cis/trans Isomers of Dimeric Dialkylaluminum and Dialkylgallium Hydrazides

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The reaction of diethylaluminum hydride with the hydrazine derivatives 1-aminopyrrole and 1-aminopiperidine afforded the corresponding dialkylaluminum hydrazides (**1** and **2**) by the release of elemental hydrogen. Both products are dimeric in the solid state. While **1** adopts a *cis* arrangement of the pyrrole groups, a *trans* configuration was determined for the piperidine compound **2**. Only **1** gives an equilibrium mixture of *cis* and *trans* isomers in solution. Similar compounds (**3** and **4**) were obtained by the treatment of the same hydrazines with di(*tert*-butyl)gallium hydride. Both products exhibit the *trans* configuration in the solid state, but interestingly only the piperidine derivative **4** shows a *cis*/*trans* equilibrium in solution.

Key words: Aluminum, Gallium, Hydrazides, Heterocycles, *cis*/*trans* Isomers

Introduction

Organoaluminum, -gallium and -indium hydrazides are suitable precursors for the deposition of the corresponding metal nitrides by thermolysis reactions [1]. Furthermore they are of particular interest because the hydrazido ligands show a very interesting coordination behavior. They possess two donor atoms linked by an N–N bond and form a broad variety of different structural motifs upon coordination to metal atoms [2]. The synthesis of metal hydrazides was accomplished by different preparative procedures such as salt elimination, hydrogen or alkane release. Usually the first step of these reactions comprises the formation of adducts between the coordinatively unsaturated aluminum, gallium or indium atoms and the hydrazines. Several of these adducts could be isolated and characterized by crystal structure determinations [3 – 12]. Subsequent elimination of suitable leaving groups afforded compounds with the monoanionic hydrazide units. Through bridging coordination of two metal atoms usually dimeric formula units having four-, five- or six-membered heterocycles were obtained. Monomeric compounds bearing bulky substituents, or oligocyclic and cage-like hydrazides containing dianionic ligands, are relatively rare [5, 7, 9, 13 – 27]. Hydroalumination of suitable dinitrogen compounds opened an alternative access to hydrazide dianions [22, 28, 29]. Applications of these hydrazides in secondary processes require the synthesis of a broad variety of different compounds in order to get a systematic insight into their properties such as configuration, thermal stability, solubility, volatility, and decomposition behavior. Particular decomposition pathways seem to include rearrangement processes in the hydrazido groups. Therefore, we applied hydrazines possessing rigid backbones such as 1-aminopyrrole and 1-aminopiperidine in which one nitrogen atom is part of a heterocyclic system. Some compounds derived from these hydrazines and their stereochemistry are discussed in this report.

Results and Discussion

Reactions of diethylaluminum hydride with 1-aminopyrrole and 1-aminopiperidine

Treatment of dialkylaluminum and dialkylgallium hydrides with neutral hydrazines affords dialkylelement hydrazides by the release of elemental hydrogen. No separation of salt-like by-products is required in this synthesis, and the products are usually formed in a very high purity. Here, we treated diethylaluminum hydride with equimolar quantities of 1-aminopyrrole and 1-aminopiperidine in the solvents *n*-pentane or *n*-hexane at r. t. or at -25 °C, respectively. Gas evolution occurred which was complete after few min-

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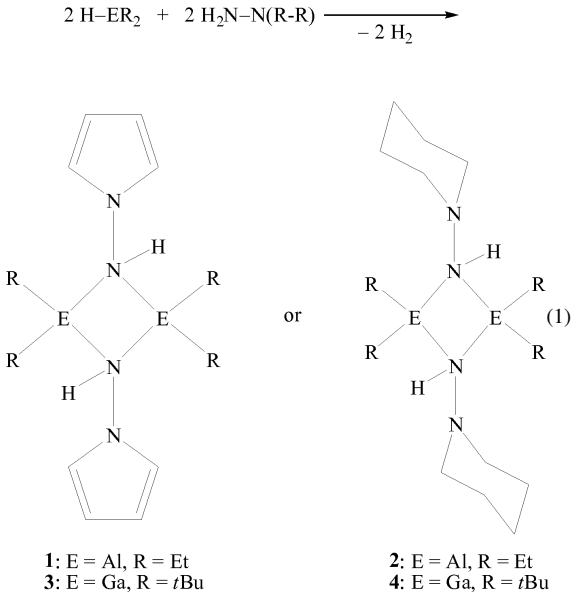

utes (Eq. 1). The product of the 1-aminopyrrole reaction (**1**) precipitated directly from the reaction mixture and was recrystallized from toluene. In contrast, 1-aminopiperidine gave a clear reaction mixture. Colorless crystals of the hydrazide **2** were obtained after concentration of the solution and cooling to +4 °C. Crystal structure determinations confirmed the formation of dimeric diethylaluminum hydrazides possessing central Al_2N_2 heterocycles in both cases. The NMR spectroscopic characterization of both products gave different results. The ^{1}H NMR spectrum of **2** showed a simple set of resonances of a single molecular form. A quartet (δ = 0.29) and a triplet (δ = 1.37) of ethyl hydrogen atoms indicated a centrosymmetric dimer and the *trans* arrangement of the piperidino groups. In contrast, an equilibrium mixture comprising two different isomers resulted for the hydrazide **1**. One component had two sets of resonances of ethyl groups (triplets at δ = 1.07 and 1.10; quartets at δ = 0.14 and −0.07), but only two resonances for the hydrogen atoms of the pyrrole ring. This pattern is in accordance with the point group C_{2v} and a *cis* arrangement of the aromatic rings. The second component showed the simple spectrum characteristic of a *trans* form similar to **2**. Thus, only the pyrrole derivative **1** shows a dynamic behavior in solution and gives different isomers upon dissolution in benzene. *cis/trans* Isomerisation has been observed previously for dimeric gallium hydrazides [7, 17, 18, 20], but for the first time it was detected for an aluminum derivative.

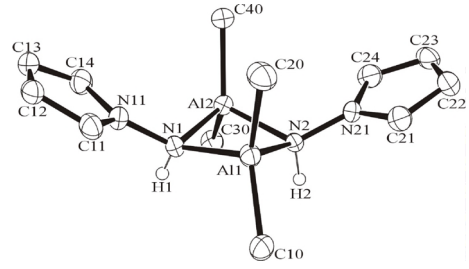

Fig. 1. Molecular structure of **1**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of N–H are omitted. Selected bond lengths (pm) and angles (deg): Al1–N1 198.1(4), Al1–N2 197.5(3), Al2–N1 198.5(4), Al2–N2 198.2(3), N1–N11 142.2(5), N2–N21 143.3(4); Al1–N1–Al2 92.1(2), Al1–N2–Al2 92.4(1), N1–Al1–N2 84.2(1), N1–Al2–N2 83.9(1).

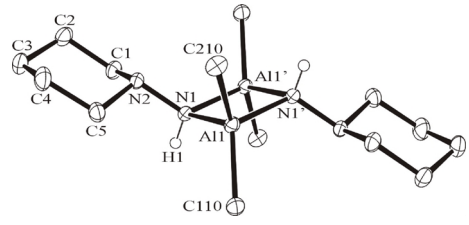

Fig. 2. Molecular structure of **2**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of N–H are omitted. Selected bond lengths (pm) and angles (deg): Al1–N1 196.73(8), Al1–N1′ 196.41(8), N1–N2 145.8(1); Al1–N1–Al1′ 92.43(3), N1–Al1–N1′ 87.57(3); Al1′ and N1′ generated by $-x+1$, $-y$, $-z+2$.

Crystal structure determinations verified the formation of dimeric diethylaluminum hydrazides for both compounds **1** and **2** (Figs. 1 and 2). However, different configurations were found. Compound **2** has a centrosymmetric molecular structure with the *trans* arrangement of the terminal N–N bonds which reflects the standard form and has been observed for most of the dimeric aluminum, gallium or indium hydrazides possessing four-membered E_2N_2 heterocycles. In contrast, **1** adopts a *cis* configuration with the N–N bonds on the same side of the central Al_2N_2 ring. This particular configuration has been observed only once before with the indium hydrazide [Me_2In–NH–N(H)CMe_3]$_2$ [24]. In accordance with the molecular symmetry, compound **2** is located on a crystallographic center of inversion with an ideal planar Al_2N_2 heterocycle, while the inner ring of **1** is folded across the Al1–Al2 axis by an angle of 30.0°. The most acute angles of the Al_2N_2 heterocycles occur at the aluminum atoms (N–Al–N 84.0 and 87.6° *versus* Al–N–Al 92.3 and 92.4°). The Al–N distances are in the expected

range (198.1 and 196.6 pm on average). The N–N distances of **1** (142.8 pm) are little shorter than those of **2** (145.8 pm) which may depend on the different hybridization of the β-nitrogen atoms.

Reactions of di(tert-butyl)gallium hydride with 1-aminopyrrole and 1-aminopiperidine

Di(*tert*-butyl)gallium hydride is the only dialkylelement hydride that shows a dismutation reaction in solution [30]. While the trimer of the hydride was detected in the solid state, an equilibrium mixture was formed upon dissolution. Three compounds were identified by NMR spectroscopy: $Ga(CMe_3)_3$, the sesquihydride $[Me_3C–GaH_2]_2[(Me_3C)_2Ga–H]_2$ and $(Me_3C)_2Ga–H$. Nevertheless this mixture usually gave clear reaction courses with the selective formation of the expected products. When we treated 1-aminopyrrol and 1-aminopiperidine with equimolar quantities of the hydride, relatively inhomogeneous reaction mixtures were obtained with gas evolution. Recrystallization of the raw products from *n*-pentane or toluene afforded the hydrazides **3** and **4** (Eq. 1) in only moderate yields of 26 and 33 %, respectively. The pyrrol derivative **3** gave only a single set of resonances in the NMR spectra. The occurrence of only one resonance of *tert*-butyl groups is in accordance with a centrosymmetric molecular structure similar to that of the aluminum compound **2**. In contrast, two isomeric forms were detected in the solutions of the piperidine derivative **4**. The NMR data are once more consistent with an equilibrium between *cis* and *trans* isomers. The *cis* form with both piperidino ligands on the same side of the inner Ga_2N_2 heterocycle is easily identified by the occurrence of two different resonances of the *tert*-butyl groups attached to gallium.

Crystal structure determinations of **3** and **4** (Figs. 3 and 4) verified the dimeric formula units possessing central Ga_2N_2 heterocycles. The molecules of compound **3** are severely disordered with two equivalent position of each pyrrole ring above and below the average molecular plane. Nevertheless, owing to the planarity of the inner ring we assume the centrosymmetric configuration as the most probable one which is similar to compound **4** and is shown in Fig. 3. In accordance with the aluminum compounds described above, the Ga–N distances are slightly longer for the pyrrole derivative (207.0 pm *versus* 204.3 pm). The nitrogen atoms of the Ga_2N_2 heterocycles have a tetrahedral coordination sphere. Those embedded in the aromatic pyrrole ring are in a trigonal planar configuration

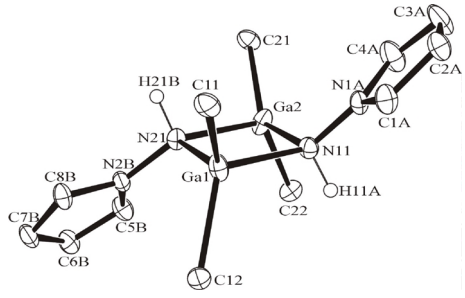

Fig. 3. Molecular structure of **3**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of NH are omitted. Only one of the disordered pyrrol positions is shown. Selected bond lengths (pm) and angles (deg): Ga1–N11 207.3(2), Ga1–N21 205.9(2), Ga2–N11 207.0(2), Ga2–N21 207.8(2); Ga1–N11–Ga2 97.85(9), Ga1–N21–Ga2 98.02(8), N11–Ga1–N21 82.26(7), N11–Ga2–N21 81.88(7).

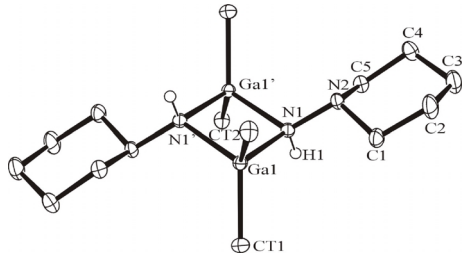

Fig. 4. Molecular structure of **4**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of NH are omitted. Selected bond lengths (pm) and angles (deg): Ga1–N1 204.0(2), Ga1–N1′ 204.6(2), N1–N2 145.3(2); Ga1–N1–Ga1′ 96.56(6), N1–Ga1–N1′ 83.44(6); Ga1′ and N1′ generated by $-x$, $-y$, $-z+2$.

(sum of the angles 360°), while the piperidine nitrogen atoms exhibit a pyramidal surrounding (sum of the angles 327.6°). The most acute angles of the Ga_2N_2 heterocycles were detected at the gallium atoms (82.1 and 83.4 *versus* 97.9 and 96.6°at N).

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over $LiAlH_4$; toluene over Na/benzophenone). $Et_2Al–H$ [31], $(Me_3C)_2Ga–H$ [30] and 1-aminopyrrole [32] were obtained according to literature procedures. Commercially available 1-aminopiperidine (Aldrich) was degassed prior to use.

*Reaction of Et_2Al-H with 1-aminopyrrole; synthesis of **1***

1-Aminopyrrole (0.37 mL, 0.385 g, 4.69 mmol) was added to a solution of $Et_2Al–H$ (0.50 mL, 0.400 g, 4.65 mmol) in 25 mL of *n*-pentane at r. t. Gas evolution

occurred for about 5 min, and a colorless solid precipitated. The suspension was stirred for 18 h. The solvent was removed in vacuum, and the residue was extracted with toluene. The remaining solid was removed. Colorless crystals of **1** were obtained upon cooling of the clear solution to −15 °C. Yield: 0.297 g (38 %). M. p. (under argon, sealed capillary): 140 °C. – IR (paraffin; CsBr plates; cm^{-1}): ν = 3163 m ν(NH); 2953 vs, 2922 vs, 2853 vs (paraffin); 1525 w (pyrrole); 1460 vs, 1377 s (paraffin); 1302 w, 1269 vw $\delta(CH_3)$; 1231 vw, 1200 vw, 1167 vw; 1082 w, 1069 m, 988 w, 962 m, 924 w, 858 w, 847 vw ν(CC), ν(NN), ν(NC); 716 s (paraffin); 669 w, 627 w, 584 w, 462 w ν(AlC), $\nu(Al_2N_2)$. – ^{1}H NMR (400 MHz, C_6D_6): *cis* isomer: *d* = 6.44 (m, 4H, NC*H*CH), 6.10 (m, 4H, NCHC*H*), 3.91 (s, 2H, NH), 1.10 and 1.07 (each: t, 3H, CH_2CH_3), 0.14 and −0,07 (each: q, 2H, CH_2CH_3); *trans* isomer: δ = 6.46 (m, 4H, NC*H*CH), 6.11 (m, 4H, NCHC*H*), 4.40 (s, 2H, NH), 1.03 (t, 12H, CH_2CH_3), 0.09 and −0.01 (each: q, 4H, diastereotopic CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): *cis* isomer: δ = 120.9 (N*C*HCH), 107.6 (NCH*C*H), 9.0 and 8.8 (CH_2CH_3), 0.5 and −1.4 (CH_2CH_3); *trans* isomer: δ = 120.7 (N*C*HCH), 107.4 (NCH*C*H), 8.6 (CH_2CH_3), −0.1 (CH_2CH_3). – MS (EI, 20 eV, 40 °C): *m/z* (%) = 303 (100) $[M-Et]^+$, 245 (23) $[M-3Et]^+$.

Reaction of Et_2Al–H with 1-aminopiperidine; synthesis of ***2***

Et_2AlH (0.20 mL, 0.160 g, 1.86 mmol) was dissolved in 25 mL of *n*-hexane and treated with 1-aminopiperidine (0.20 mL, 0.186 g, 1.86 mmol) at −25 °C. Gas evolution was complete after about 5 min. The reaction mixture was slowly warmed to r. t., concentrated and cooled to +4 °C to obtain colorless crystals of **2**. Yield: 0.138 g (40 %). M. p. (under argon, sealed capillary): 86 °C. – IR (paraffin; CsBr plates; cm^{-1}): ν = 3115 w ν(N–H); 2922 vs, 2853 vs (paraffin); 1456 vs (paraffin); 1406 w $\delta(CH_3)$; 1377 s (paraffin); 1310 vw, 1281 w, 1271 w $\delta(CH_3)$; 1236 vw, 1194 w, 1152 w; 1107 w, 1063 w, 1036 m, 988 m, 952 w, 923 m, 856 s, 773 m ν(CC), ν(CN), ν(NN); 721 m (paraffin); 671 s, 644 vs, 527 vw, 447 w δ(CC), ν(AlC), $\nu(Al_2N_2)$. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 3.00 (bs, 4H, H_{eq} of NCH_2), 2.18 (s, 2H, N*H*), 1.66 (bs, 4H, H_{ax} of NCH_2), 1.47 (bs, 8H, $NCH_2CH_2CH_2$), 1.37 (t, 12H, CH_2CH_3), 1.23 (bs, 2H, H_{eq} of $NCH_2CH_2CH_2$), 1.03 (bs, 2H, H_{ax} of $NCH_2CH_2CH_2$), 0.29 (q, 8H, CH_2CH_3). – ^{13}C NMR (C_6D_6, 100 MHz): δ = 62.7 (N*C*CC), 26.2 (NC*C*C), 23.2 (NCC*C*), 9.8 (CH_2CH_3), 0.2 (CH_2CH_3). – MS (EI, 20 eV, 30 °C): *m/z* (%) = 368 (2) $[M]^+$, 339 (55) $[M-Et]^+$, 310 (31) $[M-2Et]^+$, 281 (100) $[M-3Et]^+$.

Reaction of $(Me_3C)_2$Ga–H with 1-aminopyrrole; synthesis of ***3***

$(Me_3C)_2$Ga–H (0.304 g, 1.65 mmol) was dissolved in 50 mL of *n*-pentane and treated with 1-aminopyrrole (0.13 mL, 0.134 g, 1.64 mmol) at r. t. Gas evolution was complete after about 5 min. The clear solution was stirred for 2 h and concentrated. Cooling to −20 °C gave a colorless solid which was recrystallized from *n*-pentane for further purification to yield colorless crystals of **3** (+20/−20 °C). Yield: 0.113 g (26 %). M. p. (under argon, sealed capillary): decomposition above 220 °C. – IR (paraffin; CsBr plates; cm^{-1}): ν = 3171 w ν(N–H); 2897 vs, 1451 vs, 1377 vs (paraffin); 1306 m $\delta(CH_3)$; 1169 w, 1080 w, 1067 w, 1007 w, 962 s, 939 w; 860 w, 847 w, 812 w ν(NN), ν(CC), ν(CN); 708 s (paraffin); 590 w, 554 w, 447 w ν(GaN), ν(GaC). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 6.66 (pseudo-t, 4H, NC*H*CH), 6.13 (pseudo-t, 4H, NCHC*H*), 5.44 (s, 2H, N*H*), 1.11 (s, 36H, CMe_3). – ^{13}C NMR (C_6D_6, 50 MHz): δ = 121.2 (N*C*C), 107.3 (NC*C*), 31.3 (C*Me*$_3$), 24.9 (*C*Me_3).

Reaction of $(Me_3C)_2$Ga–H with 1-aminopiperidine; synthesis of ***4***

$(Me_3C)_2$Ga–H (0.625 g, 3.38 mmol) was dissolved in 30 mL of *n*-hexane and treated with 1-aminopiperidine (0.37 mL, 0.343 g, 3.43 mmol) at r. t. Gas evolution was complete after about 5 min. The clear solution was stirred for 18 h. A colorless solid precipitated after concentration and cooling to +4 °C. Colorless crystals of **4** were obtained by recrystallization from toluene (+20/+4 °C). Yield: 0.312 g (33 %). M. p. (under argon, sealed capillary): decomposition above 232 °C. – IR (paraffin; CsBr plates; cm^{-1}): ν = 3107 w ν(NH); 2920 vs, 2847 vs (paraffin); 1580 vw; 1454 vs, 1377 vs (paraffin); 1264 m $\delta(CH_3)$; 1230 m, 1167 w, 1150 m, 1101 m, 1063 w, 1034 s; 1009 m, 968 vw, 920 s, 881 vs, 856 m, 812 vs, 773 s ν(CC), ν(CN), ν(NN); 723 m (paraffin); 646 vw; 598 s, 567 vs, 538 m, 442 m, 426 s ν(GaN), ν(GaC). – ^{1}H NMR (C_6D_6, 400 MHz): *cis* isomer: δ = 3.09 (bs, 4H, H_{eq} of NCH_2), 2.93 (s, 2H, NH), 1.64 (bs, 4H, H_{ax} of NCH_2), 1.53 (s, 18H, C*Me*$_3$), 1.45 (bs, 8H $NCH_2CH_2CH_2$), 1.33 (bs, 2H, H_{eq} of $NCH_2CH_2CH_2$), 1.21 (s, 18H, C*Me*$_3$), 0.86 (bs, 2H, H_{ax} of $NCH_2CH_2CH_2$); *trans* isomer: δ = 3.20 (s, 2H, NH), 3.10 (bs, 4H, H_{eq} of NCH_2), 1.65 (bs, 4H, H_{ax} of NCH_2), 1.44 (bs, 8H, $NCH_2CH_2CH_2$), 1.34 (s, 36H, C*Me*$_3$), 1.33 (bs, 2H, H_{eq} of $NCH_2CH_2CH_2$), 0.86 (bs, 2H, H_{ax} of $NCH_2CH_2CH_2$). – ^{13}C NMR (C_6D_6, 100 MHz): *cis* isomer: δ = 64.2 (N*C*CC), 33.2 and 32.1 (C*Me*$_3$), 25.9 and 22.8 (*C*Me_3), 26.1 (NC*C*C), 23.0 (NCC*C*); *trans* isomer: δ = 63.9 (N*C*CC), 33.0 (C*Me*$_3$), 26.4 (NC*C*C), 24.0 (*C*Me_3), 23.1 (NCC*C*). – MS (EI, 20 eV, 80 °C): *m/z* (%) = 507 (9), 509 (12), 511 (5) $[M-t\text{-Bu}]^+$, 397 (9), 399 (10), 401 (4) $[M-2NC_5H_{10}]^+$, 282 (13), 284 (9) $[0.5M]^+$.

Crystal structure determinations

Single crystals were obtained by recrystallization from saturated solutions (**1**: toluene, −15 °C; **2**: *n*-hexane, +4 °C;

Table 1. Crystal data, data collection, and structure refinement.

	1	**2**	**3**	**4**
Crystal data				
Empirical formula	$C_{16}H_{30}Al_2N_4$	$C_{18}H_{42}Al_2N_4$	$C_{24}H_{46}Ga_2N_4$	$C_{26}H_{58}Ga_2N_4$
M_r	332.40	368.52	530.08	566.20
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group[a]	$P2_1/n$; no. 14	$P2_1/c$; no. 14	$P2_1/n$; no. 14	$P2_1/c$; no. 14
a, pm	808.80(5)	935.19(5)	899.4(1)	914.8(2)
b, pm	1432.42(7)	1221.02(7)	1919.2(3)	1646.1(3)
c, pm	1702.3(1)	994.85(6)	1608.1(2)	999.3(2)
β, deg	96.814(4)	90.680(1)	102.934(3)	104.192(3)
V, $\times 10^{-30}$ m^3	1958.2(2)	1135.9(1)	2705.5(7)	1458.8(4)
ρ_{calc}, g cm^{-3}	1.127	1.077	1.301	1.289
Z	4	2	4	2
$F(000)$, e	720	408	1120	608
Radiation; λ, pm	CuK_α; 154.184	MoK_α; 71.073	MoK_α; 71.073	MoK_α; 71.073
μ, mm^{-1}	1.346 (CuK_α)	0.136 (MoK_α)	2.008 (MoK_α)	1.866 (MoK_α)
Data collection				
T, K	153(2)	153(2)	153(2)	153(2)
Unique reflections	3438	3670	7858	4233
Reflections $I \geq 2\sigma(I)$	2556	3094	5190	3565
Refinement				
Refined parameters	211	115	529	186
Final R				
R^b $[I \geq 2\sigma(I)]$	0.069	0.032	0.042	0.032
$wR2^c$ (all data)	0.175	0.095	0.096	0.079
ρ_{fin} (max/min), e Å^{-3}	0.43/−0.26	0.34/−0.16	0.66/−0.57	0.62/−0.29

[a] Ref. [34]; [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [c] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

3: *n*-pentane, −20 °C; **4**: toluene, +4 °C). Data collections were performed on a Bruker Smart Apex diffractometer. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations based on F^2 [33]. The hydrogen atoms of methyl groups were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. The molecules of compounds **2** and **4** reside on crystallographic centers of inversion. The aminopyrrole ligands of compound **3** were disordered. The atoms were refined on split positions with site occupancy factors of 0.5. One *tert*-butyl group of **4** (CT2) showed a rotational disorder; the methyl groups were refined on split positions (0.503 to 0.497).

CCDC 696057 (**1**), 696058 (**2**), 696059 (**3**) and 696060 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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