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Trimerization of Phenylacetonitrile. $InMe_3$ as a Base for C−H Acidic Nitriles

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The reaction of phenylacetonitrile with $InMe_3$ in boiling toluene in a molar ratio of 3:1 leads to a trimerization of the nitrile with evolution of methane. The presence of CsF accelerates the reaction. The colorless product was recrystallized from toluene/TMEDA to give 2-amino-1-[Me_2In(TMEDA)]-4-amino-3,5-diphenyl-6-benzylpyridine (**6**). A similar reaction of Ph_2CHCN with $InMe_3$ in boiling toluene gives not the product of a trimerization but a metalla-substituted ketenimine which crystallizes after addition of THF as the dimer $[Ph_2C{=}C{=}NInMe_2(THF)]_2$ (**7**). The reaction was monitored by ^1H NMR spectroscopy, exhibiting a equilibrium with a 0.5(**7**) to nitrile ratio of 82:18 mol %. CsF accelerates this reaction as well. Quite similarly, the reaction between $GaMe_3$ and Ph_2CHCN proceeds to give $[Ph_2C{=}C{=}NGaMe_2]_2$ (**8**), but the position of the equilibrium 0.5(**8**):Ph_2CHCN is more unfavorable (34:66 mol %). A complete transfer to **7** or **8** was observed when $[Ph_2C{=}C{=}NLi(OEt_2)_2]_2$ (**9**) was added to Me_2InCl or Me_2GaCl. **6**, **7**, **9**, and Ph_2CHCN were characterized by NMR and vibrational spectroscopy as well as by X-ray structure analyses. According to these, **6** shows a delocalization of π-electrons over the six-membered ring and the amino/amido functions. The In atom possesses coordination number (CN) 5 with an In−N single bond of 2.180(3) Å and two weak donor−acceptor bonds of 2.439(3) Å (pyridine) and 2.533(3) Å (TMEDA). The ketenimine sequence in **7** shows C=C distances of 1.35 Å and C=N distances of 1.20 Å (mean values). The unit cell of the dimer **9** consists of two crystallographically unique molecules with almost planar four-membered Li_2N_2 rings.

Introduction

Recently we were able to elucidate the reaction between the metalanes MMe_3 (M = Al, Ga, In, Tl) and acetonitrile.[1−4] In the case of Al (**1**), Ga (**2**), and In (**3**) the generation of a six-membered heterocyle with evolution of methane was observed (see Figure 1). We could show that halide ions acting as catalysts by forming intermediate metalates of the types $[XMMe_3]^-$ and $[Me_3MXMMe_3]^-$,[5] especially when cesium salts were used. Only the metalane $TlMe_3$ acts as a simple Lewis acid, initiating the well-known nitrile trimerization[6] to a 1,3,5-triazine (**4**; Figure 1). The NCCCN sequence of the heterocycle is part of a ligand which recently was used very often to stabilize organometal fragments or low-valent metal ions[7] and which can be derived from the acac (acetylacetonate) ligand. The iminium protons in **2** can be abstracted with ^nBuLi, followed by silylation with Me_3SiCl to give the corresponding N−$SiMe_3$ heterocycle (**5**; Figure 1).[1] A very recent study of the interaction of Co^{III} centers with acetonitrile in the presence of a tosylamide anion leads to identical trimerization.[8]

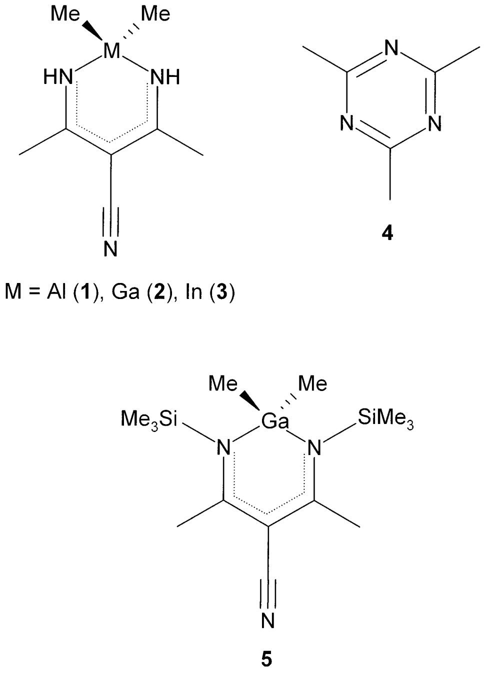

Figure 1. Schematic representation of **1**−**5**.

Therefore, the question is, which intermediate is present during the reaction and is it possible to use

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other nitriles for this trimerization? To answer the questions, we decided to use the phenyl-substituted acetonitriles $PhCH_2CN$ and Ph_2CHCN. However, if a oligomerization occurs, the products must be different now, because those nitriles have less than three acidic protons for abstraction and H-shift, respectively.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvents were performed using standard methods.[9] $GaMe_3$ and $InMe_3$ were donated by the group of Prof. Dr. J. Lorberth. $PhCH_2CN$ and Ph_2CHCN were purchased from Aldrich and Merck-Schuchardt ($PhCH_2CN$ was distilled and stored under argon; Ph_2CHCN was recrystallized from THF and stored under argon). Me_2GaCl and Me_2InCl were prepared according to literature procedures.[10,11]

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-200 spectrometer (^{1}H, 200.135 MHz; ^{13}C, 50.324 MHz). The standard is TMS (external) with δ 0.0 ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). The Raman spectra (RE) was recorded on a Jobin Yvon spectrometer (LABRAM HR800; He−Ne laser; 633 nm). The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected).

Synthesis of 2-Amino-1-[Me_2In(TMEDA)]-4-amino-3,5-diphenyl-6-benzylpyridine (6). A 0.86 g (7.3 mmol) amount of $PhCH_2CN$ in 5 mL of toluene was added dropwise to a solution of 1.17 g (7.3 mmol) of $InMe_3$ in 40 mL of toluene at 20 °C. The mixture was heated under reflux for 5 days and then filtered at room temperature. The filtrate was concentrated under vacuum, and 10 mL of DME was added. The solution was covered with a small amount of TMEDA and stored at −20 °C. Colorless crystals of **6** were obtained during a period of 6 weeks (0.73 g, 42% yield; in the melting point determination, crystals of **6** became opaque at ca. 50 °C and shrank to a white mass which showed no change up to 310 °C). ^{1}H NMR (THF-d_8; ppm): 0.01 (s, 6 H, $\mathrm{InC}H_3$), 1.64 (s, 2 H, $\mathrm{C}H_2\mathrm{Ph}$), 2.50 (s, br, 12 H, $\mathrm{C}H_3$, TMEDA), 3.11 (m, 4 H, $\mathrm{C}H_2$, TMEDA), 4.40 (s, 2 H, $\mathrm{N}H_2$), 5.71 (s, br, 1 H, N*H*), 6.93−7.37 (m, 15 H, *H* phenyl). ^{13}C NMR (THF-d_8; ppm): 0.69 ($\mathrm{In}C\mathrm{H_3}$), 41.3 (s, $C\mathrm{H_2}$, TMEDA), 42.5 (s, $C\mathrm{H_2}$), 47.1 (s, $C\mathrm{H_3}$, TMEDA), 125.9, 127.7, 128.0 (C^4, phenyl), 128.2, 129.4, 129.6, 130.2, 131.6, 132.1 ($C^{2/6}$, $C^{3/5}$, phenyl), 129.5, 136.9, 138.5, (C^1, phenyl), 141.9 ($\mathrm{H_2NC}C\mathrm{(Ph)CCH_2Ph}$, pyridine), 150.2 ($\mathrm{H_2NC}C\mathrm{CNH}$, pyridine), 155.5 (N*C*, pyridine), 156.4 ($\mathrm{H_2N}C$, pyridine), 238.2 (HN*C*, pyridine). IR (Nujol, cm^{-1}): 3478 (w, $\nu(NH_2)$), 3438 (w, $\nu(NH_2)$), 3384 (w, ν(NH)), 2724 (vw), 1621 (m, ν(N=C), HNC), 1602 (m, ν(N=C), H_2NC), 1582 (m), 1560 (m), 1307 (m), 1260 (m), 1152 (w), 1073 (m), 1026 (m), 938 (m), 800 (m), 764 (m), 704 (m), 513 (m, $\nu(InC_2)$), 451 (m, ν(InN)), 400 (m, ν(InN)), 243 (vw), 129 (vw). EI-MS (*m*/*z* (relative intensity), fragment): 351 (100) $(M - TMEDA - InMe_2 - C_7H_7)^+$; 274 (4) $(M - TMEDA - InMe_2 - C_7H_7 - Ph)^+$; 235 (76) $(InN_4C_4H_{16})^+$; 218 (35) $(InN_3C_4H_{13})^+$; 116 (14) $(TMEDA)^+$; 115 (2) $(In)^+$; 91 (12) $(C_7H_7)^+$; 77 (4) $(Ph)^+$. Anal. Calcd: C, 66.57; H, 7.16; N, 9.95. Found: C, 66.37; H, 6.98; N, 9.91.

Synthesis of $[Ph_2C{=}C{=}NInMe_2(THF)]_2$ (7). Method A (typical experiment without CsF): 1.76 g (11.0 mmol) of $InMe_3$ was dissolved in 25 mL of toluene. The solution was dropped into a solution of 2.13 g (11.0 mmol) of Ph_2CHCN. A weak gas evolution was observed (no preceptible warming of the solution, probably CH_4). The mixture was heated under reflux for 48 h. The solvent was removed under vacuum, and the residue was dissolved in 20 mL of THF. The mixture was filtered, and the filtrate was stored at −20 °C. After several days colorless plates of **7** were obtained (2.4 g, 53% yield; in the melting point determination, crystals of **7** became soft and opaque at ca. 40 °C and the white mass melted at 164 °C). The coordinated solvent can be removed under vacuum.

If 1 mol % CsF, was added the yield increases to 90% under the same conditions.

Method B: 1.16 g (5.82 mmol) of Ph_2CCNLi was dissolved in 25 mL of Et_2O, and the solution was added at 0 °C to 1.05 g (5.82 mmol) of Me_2InCl in 25 mL of Et_2O. The reaction is exothermic, and the precipitation of LiCl was observed. The mixture was stirred for 10 h. The suspension was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in 20 mL of THF and stored at −20 °C. After several days colorless plates of **7** could be isolated (2.0 g, 87% yield). ^{1}H NMR (THF-d_8; ppm): −0.48 (s, 12 H, $\mathrm{InC}H_3$), 1.60 (m, 8 H, $\mathrm{C}H_2\mathrm{C}H_2$, THF), 3.49 (m, 8 H, $\mathrm{OC}H_2$, THF), 6.68 (m, pseudo-triplet, 4 H, $C^4{-}H$, phenyl), 7.06 (m, pseudo-triplet, 8 H, $C^{3/5}{-}H$, phenyl), 7.25 (m, pseudo-doublet, 8 H, $C^{2/6}{-}H$, phenyl). ^{13}C NMR (THF-d_8; ppm): −7.7 ($\mathrm{In}C\mathrm{H_3}$), 25.1 ($C\mathrm{H_2}C\mathrm{H_2}$, THF), 55.0 ($\mathrm{N{=}C{=}}C$), 66.9 ($\mathrm{O}C\mathrm{H_2}$, THF), 122.0, 128.2 ($C^{2/6}$, $C^{3/5}$, phenyl), 129.3 (C^4, phenyl), 141.2 ($\mathrm{N{=}}C\mathrm{{=}C}$), 143.8 ($C^1$, phenyl). IR (Nujol, cm^{-1}): 2167 m (ν_{as}(out-of-phase C=C=N)); 1949 w, 1873 m, 1804 m, 1747 w, 1667 w, 1594 m, 1490 s, 1455 s, 1378 s, 1345 w, 1236 m (ν_s(out-of-phase C=C=N)), 1178 m, 1032 m, 1006 vw, 972 w, 913 w, 850 m, 811 vw, 753 s, 699 s, 649 m, 628 m, 614 w, 537 s ($\nu_{as}(InC_2)$), 515 m, 489 w ($\nu_s(InC_2)$), 473 m, 454 w ($\nu_{ring}(In_2N_2)$), 406 w, 345 w, 294, 258 vw, 225 w, 200 w, 151 m, 133 m. RE (crystalline; cm^{-1}): 3073 w, 3064 w, 3057 s, 3051 w, 3044 m, 2166 w (ν_{as}(in-phase C=C=N)), 1596 m, 1240 w (ν_s(in-phase C=C=N)), 1199 m, 1167 m, 1157 w, 1034 w, 1027 m, 1010 s, 813 w, 771 m, 703 w, 647 w, 627 s, 613 s, 535 m ($\nu_{as}(InC_2)$), 493 w ($\nu_s(InC_2)$), 404 s, 298 w ($\nu_{ring}(In_2N_2)$), 243 vw, 227 vw, 188 m, 124 s, 116 s. EI-MS (*m*/*z* (relative intensity), fragment): 193 (100) $(HNCCPh_2)^+$; 166 (52) $(CPh_2)^+$; 115 (10) $(In)^+$; 77 (10) $(Ph)^+$. Anal. Calcd (THF-free material): C, 57.00; H, 4.78; N, 4.15. Found: C, 57.10; H, 4.94; N, 4.09.

The NMR and IR spectra of **7** isolated from method A (with or without CsF) were identical; all the reactions were monitored in sealed NMR tubes as well.

Synthesis of $[Ph_2C{=}C{=}NGaMe_2]_2$ (8). Method B: 2.58 g (13.0 mmol) of Ph_2CCNLi was dissolved in 25 mL of Et_2O and given at 0 °C to 1.75 g (12.9 mmol) of Me_2GaCl in 25 mL of Et_2O. The reaction was exothermic, and LiCl precipitated. The mixture was stirred for 15 h and filtered. The filtrate was evaporated to dryness. The residue was dissolved in THF and stored at −20 °C. After several days colorless crystals of **8** could be isolated (3.4 g, 73% yield; mp 154 °C). ^{1}H NMR (THF-d_8; ppm): −0.32 (s, 12 H, $\mathrm{GaC}H_3$), 6.86 (m, pseudo-triplet, 4 H, $C^4{-}H$, phenyl), 7.31 (m, pseudo-triplet, 8 H, $C^{3/5}{-}H$, phenyl), 7.56 (m, pseudo-doublet, 8 H, $C^{2/6}{-}H$, phenyl). ^{13}C NMR (THF-d_8; ppm): −4.1 ($\mathrm{Ga}C\mathrm{H_3}$), 55.1 ($\mathrm{N{=}C{=}}C$), 122.4, 128.6 ($C^{2/6}$, $C^{3/5}$, phenyl), 128.0 (C^4, phenyl), 140.0 (br, $\mathrm{N{=}}C\mathrm{{=}C}$), 143.2 ($C^1$, phenyl). IR (Nujol; cm^{-1}): 2188 (ν_{as}(out-of-phase C=C=N)), 1952 m, 1873 m, 1804 m, 1748 m, 1652 m, 1597 s, 1493 vs, 1344 s, 1322 s, 1281 s, 1262 vs, 1224 m (ν_s(out-of-phase C=C=N)), 1207 vs (br), 1179 vs, 1079 vs, 1053 vs (br), 973 m, 944 vw, 905 vs, 888 vs, 803 vs, 703 vs, 616 vs ($\nu_{as}(GaC_2)$), 575 vs ($\nu_s(GaC_2)$), 534 vs, 457 s ($\nu_{ring}(Ga_2N_2)$), 395 s ($\nu_{ring}(Ga_2N_2)$),

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Table 1. Crystallographic Data for 6, 7, 9, and Ph_2CHCN

	6	**7**	**9**	Ph_2CHCN
instrument	IPDS I (Stoe)	IPDS II	IPDS II	IPDS II
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
formula	$C_{39}H_{50}InN_5$	$C_{40}H_{48}In_2N_2O_2$	$C_{44}H_{60}N_2O_4Li_2$	$C_{14}H_{11}N$
fw	703.68	818.47	694.85	193.25
cryst size (mm)	0.52 × 0.11 × 0.06	0.43 × 0.24 × 0.06	0.2 × 0.15 × 0.06	0.71 × 0.15 × 0.07
a (Å)	11.065(1)	10.288(1)	13.790(2)	10.720(2)
b (Å)	12.786(2)	12.973(2)	15.279(3)	6.297(1)
c (Å)	14.356(2)	15.105(2)	22.582(4)	16.385(2)
α (deg)	65.98(1)	75.30(1)	100.32(1)	
β (deg)	81.43(1)	73.56(1)	107.05(1)	107.28(1)
γ (deg)	77.94(1)	83.82(1)	101.77(1)	
V (Å^3)	1809.6(4)	1868.9(4)	4306(1)	1056.1(3)
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
No.[28]	2	2	2	14
Z	2	2	4	4
ρ_{calcd} (g/cm^3)	1.291	1.454	1.072	1.214
temp (K)	193	193	193	193
μ (cm^{-1})	6.9	12.7	0.7	0.7
$2\theta_{max}$ (deg)	52.63	52.62	52.83	52.54
h, k, l values	$-13 \le h \le 13$	$-12 \le h \le 11$	$-17 \le h \le 17$	$-13 \le h \le 13$
	$-15 \le k \le 15$	$-16 \le k \le 15$	$-19 \le k \le 19$	$-7 \le k \le 7$
	$-17 \le l \le 17$	$-18 \le l \le 18$	$-27 \le l \le 28$	$-20 \le l \le 20$
no. of rflns	15 960	21 410	63 273	13 704
no. of unique rflns (R_{int})	7130 (0.0647)	7531 (0.0846)	17 410 (0.1698)	2133 (0.0592)
no. of rflns with $F_o > 4\sigma(F_o)$	6136	6033	3367	1456
no. of params	426	421	845	181
R_1[a]	0.0465	0.0431	0.0775	0.0361
wR_2 (all data)[b]	0.1252[c]	0.1145[d]	0.2557[e]	0.089[f]
max/min resid electron density (e/Å^3)	1.00/−1.17	0.72/−0.98	0.26/−0.26	0.17/−0.14

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_c|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0862P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0763)^2]$. [e] $w = 1/[\sigma^2(F_o^2) + (0.0931P)^2]$. [f] $w = 1/[\sigma^2(F_o^2) + (0.0583P)^2]$.

325 s, 248 s, 155 m. EI-MS (m/z (relative intensity), fragment): 317 (8) $(Me_2GaNCCPh_2(CN))^+$; 193 (100) $(HNCCPh_2)^+$; 178 (7) $(CCPh_2)^+$; 166 (34) $(CPh_2/Ga_2N_2)^+$; 77 (13) $(Ph)^+$; 69 (1) $(Ga)^+$. Anal. Calcd: C, 65.81; H, 5.52; N, 4.80. Found: C, 65.94; H, 6.62; N, 4.91.

Synthesis of $[Ph_2C{=}C{=}NLi(OEt_2)_2]_2$ (9). A 7.0 g portion (36.2 mmol) of Ph_2CHCN was dissolved in 50 mL of Et_2O and cooled to −78 °C. A 22.6 mL (36.2 mmol) of a 1.6 M solution of ^nBuLi in *n*-hexane was added dropwise over 30 min. The mixture was warmed to 20 °C and stirred for an additional 5 h. After 1 h of heating under reflux conditions the solvent was evaporated under vacuum. The residue was dissolved in a small portion of Et_2O and stored at −20 °C. After 1 day colorless crystals of **9** could be isolated (11.6 g, 92.2% yield; in the melting point determination, crystals of **9** were carefully dried under a stream of argon, the material became soft and opaque at ca. 30 °C, and the white mass melted at 152 °C). The coordinated solvent can be removed under vacuum to give a colorless powder. ^1H NMR (THF-d_8; ppm): 1.00 (t, 24 H, OCH_2CH_3), 3.25 (q, 16 H, OCH_2CH_3), 6.25 (m, pseudo-triplet, 4 H, $C^4{-}H$, phenyl), 6.80 (m, pseudo-triplet, 8 H, $C^{3/5}{-}H$, phenyl), 7.10 (m, pseudo-doublet, 8 H, $C^{2/6}{-}H$, phenyl). ^{13}C NMR (THF-d_8; ppm): 15.2 (CH_3, Et_2O), 54.0 ($N{=}C{=}C$), 65.8 (OCH_2, Et_2O), 116.0 (C^4, phenyl), 121.5, 127.7 ($C^{2/6}$, $C^{3/5}$), 139.8 (br, $N{=}C{=}C$), 144.3 (C^1). IR (Nujol, cm^{-1}): 2726 vw, 2023 vs, br (ν_{as}(out-of-phase)), 1652 w, 1586 s, 1334 m, 1306 m, 1261 m (ν_s(out-of-phase)) 1184 m, 1154 m, 1108 m, 1093 m, 1062 s, 1028 m, 993 m, 944 vw, 916 w, 884 w, 839 w, 795 w, 756 vs, 740 s, 693 vs, 668 m, 658 w, 639 vw, 619 vw, 585 w, 510 s, 457 s, 374 s, 348 s, br ($\nu_{ring}(Li_2N_2)$). EI-MS (m/z (relative intensity), fragment): 193 (100) $(HNCCPh_2)^+$; 178 (2) $(C_2Ph_2)^+$; 166 (17) $(CPh_2)^+$; 77 (39) $(Ph)^+$. Anal. Calcd: C, 76.05; H, 8.70; N, 4.03. Found: C, 75.95; H, 8.86; N, 3.93.

Ph_2CHCN. For comparison the nitrile was recrystallized from THF and investigated by NMR, IR, and RE spectroscopy as well as by X-ray structure analysis. ^1H NMR (THF-d_8, ppm): 5.60 (s, 1 H, CHCN), 7.17 (m, 10 H, H phenyl). ^{13}C NMR (THF-d_8; ppm): 42.2 (CHCN), 113.4 (CHCN), 122.4, 128.2 (^4C, phenyl), 128.6 ($^{2/6}C$, $^{3/5}C$, phenyl), 137.5 (^1C, phenyl). IR (Nujol, cm^{-1}): 2724 w, 2673 w, 2242 m ($\nu(C{\equiv}N)$), 1950 w, 1873 w, 1803 w, 1747 w, 1656 w, 1596 m, 1492 s, 1345 m, 1291 w, 1221 w, 1178 m, 1159 m, 1098 w, 1078 m, 1031 w, 1005 m, 971 m, 915 m, 850 m, 812 m, 744 vs, 697 vs, 649 s, 628 s, 539 s, 455 s. RE (crystalline, cm^{-1}): 3078 vw, 3062 s,3054 s, 3042 vw, 2986 vw, 2978 vw, 2936 w, 2247 s ($\nu(C{\equiv}N)$), 2235 m ($\nu(C{\equiv}N)$, Fermi resonance), 2191 vw, 1608 m, 1590 w, 1457 vw, 1267 w, 1226 vw, 1198 s, 1189 s, 1181 s, 1161 w, 1156 vw, 1035 s, 1010 vs, 975 m, 814 s, 758 s, 652 s, 632 vw, 620 m, 543 vw, 460 vw, 400 m, 347 m, 279 vw, 260 m, 206 vw, 162 w, 149 m, 136 m.

X-ray Structure Determination of 6, 7, 9, and Ph_2CHCN. The crystals were covered with a perfluorinated polyether and mounted at the top of a glass capillary under a flow of cold gaseous nitrogen. The measured intensities were corrected for Lorentz and polarization and by a numerical absorption correction (for cell parameters, instruments, and radiation see Table 1). The structures were solved by direct methods (**6**, SIR-92;[12] **7**, **9**, and Ph_2CHCN, SHELXS-97[13]). Refinement was performed against F^2 by full-matrix least squares with the program SHELXL-97.[14] The positions of the H atoms were calculated for ideal positions and refined with a common displacement parameter. A free refinement was used for the amino/amido H atoms of **6** (H1, H2, H3) and for all H atoms in Ph_2CHCN. The calculation of the bond lengths, bond angles, and U_{eq} values was performed with the program PLATON.[15] The molecules of **9** show disorder behavior for one phenyl ring C(91)−C(141)/C(92)−C(142) (occupation parameters 0.7/0.3; all phenyl rings are refined as rigid groups) and several coordi-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of 6, 7, 9, and Ph_2CHCN

Compound **6**							
In(1)−N(1)	2.180(3)	N(1)−C(1)	1.342(4)	C(1)−C(2)	1.412(5)	C(2)−C(21)	1.489(5)
In1(1)−N(3)	2.439(3)	N(2)−C(3)	1.375(4)	C(2)−C(3)	1.401(4)	C(4)−C(41)	1.502(4)
In(1)−N(4)	2.523(3)	N(3)−C(1)	1.370(4)	C(3)−C(4)	1.426(4)	C(5)−C(6)	1.517(5)
In(1)−C(7)	2.160(5)	N(3)−C(5)	1.349(4)	C(4)−C(5)	1.378(5)	C(6)−C(61)	1.509(5)
In(1)−C(8)	2.148(4)						
N(1)−In(1)−N(3)	57.72(9)	C(7)−In(1)−C(8)	131.5(2)	In(1)−N(4)−C(11)	111.8(2)	C(2)−C(3)−C(4)	120.2(3)
N(1)−In(1)−N(4)	90.01(9)	In(1)−N(1)−C(1)	101.7(2)	N(1)−C(1)−C(2)	127.6(3)	C(3)−C(4)−C(5)	117.7(3)
N(1)−In(1)−C(7)	112.6(1)	In(1)−N(3)−C(1)	89.2(2)	N(3)−C(1)−C(2)	121.0(3)	C(3)−C(4)−C(41)	120.2(3)
N(1)−In(1)−C(8)	114.5(2)	N(1)−C(1)−N(3)	111.4(3)	C(1)−C(2)−C(3)	118.1(3)	C(5)−C(4)−C(41)	122.1(3)
N(3)−In(1)−N(4)	147.37(9)	In(1)−N(3)−C(5)	150.7(2)	C(1)−C(2)−C(21)	119.9(3)	N(3)−C(5)−C(4)	123.0(3)
N(3)−In(1)−C(7)	102.2(1)	C(1)−N(3)−C(5)	119.9(3)	C(3)−C(2)−C(21)	122.1(3)	N(3)−C(5)−C(6)	113.8(3)
N(3)−In(1)−C(8)	93.1(1)	In(1)−N(4)−C(9)	108.1(2)	N(2)−C(3)−C(2)	120.2(3)	C(4)−C(5)−C(6)	123.2(3)
N(4)−In(1)−C(7)	94.4(1)	In(1)−N(4)−C(10)	109.5(2)	N(2)−C(3)−C(4)	119.5(3)	C(5)−C(6)−C(61)	113.8(3)
N(4)−In(1)−C(8)	96.8(2)						
Compound **7**							
Molecule I							
In(1)−O(1)	2.451(3)	In(1)−C(15)	2.131(4)	N(1)−C(1)	1.188(5)	C(2)−C(3)	1.479(5)
In(1)−N(1)	2.252(3)	In(1)−C(16)	2.119(4)	C(1)−C(2)	1.358(5)	C(2)−C(9)	1.459(6)
In(1)−N(1a)	2.458(3)						
O(1)−In(1)−N(1)	86.1(1)	N(1)−In(1)−C(15)	112.2(2)	C(15)−In(1)−N(1a)	96.1(2)	C(1)−N(1)−In(1a)	124.6(3)
O(1)−In(1)−C(15)	91.9(1)	N(1)−In(1)−C(16)	108.2(2)	C(16)−In(1)−N(1a)	94.9(2)	N(1)−C(1)−C(2)	179.4(4)
O(1)−In(1)−C(16)	90.8(1)	N(1)−In(1)−N(1a)	73.9(1)	In(1)−N(1)−C(1)	129.2(3)	C(1)−C(2)−C(3)	115.9(4)
O(1)−In(1)−N(1a)	160.05(9)	C(15)−In(1)−C(16)	139.6(2)	In(1)−N(1)−In(1a)	106.1(1)	C(1)−C(2)−C(9)	117.9(4)
Molecule II							
In(2)−O(2)	2.456(3)	In(2)−C(35)	2.140(4)	N(2)−C(21)	1.201(5)	C(22)−C(23)	1.489(5)
In(2)−N(2)	2.242(3)	In(2)−C(36)	2.143(4)	C(21)−C(22)	1.350(5)	C(22)−C(29)	1.477(5)
In(2)−(N2a)	2.435(3)						
O(2)−In(2)−N(2)	83.7(1)	N(2)−In(2)−C(35)	104.9(2)	C(35)−In(2)−N(2a)	93.7(1)	C(21)−N(2)−In(2a)	126.8(3)
O(2)−In(2)−C(35)	95.7(1)	N(2)−In(2)−C(36)	109.4(1)	C(36)−In(2)−N(2a)	92.4(1)	N(2)−C(21)−C(22)	178.5(4)
O(2)−In(2)−C(36)	89.8(1)	N(2)−In(2)−N(2a)	76.6(1)	In(2)−N(2)−C(21)	127.8(3)	C(21)−C(22)−C(23)	118.2(3)
O(2)−In(2)−N(2a)	159.81(9)	C(35)−In(2)−C(36)	145.7(2)	In(2)−N(2)−In(2a)	103.4(1)	C(21)−C(22)−C(29)	118.6(3)
Compound **9**							
Molecule I							
N(1)−C(1)	1.184(6)	C(15)−C(16)	1.401(6)	Li(2)−N(1)	2.05(1)	Li(1)−O(2)	1.97(1)
C(1)−C(2)	1.379(6)	Li(1)−N(1)	2.06(1)	Li(2)−N(2)	2.07(1)	Li(2)−O(3)	1.90(1)
N(2)−C(15)	1.180(6)	Li(1)−N(2)	2.03(1)	Li(1)−O(1)	1.95(1)	Li(2)−O(4)	1.98(1)
Li(1)−N(1)−Li(2)	84.2(4)	C(1)−N(1)−Li(2)	133.6(5)	O(1)−Li(1)−O(2)	114.8(6)	O(3)−Li(2)−O(4)	110.5(6)
Li(1)−N(2)−Li(2)	84.4(4)	Li(1)−N(2)−C(15)	142.6(5)	O(1)−Li(1)−N(1)	110.3(5)	O(3)−Li(2)−N(1)	110.5(6)
N(1)−Li(1)−N(2)	96.1(5)	C(15)−N(2)−Li(2)	132.9(5)	O(1)−Li(1)−N(2)	114.9(5)	O(3)−Li(2)−N(2)	121.4(6)
N(1)−Li(2)−N(2)	95.2(5)	N(1)−C(1)−C(2)	178.6(6)	O(2)−Li(1)−N(1)	109.1(4)	O(4)−Li(2)−N(1)	110.6(6)
C(1)−N(1)−Li(1)	141.2(5)	N(2)−C(15)−C(16)	179.0(6)	O(2)−Li(1)−N(2)	110.0(5)	O(4)−Li(2)−N(2)	107.6(5)
Molecule II							
N(3)−C(45)	1.181(7)	C(59)−C(60)	1.385(7)	Li(4)−N(3)	2.05(1)	Li(3)−O(6)	1.94(1)
C(45)−C(46)	1.376(8)	Li(3)−N(3)	2.07(1)	Li(4)−N(4)	2.07(1)	Li(4)−O(7)	1.96(1)
N(4)−C(59)	1.191(6)	Li(3)−N(4)	2.02(1)	Li(3)−O(5)	1.95(1)	Li(4)−O(8)	1.95(1)
Li(3)−N(3)−Li(4)	83.0(5)	C(45)−N(3)−Li(4)	138.7(6)	O(5)−Li(3)−O(6)	112.5(6)	O(7)−Li(4)−O(8)	116.6(6)
Li(3)−N(4)−Li(4)	83.6(4)	C(59)−N(4)−Li(3)	152.4(6)	O(5)−Li(3)−N(3)	108.9(5)	O(7)−Li(4)−N(3)	109.6(5)
N(3)−Li(3)−N(4)	97.0(5)	C(59)−N(4)−Li(4)	123.6(6)	O(5)−Li(3)−N(4)	109.0(5)	O(7)−Li(4)−N(4)	110.6(5)
N(3)−Li(4)−N(4)	96.0(5)	N(3)−C(45)−C(46)	179.7(7)	O(6)−Li(3)−N(3)	115.0(6)	O(8)−Li(4)−N(3)	110.7(6)
C(45)−N(3)−Li(3)	138.0(6)	N(4)−C(59)−C(60)	177.3(6)	O(6)−Li(3)−N(4)	113.3(6)	O(8)−Li(4)−N(4)	111.5(6)
Ph_2CHCN							
C(1)−N(1)	1.147(2)	C(1)−C(2)	1.470(2)	C(2)−C(3)	1.525(2)	C(2)−C(4)	1.527(2)
N(1)−C(1)−C(2)	177.9(1)	C(1)−C(2)−C(3)	109.4(1)	C(1)−C(2)−C(4)	111.6(1)	C(3)−C(2)−C(4)	112.4(1)

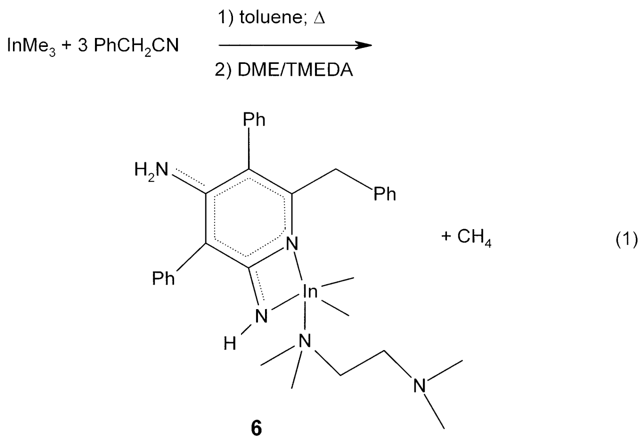
nated Et_2O molecules (for occupation parameters see the Supporting Information).

Selected bond lengths and angles of **6**, **7**, **9**, and Ph_2CHCN are given in Table 2.

Results and Discussion

The reaction of $PhCH_2CN$ with $InMe_3$ in a molar ratio of 3:1 gave under reflux conditions in toluene a product which can be derived from 2,4-diaminopyridine. Colorless crystals of **6** were formed from DME/TMEDA/toluene. The reaction can be described as trimerization of $PhCH_2CN$ with evolution of one molecule of methane (eq 1).

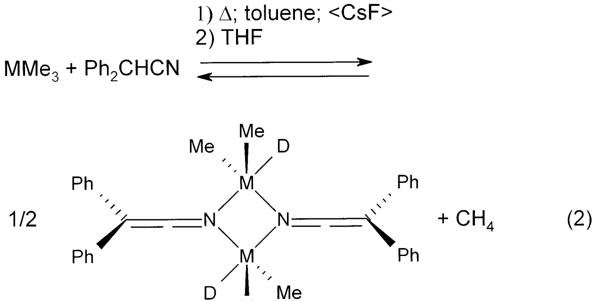
However, it was not possible to follow our reactions to the metal-containing heterocycles by NMR spectroscopy; only the starting materials and products were observed. We assumed that in all cases the initial step is a deprotonation by a metalane or the more basic metalates $[XMMe_3]^-$ and $[Me_3MXMMe_3]^-$, followed by the attack of the formed anion on further nitrile molecules. This combination of deprotonated nitrile in



6

the presence of a hard Lewis acid seems to be necessary for this type of trimerization. The six methylene protons from the three benzylnitrile molecules in eq 1 undergo different reaction pathways. One proton was abstracted for the formation of methane, three protons were used in hydrogen shifts for the generation of NH_2 and NH functions, and two protons are still present in a methylene group. All carbon atoms of the pyridine ring are substituted.

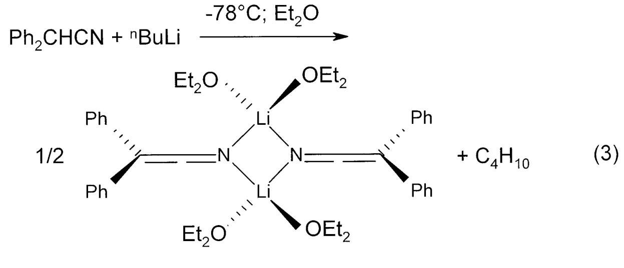
A mixture of Ph_2CHCN with MMe_3 (molar ratio 1:1; CsF as catalyst) in boiling THF lead in a slow reaction to a equilibrium. The educt Ph_2CHCN and the product $^{1}/_{2}[Ph_2C{=}C{=}NMMe_2(THF)]_2$ (**7**, **8**) form a ratio of 18:82 mol % (**7**, M = In) and 64:36 mol % (**8**, M = Ga; ratios determined in all cases by ^{1}H NMR spectroscopy in sealed NMR tubes and d_8-THF as solvent), respectively (eq 2). However, the coupling product $Ph_2(CN)C{-}C(CN)Ph_2$[16] was formed when the reaction mixture to **8** was heated for 14 days, indicating a slow radical process occurring under these conditions.



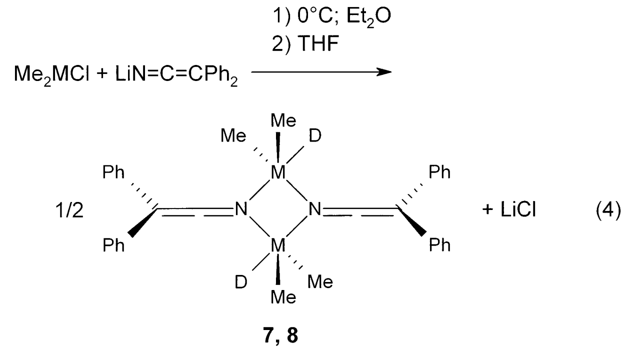
7, 8

7: M = In; D = THF; ratio 0.5 **7**:nitrile = 82:18 mol%
8: M = Ga; D = none; ratio 0.5 **8**:nitrile = 36:64 mol%

To achieve a complete transfer in **7** and **8**, we decided to synthesize the lithiated ketenimine $[Ph_2C{=}C{=}NLi(O_2Et)_2]_2$ (**9**) on the basis of the reaction of Ph_2CHCN with $^{n}BuLi$ in Et_2O (eq 3). **9** was added to solutions of Me_2MCl in Et_2O to give depending on the metal M in a metathesis reaction **7** or **8** (eq 4) after recrystallization from THF.



9



7, 8

7: M = In; D = THF
8: M = Ga; D = none

The ^{1}H and ^{13}C NMR spectra of **6** show characteristic resonances, confirming the structure found by X-ray analysis. The exocyclic NH_2 and NH functions give singlet signals at 4.40 and 5.71 ppm in the ^{1}H NMR spectrum. The short $H_2N{-}C$ and $HN{-}C$ bonds can be interpreted as a partly iminium character and should lead to downfield shifts of the corresponding ^{13}C NMR signals. Especially the HN−*C* carbon atom acts as a bridge between the pyridine nitrogen atom and the In-(H)N function is a good probe because of the downfield signal at 238.2 ppm. The C atom adjacent to the NH_2 group shows a resonance at 156.4 ppm. In crystalline **6** the two hydrogen atoms in the NH_2 function are different. Therefore, two stretching vibrations at 3478 and 3438 cm^{-1} were observed in the IR spectrum. The corresponding band ν(NH) was measured at 3384 cm^{-1}.

In accord with compound **7** a general reaction mechanism for the trimerization of the nitriles could be the creation of a ketenimine in the first step, followed by nucleophilic attack of the metal-substituted ketenimine on another molecule of nitrile. This is even more likely, since the deprotonation of $PhCH_2CN$ with $^{n}Buli$ in the presence of TMEDA gives the lithiated dimeric keteniminate $[\{(TMEDA)Li\}\{NCC(H)Ph\}]_2$.[17] Very recent studies of the diprotonation of CH_3CN in solution arrive at the same conclusion, the generation of the keteniminate $[H_2C{=}C{=}N]^-$.[18] It is known that reaction with a electrophile then leads to substituted ketenimines.[19] Therefore, reaction 3 is no surprise. The concept of a nucleophilic attack of a strong base on one or two nitrile molecules was realized by the work of M. F. Lappert

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over the last few years, leading to a variety of interesting chelating ligands with CCN or $C(CN)_2$ backbones.[6e,20] These results support our imaginations about the reaction mechanism.

The first strong indicator of a ketenimine in solution are the ^{1}H and ^{13}C NMR spectra. If the reaction is carried out according to (2), there is still a resonance for the methine proton in the ^{1}H NMR spectrum of Ph_2CHCN because of the equilibrium between $InMe_3$ and Ph_2CHCN. The ratio Ph_2CHCN:$[NCCPh_2]^-$ was determined (sealed NMR tubes) to be 18:82 (**7**) and 64:36 (**8**), respectively. Reaction 4 gave pure **7** with ^{13}C NMR parameters of 55.0 and 141.2 ppm for the phenyl-substituted and nitrogen-substituted carbon atoms. The corresponding values for **8** are 55.1 and 137.0 ppm.

The second probe is vibrational spectroscopy. The most characteristic vibrational mode of a ketenimine is the asymmetrical valence vibration $\nu_{as}(C{=}C{=}N)$, usually found between 2000 and 2200 cm^{-1}. In the case of the centrosymmetrical dimer **7** (see eq 2), the IR spectrum shows the out-of-phase absorption at 2167 cm^{-1} and the Raman spectrum (RE) the in-phase emission at 2166 cm^{-1}. The symmetrical modes are not very significant, because of their position of ca. 1200 cm^{-1} (see the Experimental Section). For the educt Ph_2CHCN $\nu(CN)$ was found at 2242 (IR), 2247, and 2235 cm^{-1} (RE; Fermi resonance). Two bands of the four In_2N_2 ring vibrations[21] were measured. Because of the rule of mutual exclusion only two ring vibrations (with mainly stretching character) were expected in the IR spectrum (observed 454 cm^{-1}) and two in the RE spectrum (observed 298 cm^{-1}). The values for the probably likewise centrosymmetrical dimer **8** are somewhat different and signify another electronic situation (2188 cm^{-1}; ν_{as}(out-of-phase $C{=}C{=}N$)). The more ionic character of the Li−N bonds in **9** compared with In(Ga)−N bonds in **7** and **8** leads to a better coupling of the C=C and C=N parts of the ketenimine sequence $C{=}C{=}N$, indicated by a shift of ν_{as}(out-of-phase) to lower wavenumbers, in this case 2023 cm^{-1}. Both **7** and **8** fragment under EI-MS conditions in such a way that only for **8** could a metal atom in a heavier fragment be detected (*m/z* 317; $(Me_2GaNCCPh_2(CN))^+$).

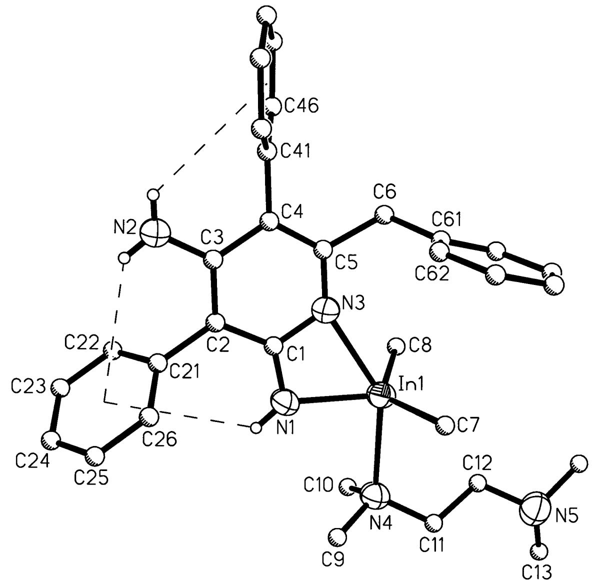

Figure 2. Molecular structure of **6** (ellipsoids at the 50% probability level; only H(1), H(2), and H(3) are drawn).

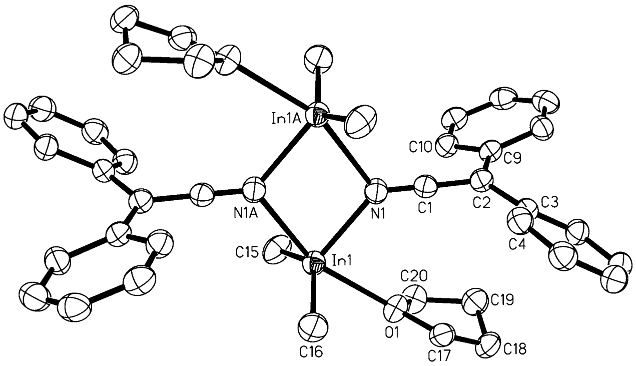

Figure 3. One of the unique centrosymmetric molecules in **7** (ellipsoids at the 40% probability level; without H atoms).

Figure 2 shows a molecule of **6** with a central planar six-membered pyridine ring. The amino and amido functions are included in the π-electron system of the pyridine ring. Clear hints of this are the short N−C distances N(1)−C(1) (1.342(4) Å) and N(2)−C(3) (1.375 Å), which are in the same range as the bond lengths N(3)−C(1) (1.370(4) Å) and N(3)−C(5) (1.349(4) Å) of the central ring. The bond In(1)−N(1) at 2.180(3) Å can be described as an In−N single bond, while In(1)−N(3) (2.439(3) Å) and In(1)−N(4) (2.523(3) Å) have the character of weak donor−acceptor interactions. In−N distances in organometalllic amides of the type $[Me_2InNR'_2]_2$ are typically between 2.22 and 2.28 Å.[22] A good comparison is **3**, at 2.20 Å for the In−N bond lengths.[3] The axial In−N bonds in the related complex $[(DMF)Cl_2InNPPh_3]_2$ have been determined to be 2.179(2) Å, whereas the In center also adopts a distorted-trigonal-bipyramidal geometry.[23] According to the C−C distances of the pyridine ring, the delocalization of the π-electron density is typical for a pyridine system (see Table 2). The pyridine ring and the planes of the adjacent phenyl rings C(21)−C(26), C(41)−C(46), and C(61)−C(66) enclose angles of 69, 71, and 90°. This leads to intramolecular N−H···π-electron hydrogen bonds involving all three imine H atoms. The closest contacts of H(1), H(2), and H(3) to the carbon atoms of the phenyl rings are between 2.51(4) and 2.90(4) Å.

The crystals of compound **7** contain two crystallographically unique centrosymmetrical molecules with a four-membered In_2N_2 ring, one of which is shown in Figure 3. Two attributes are important for a heteroallene such as a ketenimine: the planes C(phenyl ring)/C/C(phenyl ring)//N/In/In should be more or less perpendicular, and the sequence NCC should be linear with short N−C and C−C bonds. Both criteria are fulfillled. The average value for the dihedral angle is 85°, and the mean N−C and C−C distances are 1.20 and 1.35 Å, respectively. The angle of the CCN sequence has been

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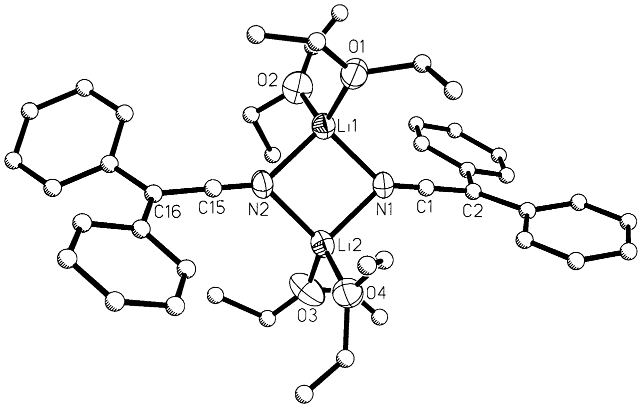

Figure 4. One of the unique molecules in **9** (ellipsoids at the 30% probability level, without H atoms; only one of the disordered positions of the phenyl rings and Et_2O molecules is given).

measured to be 179°. The structure of [{(TMEDA)Li}{N=C=C(H)Ph}]·C_6H_6 exhibits comparable lengths of 1.15(3) and 1.38(2) Å as well as an angle of 178(1)°.[17] The distances in the CCN sequence of the aryl-substituted 4-Br-C_6H_4N=C=CPh_2 are closer to the values of **7** (1.24 and 1.33 Å).[19] A distorted-trigonal-bipyramidal environment around the In atoms in **7** leads to two very different In−N bond lengths. N(1) occupies the equatorial position in the first trigonal bipyramid, leading to a value of 2.25 Å and a axial position in the adjacent polyether with 2.44 Å. Therefore, **7** can also be described as a $[Me{-}In{-}Me]^+$ ion, coordinated by ketenimido and THF ligands. A nondisturbed $[R{-}In{-}R]^+$ unit is electronically isovalent with R−Mg−R or R−Hg−R and is linear. This is approximately realized in Me_2InBr,[24] $[^iPr_2In(THF)_2][BF_4]$,[25] and $[Mes_2In][BF_4]$.[26]

The unit cell of **9** consists of two crystallographically unique molecules with almost planar Li_2N_2 four-membered rings (largest deviation of an atom from the “best plane” 5 pm; molecule I is shown in Figure 4). Interestingly, the environments of the three N atoms are strongly distorted. N(1), N(2), and N(4) are the center of very asymmetrical Li_2NC_2 sequences. The angle pairs Li(1)−N(1)−C(1)/Li(2)−N(1)−C(1) (141.2(5), 133.6(5)°), Li(2)−N(2)−C(15)/Li(3)−N(2)−C(15) (142.6(5), 132.9(5)°), and Li(3)−N(4)−C(59)/Li(4)−N(4)−C(59) (152.4(6), 123.6(6)°) are the result of the steric interactions of the CPh_2 units with the Et_2O molecules. Two things are responsible for this behavior. The Li−N bond lengths are significiantly shorter than the corresponding In−N bonds in **7**, and the Li_2N_2 planes are not perpendicular to the CPh_2 units. The mean dihedral angles in molecules I and II are 65 and 76°, respectively.

To illustrate the difference in the bond lengths in the sequence CCN between **7** and Ph_2CHCN, we investigated the nitrile by a X-ray structure determination. The difference is obvious (Figure 5). The core CCN in Ph_2CHCN shows the typical values for C≡N triple bonds (C(1)−N(1) = 1.147(2) Å) and a C(sp^3)−C(sp) single bond (C(1)−C(2) = 1.470(2) Å).

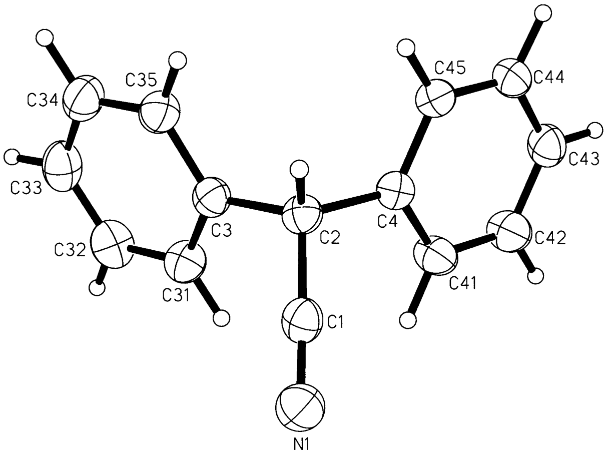

Figure 5. Graphic representation of Ph_2CHCN (ellipsoids at the 40% probability level).

Conclusion

From the results of the presented reactions, everything seems to point to the formation of a ketenimine species as the first intermediate. Depending on their basicity and steric bulk, the further attack of nitrile molecules followed by proton shifts is possible. Notably, the trimerization leads to the formation of six-π-electron systems either in the well-known open form[27] shown for **1**−**3** or in a classical Hückel aromatic species as in **6**. When the metalates $[FMMe_3]^-$ and $[Me_3MFMe_3]^-$ are not basic enough for the initial step, only the regular trimerization to 1,3,5-triazines was observed (M = Tl). Surprisingly, our trimerizations were not detected in the reactions of a nitrile such as $PhCH_2CN$ with lithium reagents, presumably because only equimolar mixtures of the starting material leading directly to the corresponding ketenimines were investigated. In addition, no strong Lewis acids such as M^{3+} (M = earth metal) and Co^{3+} were present. It may be worthwhile to reconceive this reaction, because highly substituted aromatic systems would be accessible in one-pot reactions.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond lengths and angles as well as isotropic or anisotropic displacement parameters for all atoms in **6**, **7**, **9**, and Ph_2CHCN; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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