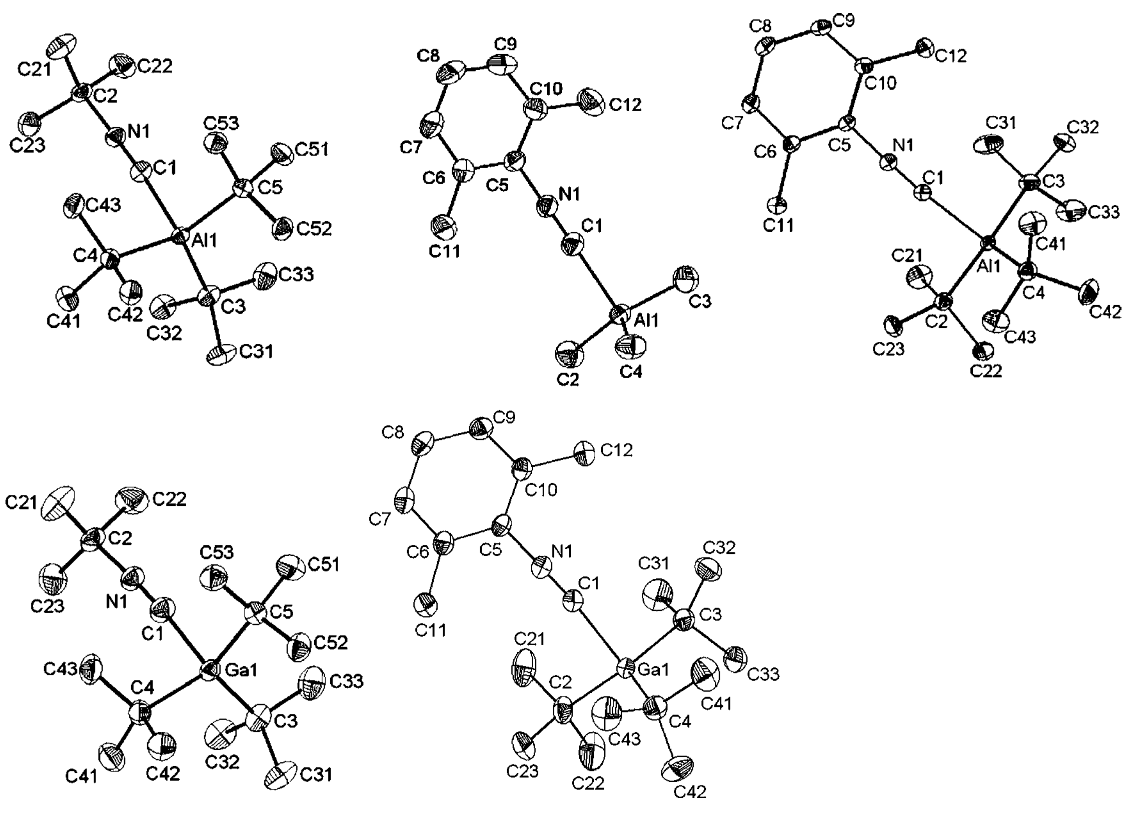


Figure 1. ORTEP drawings of (from left to right) $\mathrm{^tBu_3Al\cdot C\equiv N^tBu}$ (**4**), $\mathrm{Me_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**5**), $\mathrm{^tBu_3Al\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**8**), $\mathrm{^tBu_3Ga\cdot C\equiv N^tBu}$ (**9**), and $\mathrm{^tBu_3Ga\cdot C\equiv N(2,6\text{-}Me_2C_6H_3)}$ (**10**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Angstroms) and Angles (degrees) for 4, 5, and 8−10

complex	M−C(1)	C≡N	M−C≡N	C≡N−C
$^tBu_3Al·C≡N^tBu$ (**4**)[a]	2.122(2)	1.146(2)	174.38(13)	178.21(14)
	2.116(2)	1.147(2)	174.93(13)	178.49(14)
$Me_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**5**)	2.121(2)	1.148(3)	170.77(19)	177.7(2)
$^tBu_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**8**)	2.117(1)	1.149(1)	175.59(9)	177.04(10)
$^tBu_3Ga·C≡N^tBu$ (**9**)[a]	2.169(2)	1.145(3)	173.6(2)	178.6(2)
	2.162(2)	1.146(3)	174.1(2)	178.7(2)
$^tBu_3Ga·C≡N(2,6\text{-}Me_2C_6H_3)$ (**10**)	2.168(1)	1.148(2)	175.15(11)	177.56(13)

[a] Data provided for both independent molecules in the unit cell.

longer than the 1.113(3) Å distance observed for $(C_6F_5)_3B·C≡N^tBu$.[28] These distances are consistent with the IR data and the greater Lewis acidity of $(C_6F_5)_3B$ relative to that for the aluminum and gallium trialkyls. The $Al−C_{isocyanide}$ distances in **4**, **5**, and **8** range from 2.116(2) to 2.122(3) Å, slightly shorter than that calculated by Schaefer for $MeN≡C·AlMe_3$ (2.161 Å)[8] and considerably longer than the $Al−C_{alkyl}$ distances of 1.959(3)−1.965(3) Å for the trimethylaluminum complex **5** and 2.020(1)−2.027(1) Å for the tri-*tert*-butylaluminum complexes **4** and **8**. The $Al−C_{isocyanide}$ distances are comparable to those in $Cp_3Al·C≡N^tBu$ (2.109(2) Å)[5] and $\{Me_4C_2(C_5H_4)_2\}ClAl·C≡N^tBu$ (2.067(6) Å).[6] The $Al−C_{isocyanide}$ distances are greater than typical Al−O (1.84−2.02 Å) and Al−N (2.02−2.10 Å) distances for analogous Lewis acid−base complexes with neutral nitrogen and oxygen donors, respectively.[32,33] The Al−N distance in $Me_3Al·N≡CMe$, for example, is 2.02(1) Å.[34] The $Ga−C_{isocyanide}$ distances in **9** and **10** are only slightly longer than the corresponding $Al−C_{isocyanide}$ distances and range from 2.162(2) to 2.169(2) Å. These distances are slightly less than that calculated by Schaefer for $Me_3Ga·C≡NMe$ (2.237 Å).[8]

Isothermal Titration Calorimetry. Early measurements of gas-phase enthalpies for thermal dissociation of group 13 complexes and enthalpies for solution-phase group 13 complex formation were reviewed by Stone[35] and later work subsequently summarized by Mole.[36] In particular, Eyman and co-workers reported solution calorimetry data on enthalpies of reactions of trimethylaluminum with simple Lewis bases, such as THF, diethyl ether, amines, sulfides, phosphines, and phosphine oxides,[37−40] and Pasynkiewicz extended this work to include nitriles.[41] Similar data have been reported for triethylaluminum by Bonitz[42] and Schubert and co-workers[43] and for triphenylaluminum by Greenwood et al.[44] More recently, calorimetry has been used by Marks and co-workers to measure enthalpies of methide abstraction from dimethylmetallocenes of titanium and zirconium using $E(C_6F_5)_3$ (E = B, Al).[45] Calorimetric methods for determining organoaluminum concentrations in solution, and process streams have also been patented.[46] There are, however, no enthalpy data for reactions of organoaluminum or organogallium reagents with isocyanides.

We chose to measure enthalpies of complexation for **1**−**10** by isothermal titration calorimetry (ITC). ITC is commonly employed to determine thermodynamic information involving interactions of biomolecules, but it has been little utilized to determine thermodynamic parameters of ligand to metal binding in inorganic or organometallic systems. Advantages of ITC in comparison to other types of solution calorimetry[47] include multiple injections per experiment, small reactant volumes, and reproducibility. One of us has previously used this technique to determine the number and strength of ligand binding in samarium and yttrium halides.[48]

Corrected and uncorrected enthalpies of complexation for **1**−**10** are summarized in Table 4, and a representative titration curve is shown in Figure 2. Uncorrected enthalpies for **1**−**8** (Table 4, column 1) clearly decrease in the order $^tBu_3Al$ > $^iBu_3Al$ > Et_3Al > Me_3Al, but these enthalpies do not take into account the varying degrees of association in solution[49] and the differing enthalpies of dimerization for $^iBu_3Al$, Et_3Al, and Me_3Al. Thus, enthalpies of complexation for **1**, **2**, **5**, and **6** have

Table 4. Enthalpies of Formation of Isocyanide Complexes in *n*-Hexane at 25 °C

complex	−Δ*H* (kcal/mol) (uncorrected)	−Δ*H* (kcal/mol) (corrected)[a]	−Δ*H* (kcal/mol) (corrected)[b]
$Me_3Al·C≡N^tBu$ (**1**)	11.5 ± 0.4	21.7 ± 0.4	19.7 ± 1.5
$Et_3Al·C≡N^tBu$ (**2**)	12.8 ± 0.5	21.3 ± 0.5	19.1 ± 2.0
$^iBu_3Al·C≡N^tBu$ (**3**)	20.9 ± 0.4	20.9 ± 0.4	20.9 ± 0.4
$^tBu_3Al·C≡N^tBu$ (**4**)	24.4 ± 0.6	24.4 ± 0.6	24.4 ± 0.6
$Me_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**5**)	10.9 ± 0.5	21.1 ± 0.5	19.1 ± 1.5
$Et_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**6**)	12.4 ± 0.4	20.9 ± 0.4	18.7 ± 2.0
$^iBu_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**7**)	21.2 ± 0.6	21.2 ± 0.6	21.2 ± 0.6
$^tBu_3Al·C≡N(2,6\text{-}Me_2C_6H_3)$ (**8**)	25.9 ± 0.4	25.9 ± 0.4	25.9 ± 0.4
$^tBu_3Ga·C≡N^tBu$ (**9**)	17.0 ± 0.3	17.0 ± 0.3	17.0 ± 0.3
$^tBu_3Ga·C≡N(2,6\text{-}Me_2C_6H_3)$ (**10**)	16.8 ± 0.5	16.8 ± 0.5	16.8 ± 0.5

[a] Corrected for gas-phase enthalpies of dimerization for Me_3Al and Et_3Al.[50−52] [b] Corrected for liquid-phase enthalpies of dimerization for Me_3Al and Et_3Al.[52]

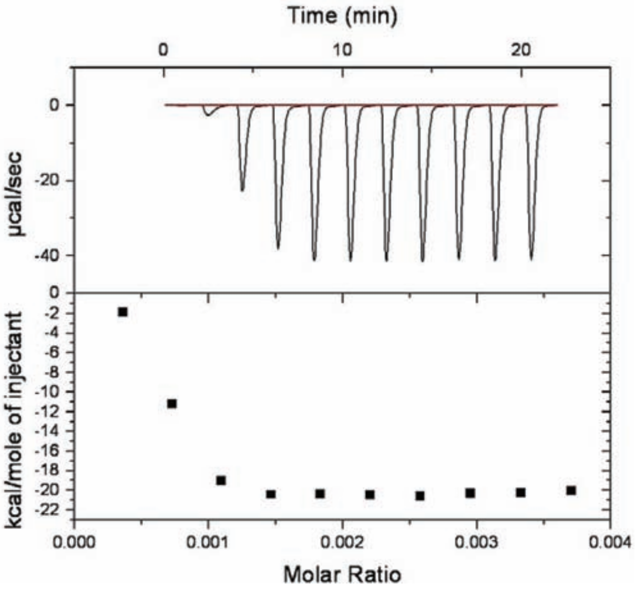


Figure 2. ITC thermogram for titration of $^iBu_3Al$ with $C≡N^tBu$. (Top) Heat change associated with addition of 5 μL aliquots of $C≡N^tBu$ (0.010 M) to $^iBu_3Al$ (1.4 mL, 0.10 M) at 25 °C. (Bottom) Binding isotherm.

been corrected (column 2) for the gas-phase enthalpy of dimerization of Me_3Al (−20.40 ± 0.34 kcal/mol dimer)[40,50,51] or Et_3Al (−16.93 ± 0.23 kcal/mol dimer),[52] as appropriate, by adding one-half the enthalpy of dimerization to the experimentally observed enthalpy of complexation. This is consistent with the approach used by Eyman[37−40] and allows direct comparison of enthalpies of complexation of various Lewis bases to trimethylaluminum (Table 5). This comparison reveals that enthalpies for isocyanide complexes **1** and **5** are comparable to those for $Me_3Al{\cdot}PEt_3$ and $Me_3Al{\cdot}PMe_3$ and less than those for most oxygen and nitrogen donors, including phosphine oxides, sulfoxides, amines, nitriles, and THF. Although these data allow direct comparison of our results to those of Eyman and others, the correction assumes that the gas-phase enthalpies of dimerization are the same as those in solution. An alternate correction has been proposed by Hay et al.,[53] who used the gas-phase enthalpy of dimerization for Me_3Al, corrected for the enthalpy of vaporization for Me_3Al monomer, as well as the monomer−dimer equilibrium constant, to estimate the solution-phase enthalpy of dimerization for Me_3Al to be only −16.3 ± 1.5 kcal/mol dimer. They similarly estimated the solution-phase enthalpy of dimerization for Et_3Al as −12.5 ± 2.0 kcal/mol dimer. On the basis of these solution-phase enthalpies of dimerization, corrected enthalpies for **1**, **2**, **5**, and **6** in column 3 of Table 4 would be approximately 2.0 kcal/mol less than those listed in column 2. The corrected value for **1** is still 3.3 kcal/mol greater than the gas-phase value calculated by Schaefer for the analogous complex $Me_3Al{\cdot}C{\equiv}NMe$ (−16.4 kcal/mol).[8]

Table 5. Enthalpies of Formation of Selected Trimethylaluminum Complexes

complex	−Δ*H* (kcal/mol) (corrected)[a]	solvent	ref
$Me_3Al{\cdot}O{=}PMe_3$	32.0 ± 0.2	benzene	39
$Me_3Al{\cdot}NMe_3$	30.0 ± 0.2	hexane	38
$Me_3Al{\cdot}O{=}PPh_3$	28.7 ± 0.2	benzene	39
$Me_3Al{\cdot}O{=}SMe_2$	28.6 ± 0.3	hexane	41
$Me_3Al{\cdot}py$	27.6 ± 0.2	hexane	38
$Me_3Al{\cdot}NEt_3$	26.5 ± 0.2	hexane	38
$Me_3Al{\cdot}N{\equiv}CPh$	25.4	heptane	41
$Me_3Al{\cdot}THF$	22.9 ± 0.2	hexane	38
$Me_3Al{\cdot}PEt_3$	22.1 ± 0.3	hexane	38
$Me_3Al{\cdot}C{\equiv}N^tBu$ (**1**)	21.7 ± 0.4	hexane	this work
$Me_3Al{\cdot}C{\equiv}N(2,6\text{-}Me_2C_6H_3)$ (**5**)	21.1 ± 0.5	hexane	this work
$Me_3Al{\cdot}PMe_3$	21.0 ± 0.3	hexane	38
$Me_3Al{\cdot}OEt_2$	20.2 ± 0.2	hexane	38
$Me_3Al{\cdot}PPh_3$	17.6 ± 0.2	hexane	38
$Me_3Al{\cdot}SMe_2$	16.6 ± 0.2	hexane	40

[a] Corrected for gas-phase enthalpy of dimerization of Me_3Al.

Triisobutylaluminum is approximately 99.5% dissociated into monomer under the conditions at which the calorimetry data were collected, 25 °C and a mole fraction of approximately 0.01. Hence, enthalpies for **3** and **7** cannot be corrected by simply adding one-half the enthalpy of dimerization (−8.2 kcal/mol dimer)[54] to the experimental data. Instead, we utilized the approach and data used by Smith for correcting the enthalpy of complexation for ${}^iBu_3Al{\cdot}THF$.[54] Smith reported enthalpies of dissociation for ${}^iBu_3Al$ as a function of temperature and ${}^iBu_3Al$ mole fraction, yielding a value of −0.017 kcal/mol at our ITC conditions. Since this correction would be less that 5% of the standard deviation of the enthalpy data, no correction was applied. Similarly, no corrections were made to the enthalpies of formation for **4**, **8**, **9**, or **10** since ${}^tBu_3Al$ and ${}^tBu_3Ga$ are monomers in solution. Corrected enthalpies (column 3) for **1**−**10** show no discernible difference in the basicity of *tert*-butylisocyanide and 2,6-dimethylphenylisocyanide but do illustrate important differences in the Lewis acidities of the aluminum and gallium alkyls. Enthalpies for ${}^tBu_3Al$ complexes **3** and **4** are approximately 4−5 kcal/mol greater than those for ${}^iBu_3Al$ complexes **3** and **7**. There is little difference between enthalpies of complexes **1**−**3** and **5**−**7**. Enthalpies for **4** and **8** exceed those for **9** and **10** by 8−9 kcal/mol, confirming the significantly greater Lewis acidity of trialkylaluminum reagents. Overall, the corrected data (column 3) suggest the following order of decreasing Lewis acidity: ${}^tBu_3Al \gg {}^iBu_3Al \geq Me_3Al \approx Et_3Al \gg {}^tBu_3Ga$.

The greater Lewis acidity of ${}^tBu_3Al$ relative to that for monomeric ${}^iBu_3Al$, Et_3Al, and Me_3Al is counterintuitive considering the electron-donating ability[55] and large steric demand of the ${}^tBu$ group.[55,56] Steric crowding in adducts of ${}^tBu_3Al$ is expected to result in lower enthalpies of complexation. Although we offer no explanation for the observed Lewis acidity of ${}^tBu_3Al$, it is our supposition that the effects of steric crowding in complexes **4** and **8** are minimized due to the slender profile of the isocyanide ligands. Unfortunately, there are no previously published calorimetric studies on enthalpies of complexation for ${}^tBu_3Al$ to which we can compare the present ITC results. Enthalpies of complexation for ${}^tBu_3Al{\cdot}E^iPr_3$ (E = P, As, Sb, Bi),[57] $Me(BHT)_2Al{\cdot}L$ (L = Et_2O, THF, py),[58] ${}^tBu_2(ArO)Al{\cdot}L$ (L = py and bipyridyl derivatives),[59] and ${}^tBu_2(ArO)Ga{\cdot}py$[60] complexes have been determined from the temperature dependence of equilibrium constants for ligand dissociation using NMR spectroscopy, but no isocyanide complexes were investigated. The ${}^tBu_3Al{\cdot}E^iPr_3$ compounds have much lower enthalpies of complexation (E = P, 12.2 kcal/mol; E = As, 9.9 kcal/mol; E = Sb, 7.8 kcal/mol; E = Bi, 6.9 kcal/mol)[57] than we observed for isocyanide complexes **4** (24.4 ± 0.6 kcal/mol) and **8** (25.9 ± 0.4 kcal/mol), which is not surprising considering the weaker donating ability and large steric demand of the heavier pnictogen bases E^iPr_3 (E = P, As, Sb, Bi). ITC determination of enthalpies of complexation for adducts of ${}^tBu_3Al$ and other three-coordinate aluminum alkyls will be the subject of future work.

Thermal Stability and Insertion Chemistry. On the basis of the results of their computational study, Schaefer and coworkers[8] suggested that isocyanide complexes of aluminum and gallium are prone to elimination and alkyl transfer reactions. We find, however, that compounds **1**−**10** are stable at room temperature under an inert atmosphere for up to 3 years with no change in their ^1H NMR spectra. Complexes **2**, **3**, **6**, and **7** do slowly discolor to green and red when stored under nitrogen for several months, but there is no concomitant change in their ^1H NMR spectra.

To probe the possibility of insertion or elimination reactions at higher temperatures, solutions of isocyanide complexes in C_6D_6 were monitored by NMR spectroscopy at 80 and 100 °C. Solutions of **1**−**10** showed no reaction over 24 h at 80 °C. Similarly, none of the complexes underwent reaction over 24 h at 100 °C, except for **2** and **3**, which decomposed to a mixture of unidentified products. To check for reactivity under harsher conditions, complex **4** was refluxed in toluene to give a bright yellow solution. Removal of volatiles yielded a yellow oily mixture of compounds which we were unable to identify by NMR spectroscopy. Attempted separation and purification by recrystallization from THF yielded a few crystals of $[^tBu_2AlC(H){=}N^tBu]_2$ as identified by X-ray crystallography. Metric parameters matched those reported by Uhl.[61] Since $^tBu_3Al$ is known to undergo β-hydride elimination at elevated temperatures to form $^tBu_2AlH$ and 2-methylpropene,[62] we hypothesize that $[^tBu_2AlC(H){=}N^tBu]_2$ was formed by insertion of the isocyanide into the Al−H bond of $^tBu_2AlH$ formed during the extended thermolysis. Although we have not performed a full investigation of the thermal stability of **1**−**10** nor their decomposition products, it is apparent that these complexes are stable to insertion and elimination reactions at room temperature and upon heating to 80 °C. At or above 100 °C, decomposition does occur, possibly by one or more of the routes outlined by Schaefer.[8]

CONCLUSIONS

Ten new isocyanide complexes of trialkylaluminum and tri-*tert*-butylgallium have been prepared. The complexes are stable if protected from oxygen and protic reagents, and there is no evidence for decomposition by isocyanide insertion, elimination, or other pathways below 80 °C. Decomposition to unidentified products is evident above 100 °C. Enthalpies of Lewis base coordination to R_3Al or $^tBu_3Ga$ are comparable to those for complexation of PMe_3 or PEt_3 to the same metal alkyls. Enthalpy data suggest the following order of decreasing Lewis acidity: $^tBu_3Al \gg {}^iBu_3Al \geq Me_3Al \approx Et_3Al \gg {}^tBu_3Ga$. We are currently further examining the Lewis acidity of three-coordinate organoaluminum reagents by ITC.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIFs for compounds **4**, **5**, and **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

We thank the National Science Foundation (Grant CHE-0407542 to M.R.M.) for partial support of this research. The CCD facility of the Ohio Crystallography Consortium located at the University of Toledo was established with grants from the Ohio Board of Regents and ONR.

REFERENCES

(1) Mason, M. R.; Song, B.; Kirschbaum, K. *J. Am. Chem. Soc.* **2004**, *126*, 11812.

(2) Mason, M. R.; Song, B.; Han, Y.; Hu, X. *Inorg. Chim. Acta* **2008**, *361*, 3332.

(3) Hesse, G.; Witte, H.; Mischke, P. *Angew. Chem., Int. Ed.* **1965**, *4*, 355.

(4) Meller, A.; Batka, H. *Monatsh. Chem.* **1970**, *101*, 627.

(5) Fisher, J. D.; Wei, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324.

(6) Shapiro, P. J.; Lee, S.-J.; Perrotin, P.; Cantrell, T.; Blumenfeld, A.; Twamley, B. *Polyhedron* **2005**, *24*, 1366.

(7) Hoberg, H.; Bukowski, P. *Liebigs Ann. Chem.* **1975**, 1124.

(8) Timoshkin, A. Y.; Schaefer, H. F. III *J. Am. Chem. Soc.* **2003**, *125*, 9998.

(9) Uhl, W.; Matar, M. *Z. Naturforsch. B* **2004**, *59*, 1214.

(10) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906.

(11) (a) Zheng, W.; Stasch, A.; Prust, J.; Roesky, H. W.; Cimpoesu, F.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3461. (b) Pi, C.; Wan, L.; Wu, H.; Gu, Y.; Zheng, W.; Weng, L.; Chen, Z.; Wu, L. *Organometallics* **2009**, *28*, 1263.

(12) Uhl, W.; Hannemann, F.; Wartchow, R. *Organometallics* **1998**, *17*, 3822 and references therein.

(13) Shapiro, P. J.; Vij, A.; Yap, G. P. A; Rheingold, A. L. *Polyhedron* **1995**, *14*, 203.

(14) Li, X.; Ni, C.; Song, H.; Cui, C. *Chem. Commun.* **2006**, 1763.

(15) Li, X.; Cheng, X.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1039.

(16) Uhl, W.; Schütz, U.; Hiller, W.; Heckel, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 823.

(17) (a) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708.

(18) Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.

(19) Stephany, R. W.; de Bie, M. J.; Drenth, W. *Org. Magn. Reson.* **1974**, *6*, 45.

(20) *SMART 5.630, Software for the CCD Detector System*; Bruker AXS Inc.: Madison, WI, 2003.

(21) *SAINT 6.45A, Software for the CCD Detector System*; Bruker AXS Inc.: Madison, WI, 2003.

(22) Sheldrick, G. M. *SADABS, Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1996.

(23) Sheldrick, G. M. *TWINABS*; University of Göttingen: Göttingen, Germany, 2008.

(24) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(25) *RLATT 3.0*; Bruker AXS Inc.: Madison, WI, 2000.

(26) *GEMINI 1.02*; Bruker AXS Inc.: Madison, WI, 1999.

(27) Minelli, M.; Maley, W. J. *Inorg. Chem.* **1989**, *28*, 2954.

(28) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

(29) Watari, F. *Inorg. Chem.* **1982**, *21*, 1442.

(30) Casanova, J.; Schuster, R. E. *Tetrahedron Lett.* **1964**, 405.

(31) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1196.

(32) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1997**, *543*, 1.

(33) Robinson, G. H. *Coordination Chemistry of Aluminum*; VCH Publishers: New York, 1993; Chapter 1.

(34) Atwood, J. L.; Seale, S. K.; Roberts, D. H. *J. Organomet. Chem.* **1973**, *51*, 105.

(35) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101.

(36) Mole, T.; Jeffery, E. A. *Organoaluminium Compounds*; Elsevier: Amsterdam, 1972; pp 109−112.

(37) Henrickson, C. H.; Nykerk, K. M.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1028.

(38) Henrickson, C. H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1047.

(39) Nykerk, K. M.; Eyman, D. P. *Inorg. Nucl. Chem. Letters* **1968**, *4*, 253.

(40) Henrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461.

(41) Starowieyski, K.; Pasynkiewicz, S.; Boleslawski, M. *J. Organomet. Chem.* **1967**, *10*, 393.

(42) Bonitz, E. *Chem. Ber.* **1955**, *88*, 742.

(43) Hoeg, D. F.; Liebman, S.; Schubert, L. *J. Org. Chem.* **1963**, *28*, 1554.

(44) Greenwood, N. N.; Perkins, P. G.; Twentyman, M. E. *J. Chem. Soc. (A)* **1969**, 249.

(45) (a) Stahl, N. G.; Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10898. (b) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358.

(46) (a) Gallant, R. P.; Smith, I. L.; Tedder, J. B., Jr.; Crasto, L. T.; Daniels, G. A. U.S. Patent 5 518 932, 1996. (b) Boehm, L. U.S. Patent 4 152 117, 1979.

(47) For a few examples of applications of solution calorimetry to inorganic and organometallic chemistry, see: (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (b) Nolan, S. P. Bonding Energetics of Organometallics. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed; Wiley: New York, 1994. (c) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503. (d) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (e) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

(48) (a) Teprovich, J. A. Jr.; Prasad, E.; Flowers, R. A. II *Angew. Chem., Int. Ed.* **2007**, *46*, 1145. (b) Shotwell, J. B.; Sealy, J. M.; Flowers, R. A. II *J. Org. Chem.* **1999**, *64*, 5251. (c) Shotwell, J. B.; Flowers, R. A. II *Tetrahedron Lett.* **1998**, *39*, 8063.

(49) (a) Mason, M. R. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, B., Ed.; John Wiley and Sons: New York, 2005; Vol. *1*, pp 185−210. (b) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *16*, 111.

(50) (a) Laubengayer, A. W.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 477. (b) Smith, M. B. *J. Organomet. Chem.* **1972**, *46*, 31.

(51) A comparable dimerization energy of −20.9 kcal/mol has been calculated for Me_3Al, see: Tossell, J. A. *Organometallics* **2002**, *21*, 4523.

(52) Smith, M. B. *J. Phys. Chem.* **1967**, *71*, 364.

(53) Hay, J. N.; Hooper, P. G.; Robb, J. C. *J. Organomet. Chem.* **1971**, *28*, 193.

(54) Smith, M. B. *J. Organomet. Chem.* **1970**, *22*, 273.

(55) Keys, A.; Brain, P. T.; Morrison, C. A.; Callender, R. L.; Smart, B. A.; Wann, D. A.; Robertson, H. E.; Rankin, D. W. H.; Barron, A. R. *Dalton Trans.* **2008**, 404.

(56) (a) Cowley, A. R.; Downs, A. J.; Marchant, S.; Macrae, V. A.; Taylor, R. A.; Parsons, S. *Organometallics* **2005**, *24*, 5702. (b) Woski, M.; Mitzel, N. W. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 269.

(57) Kuczkowski, A.; Schulz, S.; Nieger, M.; Schreiner, P. R. *Organometallics* **2002**, *21*, 1408.

(58) (a) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63. (b) Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830.

(59) (a) Ogrin, D.; van Poppel, L. H.; Barron, A. R. *Dalton Trans.* **2005**, 1722. (b) Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, *20*, 5119. (c) Francis, J. A.; McMahon, N.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 4399.

(60) van Poppel, L. H.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **2003**, *125*, 11006.

(61) Uhl, W.; Matar, M. *Z. Naturforsch. B.: Chem. Sci.* **2004**, *59*, 1214.

(62) (a) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, 715. (b) Lehmkuhl, H. *Liebigs Ann. Chem.* **1968**, *719*, 40. (c) Lehmkuhl, H. *Angew. Chem.* **1964**, *76*, 817.