Hydrazine Adducts of Tri(tert-butyl)aluminum, -gallium and -indium – a Systematic Approach

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Treatment of the monomeric trialkylelement compounds Al(CMe₃)₃, Ga(CMe₃)₃, and In(CMe₃)₃ with different hydrazines H₂N–N(H)R (R = Me, CMe₃, C₆H₅) yielded the corresponding adducts (Me₃C)₃E ← NH₂–N(H)R, 1 to 9, in almost quantitative yields. All products were characterized by crystal structure determinations and shown to have the NH₂ group of the hydrazine ligands attached to the central Group 13 atom. These adducts are excellent starting compounds for the generation of hydrazides by thermolysis with release of butane.

Key words: Aluminum, Gallium, Indium, Hydrazines, Adducts

Introduction

Alkylaluminum, -gallium or -indium hydrazides are suitable starting compounds for the generation of the corresponding element nitrides by thermolysis [1]. Furthermore, they found increased interest in recent literature owing to the fascinating coordination behavior of the bifunctional hydrazido ligands, which resulted in the formation of a broad variety of heterocyclic or cage-like compounds. Their synthesis was accomplished via several efficient routes, which essentially comprise hydrogen or alkane elimination, salt elimination and hydroalumination reactions [2–25]. The formation of adducts was postulated as a reasonable initiating step in particular for the first two types of elimination reactions. However, these adducts were isolated and thoroughly characterized in few cases only [5, 9, 16–19, 22, 23, 25]. Steric interactions determine the coordination mode, and usually the less shielded NH₂ nitrogen atom of the hydrazide ligands is attached to the central aluminum or gallium atoms. A single exception was recently observed with the compound Me₃Ga ← N(H)(Me)–NH₂ in which the more basic alkylated nitrogen atom is coordinated to the gallium atom [25]. The formation of this particular compound may be favored by the low steric shielding of acceptor and donor atoms. Systematic investigations into the coordination of tri(tert-butyl)element compounds (E = Al, Ga, In) by different hydrazines H₂N–N(H)R (R = Me, CMe₃, C₆H₅) should allow for a concise understanding of steric or electronic influences on the structures and properties of these adducts. A different reactivity pattern may appear owing to the strongly differing polarities of the E–C bonds. For instance, AlMe₃ or InMe₃ did not yield stable adducts with methylhydrazine at all. Instead spontaneous release of methane occurred below r. t. [25]. GaMe₃ and methylhydrazine gave an adduct as described above, and heating was required to initiate a secondary reaction. These compounds are potentially useful precursors for the generation of hydrazides or the corresponding nitrides by thermolysis, because only volatile by-products may be formed. Furthermore, tert-butyl substituents are particularly suitable leaving groups for these purposes, because butane may be eliminated by direct deprotonation of the hydrazido ligands or β-elimination may occur followed by release of elemental hydrogen.

Results and Discussion

Synthesis of the adducts (Me₃C)₃E←NH₂–N(H)R 1 to 9

A standard procedure was applied for the synthesis of all adducts. The tri(tert-butyl) element compounds were dissolved in n-pentane or n-hexane and treated with equimolar quantities of the respective hydrazine at r. t. (Eq. 1). After stirring for 1 h the solvents were removed in a vacuum to obtain the products in high purity and in almost quantitative yield. Two alkylaluminum (1 and 2) and alkylgallium adducts (4 and 5)
remained as amorphous solids, while all other compounds (3, 6 to 9) are colorless liquids at r.t. They could be distilled in vacuum without decomposition. Recrystallization from pentane or hexane afforded colorless crystals, some of which melted below r.t. Nevertheless, we were able to mount crystals of all compounds on the diffractometer and determine their structures (see below). The NMR spectroscopic characterization gave the correct integration ratio of peak intensities in all cases. The 1H NMR spectra of the methylhydrazine adducts 1, 4 and 7 showed doublets of the hydrazine methyl groups caused by coupling to the hydrogen atoms of the neighboring N–H moieties. However, with exception of the aluminum adduct 1, the quartets expected for these atoms were not clearly resolved owing to the generally broad resonances of hydrogen atoms attached to nitrogen. For the same reason the H-H coupling constants across the N–N bonds were not detected unambiguously in several cases. A splitting of the N–H resonances into doublets and triplets occurred for compounds 2 (3JH–H = 5.8 Hz), 3 (4.2 Hz), 8 (5.4 Hz) and 9 (4.0 Hz). In the alkylhydrazine adducts the chemical shifts of the NH and NH2 groups were about δ = 2.7 and 3.4 on average, while in the phenylhydrazine adducts the N–H protons in geminal position to the aromatic rings were considerably shifted to lower field (δ = 3.9 for NH2 and 5.1 for N–H). The mass spectra showed reasonable fragmentation patterns for most of the aluminum and gallium compounds. An interesting spectrum was obtained for the indium adduct 7 (methylhydrazine). Under relatively mild conditions (25 °C) it showed the characteristic masses of heterocyclic diindium compounds such as [(Me3C)2In(N(H)–N(H)Me)2 which are expected to be formed by thermolysis.

Crystal structure determinations

All adducts (1 to 9) were characterized by crystal structure determinations. Three representative examples (1: E = Al, R = Me; 5: E = Ga, R = CMe3; 9: E = In, R = C6H5) are depicted in Figs. 1 to 3. Table 1 contains important bond lengths and angles. In all cases the NH2 nitrogen atoms of the hydrazine ligands are coordinated to the central atoms. This result does not reflect the stronger basicity of the alkylated nitrogen atoms, but may be due to weaker steric interactions (see Introduction). The bond parameters are essentially unaffected by the different alkyl or aryl groups attached to the hydrazine ligands. The aluminum, gallium or indium atoms possess a distorted tetrahedral surrounding with relatively large angles between the bulky tert-butyl groups (about 116°).
Table 1. Important bond lengths (pm) and angles (deg) of the hydrazine adducts 1 to 9.

<table>
<thead>
<tr>
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<tbody>
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<td>(Me3C)3Al←NH2–N(H)Me 1</td>
<td>144.6(2)</td>
<td>205.4(1)</td>
<td>202.6</td>
<td>115.8</td>
<td>97.2/104.4</td>
<td>118.10(9)</td>
</tr>
<tr>
<td>(Me3C)3Al←NH2–N(H)CMe3 2*</td>
<td>144.2(3)</td>
<td>206.4(2)</td>
<td>202.8</td>
<td>115.8</td>
<td>96.5/104.7</td>
<td>116.0(2)</td>
</tr>
<tr>
<td>(Me3C)3Al←NH2–N(H)C6H5 3</td>
<td>142.4(2)</td>
<td>206.5(1)</td>
<td>202.6</td>
<td>116.2</td>
<td>96.7/103.6</td>
<td>117.44(9)</td>
</tr>
<tr>
<td>(Me3C)3Ga←NH2–N(H)Me 4</td>
<td>143.2(4)</td>
<td>214.7(2)</td>
<td>205.0</td>
<td>116.3</td>
<td>95.8/103.8</td>
<td>117.8(2)</td>
</tr>
<tr>
<td>(Me3C)3Ga←NH2–N(H)CMe3 5</td>
<td>139.8(4)</td>
<td>216.1(3)</td>
<td>204.2</td>
<td>116.5</td>
<td>97.1/102.8</td>
<td>117.9(2)</td>
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<tr>
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<td>142.6(5)</td>
<td>218.2(4)</td>
<td>203.3</td>
<td>116.7</td>
<td>98.7/104.4b</td>
<td>115.1(3)</td>
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<tr>
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<td>141.6</td>
<td>238.6</td>
<td>221.6</td>
<td>117.7</td>
<td>98.7</td>
<td>116.0</td>
</tr>
<tr>
<td>(Me3C)3In←NH2–N(H)CMe3 8</td>
<td>143.7(2)</td>
<td>239.7(2)</td>
<td>221.5</td>
<td>117.4</td>
<td>99.3</td>
<td>114.2(1)</td>
</tr>
<tr>
<td>(Me3C)3In←NH2–N(H)C6H5 9</td>
<td>142.3(2)</td>
<td>242.0(2)</td>
<td>221.9</td>
<td>118.1</td>
<td>98.0</td>
<td>116.4(1)</td>
</tr>
</tbody>
</table>

* Disordered hydrazine ligand; b two angles at 99°; c four independent molecules.

**Fig. 2.** Molecular structure of the tert-butylhydrazine adduct 5 (E = Ga). The displacement ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of N–H are omitted for clarity.

**Fig. 3.** Molecular structure of the phenylhydrazine adduct 9 (E = In). The displacement ellipsoids are drawn at the 40% probability level; hydrogen atoms with the exception of NH2 are omitted for clarity.

The title compounds will be employed in future investigations for the generation of hydrazides and finally of the corresponding element nitrides. Their volatility may allow for the deposition of the nitrides from the gas phase. Preliminary experiments in particular with the aluminum adducts gave the corresponding hydrazides [(Me3C)2Al–N(H)–N(H)–R]2. The decomposition of the trialkylindium methylhydrazine adduct 7 under the conditions of mass spectrometry gave a further hint that thermolysis of these adducts may be successfully applied to produce interesting secondary products by butane elimination.

**Experimental Section**

All procedures were carried out under purified argon in dried solvents (n-pentane and n-hexane over LiAlH4). Commercially available methylhydrazine and phenylhydrazine were distilled prior to use and stored under argon. MOCHEM GmbH kindly supported us with tert-butylhydrazine and tri(tert-butyl)gallium. Tri-(tert-butyl)gallium was obtained according to a literature procedure [27]. The synthesis of tri(tert-butyl)aluminum is described in the literature [28]. We applied a slightly modified procedure (see below) which gave the product in a considerably higher yield.
Tri(tert-butyl)aluminum

Aluminum tribromide (25.5 g, 0.0956 mol) was dissolved in 150 mL of n-pentane and added dropwise to a cooled solution (−80 °C) of tert-butyllithium in n-pentane (1.6 M, 179.3 mL, 0.286 mol). The suspension was slowly warmed to r.t. and filtered. The solid was washed with n-pentane, and the solvent of the filtrate was removed in a vacuum. The remaining viscous liquid was distilled in a vacuum (10−3 Torr) at r.t. into a trap cooled by liquid nitrogen. Yield: 13.65 g (72%). Characterization: See [28].

Syntheses of the adducts (Me₃C)₃E−NH₂−N(H)R 1 to 9: general procedure

The respective trialkylelement compound (about 0.5 g) was dissolved in 30 mL of n-pentane or n-hexane and treated with equimolar quantities of the hydrazine derivative without a solvent at r.t. The solution was stirred for 0.5 h. The solvent was removed in a vacuum to yield the products in a high purity and an almost quantitative yield. Crystals were obtained by recrystallization from pentane or hexane or after concentration of the reaction mixtures and cooling of the solutions to −30 °C. The crystals of compounds 3 and 6 to 9 melted upon warming to r.t. In these cases distillation in a vacuum was successful without decomposition (up to 120 °C oil bath temperature/10−3 Torr).

Characterization of (Me₃C)₃Al−NH₂−N(H)CH₃ (1)

M.p. (under argon, sealed capillary) 52 °C. – IR (paraffin; CsBr plates): ν = 3348 s, 3258 s, 3198 w, 3150 w ν(NH); 2951 vs, 2922 vs, 2853 vs, 2693 m, 2621 w (paraffin); 1591 s δ(NH); 1462 vs, 1377 vs, 1362 sh (paraffin); 1273 w, 1248 m δ(CH₃); 1215 w, 1177 m, 1127 s, 1074 w, 1001 s, 935 s, 810 vs, 789 sh νₐ(AlC), ν(CN), ν(NN), νₓ(AlC); 723 w (paraffin); 644 s, 575 m, 527 w, 469 w ν(AlC), ν(AlN), δ(CC₃) cm⁻¹. – 1H NMR (400 MHz, C₆D₆): δ = 3.30 (s, br. 2 H, NH₂), 2.88 (q, br. J₃H–H = 5.6 Hz, 1 H, NH), 1.66 (d, J₃H–H = 5.6 Hz, 3 H, NMe), 1.15 (s, 27 H, t-Bu). – 13C {¹H} NMR (100 MHz, C₆D₆): δ = 41.3 (NMe), 32.4 (CMMe₃), 16.5 (br, AlC). – MS (EI, 20 eV, 50 °C): m/z (% = 198 (21) [Al(t-Bu)+]⁺, 187 (100) [M–t-Bu]+, 141 (28) [Al(t-Bu)+]⁺, 46 (4) [H₂NNHMe]⁺. – 1H NMR (400 MHz, C₆D₆): δ = 3.58 (br, 2 H, NH₂), 2.77 (br., 1 H, NH), 1.30 (s, 27 H, Ga–t-Bu), 0.62 (s, 9 H, N–t-Bu). – 13C {¹H} NMR (100 MHz, C₆D₆): δ = 53.4 (NC), 33.0 (GaCMMe₃), 25.6 (NCMe₃); Ga–C not detected. – MS (EI, 20 eV, 25 °C): m/z (% = 229 (21), 231 (14) [M–Ga]+, 183 (100), 185 (89) [Ga(t-Bu)+]⁺; 46 (4) [H₂NNHMe]⁺. – Chemical characterization of (Me₃C)₃Ga−NH₂−N(H)CH₃ (4)

M.p. (under argon, sealed capillary) 44 °C. – IR (paraffin; CsBr plates): ν = 3352 w, 3312 w ν(NH); 2949 vs, 2922 vs, 2855 vs, 2828 vs (paraffin); 1599 m δ(NH); 1464 vs, 1379 m (paraffin); 1360 m, 1250 w δ(CH₃); 1225 w, 1109 m, 1069 w, 1009 w, 937 w, 810 vs, 789 m νₐ(AlC), ν(CN), ν(NN), νₓ(AlC); 721 w (paraffin); 687 w, 594 w, 528 w, 469 w δ(CC₃), ν(GaC), ν(GaN) cm⁻¹. – 1H NMR (400 MHz, C₆D₆): δ = 3.07 (br, 2 H, NH₂), 2.70 (br., 1 H, NH), 1.78 (d, J₃H–H = 4.6 Hz, 3 H, NMe), 1.23 (s, 27 H, t-Bu). – 13C {¹H} NMR (100 MHz, C₆D₆): δ = 42.0 (NMe), 32.8 (CMGa); Ga–C not detected. – MS (EI, 20 eV, 25 °C): m/z (% = 229 (21), 231 (14) [M–Ga]+, 183 (100), 185 (89) [Ga(t-Bu)+]⁺; 46 (4) [H₂NNHMe]⁺. – Characterization of (Me₃C)₃Ga−NH₂−N(H)CH₃ (5)

M.p. (under argon, sealed capillary) 44 °C. – IR (paraffin; CsBr plates): ν = 3359 m ν(NH); 2922 vs, 2855 vs, 2826 vs (paraffin); 1595 m δ(NH); 1464 vs, 1366 vs (paraffin); 1269 wv, 1227 s, 1213 s, 1151 vs, 1070 wv, 1036 s, 1007 s, 935 m, 908 w, 810 vs, 791 s δ(CH₃), νₐ(AlC), ν(CN), ν(NN), νₓ(AlC); 719 s (paraffin); 689 w, 604 m, 530 m, 446 w ν(GaC), ν(GaN), δ(CC₃) cm⁻¹. – 1H NMR (400 MHz, C₆D₆): δ = 3.58 (br, 2 H, NH₂), 2.77 (br., 1 H, NH), 1.30 (s, 27 H, Ga–t-Bu), 0.62 (s, 9 H, N–t-Bu). – 13C {¹H} NMR (100 MHz, C₆D₆): δ = 53.4 (NC), 33.0 (GaCMMe₃), 25.6 (NCMe₃); Ga–C not detected. – MS (EI, 20 eV, 25 °C): m/z (% = 271 (25), 273 (14) [M–Ga]+; 240
Table 2. Crystal data and numbers pertinent to data collection and structure refinement of 1 to 9.

<table>
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<th>Crystal data</th>
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<th>Characterization of (Me₃C)₃Ga</th>
<th>Characterization of (Me₃C)₃In</th>
<th>Characterization of (Me₃C)₃Ga</th>
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<td>C₁₃H₃₃GaN₂</td>
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<tr>
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<td>0.930/</td>
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<td>(e - \tilde{e})</td>
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\(^a\) \(R = \Sigma|F_o| - |F_c|/\Sigma|F_o|\) \(\text{wR}^2 = (\Sigma|w(F_o^2 - F_c^2)^2|/\Sigma|w(F_o^2)^2|)^{1/2}\).

(5), 242 (3) [Ga(t-Bu)₃]⁺, 183 (100), 185 (67) [Ga(t-Bu)₂]⁺, 88 (5) [H₂N(CH₂)₂⁺].

Characterization of (Me₃C)₃Ga–NH₂–H(NH)CH₃ (6)

Liquid at r.t. – IR (paraffin; CsBr plates): \(\nu = 3389\) vs, 3312 m, 3279 w, 3233 w, 3167 w v(NH); 2953 vs, 2922 vs, 2852 vs (paraffin); 1979 vw, 1925 w, 1830 w, 1765 w, 1693 m (phenyl); 1599 vs \(\delta\) (NH); 1497 m (phenyl); 1454 vs, 1379 vs (paraffin); 1312 m, 1258 s \(\delta\) (CH₃); 1186 vs, 1157 vs, 1103 w, 1076 s, 1045 m, 1013 m, 934 s, 880 m, 847 m, 802 w, 752 vs vₐₐ(C≡N) v(CN), v(NH), vₐₐ(C≡N); 691 s, 669 m, 652 w, 592 w, 528 w, 492 w, 433 w v(CC₃), v(CC₃), \(\delta\) (CC₃) cm\(^{-1}\). – ¹H NMR (400 MHz, C₆D₆): \(\delta = 7.02\) (pseudo-t, 2 H, m of phenyl), 6.76 (pseudo-t, 1 H, p-H of phenyl), 6.26 (d, 2 H, o-H of phenyl), 4.89 (br, 1 H, NH), 3.67 (br, 2 H, NH₂), 1.24 (s, 27 H, Ga-t-Bu). – ¹³C [¹H] NMR (100 MHz, C₆D₆): \(\delta = 149.3\) (ipso-C of phenyl), 129.6, 121.3 and 112.9 (o-, m- and p-phenyl of phenyl), 32.7 (GaMe₃); – MS (EI, 20 eV, 25 °C); m/z (%) = 183 (43), 185 (29) [Ga(t-Bu)₂]⁺, 108 (100) [H₂N(NH₂)⁺].

Characterization of (Me₃C)₃In–NH₂–H(NH)CH₃ (7)

Liquid at r.t. – IR (paraffin; CsBr plates): \(\nu = 3347\) vw v(NH); 2922 vs, 2853 vs, 2835 vs (paraffin); 1603 w \(\delta\) (NH); 1460 vs, 1381 m (paraffin); 1360 s, 1255 w, 1240 m \(\delta\) (CH₃); 1190 m, 1160 m, 1056 w, 1056 w, 937 m, 880 vw, 831 m, 808 m, 746 w vₐₐ(C≡N), v(CN), v(NH), vₐₐ(C≡N); 646 vw, 542 vw, 474 vw v(InC), v(InN), v(CC₃); 1225 w, 1225 w, 1177 s, 1172 s, 1069 s, 907 m, 806 vs, 789 w vₐₐ(C≡N), v(CN), v(NH), vₐₐ(C≡N); 716 s (paraffin) 555 m, 501 w, 440 vw v(InC), v(InN), v(CC₃) cm\(^{-1}\). – ¹H NMR (400 MHz, C₆D₆): \(\delta = 3.30\) (d, 3 J₁-H = 5.4 Hz, 2 H, H, NH₂), 2.63 (t, 3 J₁-H = 5.4 Hz, 1 H, NH), 1.42 (s, 27 H, In-t-Bu), 0.59 (s, 9 H, N-t-Bu). – ¹³C [¹H] NMR (100 MHz, C₆D₆): \(\delta = 53.6\) (NC), 34.1 (InC), 34.0 (CMe₃); – MS (EI, 20 eV, 25 °C); m/z (%) = 547 (8) [In₂(CMe₃)₄(NH–NHMe)₂–H]⁺, 491 (95) [In₂(CMe₃)₄(NH₂)₂]⁺, 229 (100) [In(t-Bu)₂]⁺, 46 (2) [H₂N(NH₂)⁺].

Characterization of (Me₃C)₃In–NH₂–N(H)CH₃ (8)

Liquid at r.t. – IR (paraffin; CsBr plates): \(\nu = 3339\) vw v(NH); 3237 w v(NH); 2920 vs, 2857 vs, 2814 vs (paraffin); 1599 m \(\delta\) (NH); 1462 vs (paraffin); 1391 m \(\delta\) (CH₃); 1375 s (paraffin); 1360 s, 1225 m \(\delta\) (CH₃); 1213 m, 1190 w, 1157 m, 1132 s, 1028 s, 1007 s, 935 m, 907 m, 806 vs, 789 w vₐₐ(C≡N), v(CN), v(NH), vₐₐ(C≡N); 716 s (paraffin) 555 m, 501 w, 440 vw v(InC), v(InN), v(CC₃) cm\(^{-1}\). – ¹H NMR (400 MHz, C₆D₆): \(\delta = 3.30\) (d, 3 J₁-H = 5.4 Hz, 2 H, H, NH₂), 2.63 (t, 3 J₁-H = 5.4 Hz, 1 H, NH), 1.42 (s, 27 H, In-t-Bu), 0.59 (s, 9 H, N-t-Bu). – ¹³C [¹H] NMR (100 MHz, C₆D₆): \(\delta = 53.6\) (NC), 34.1 (InC), 25.6 (NMe₃); – MS (EI, 20 eV, 35 °C); m/z (%) = 286
(4) [In(t-Bu)3]⁺, 229 (100) [In(t-Bu)2]⁺, 88 (5) [H₂NHNH-t-Bu]⁺.

Characterization of (Me₃C)₃In—NH₂—N(H)C₆H₅ (9)

Liquid at r.t. – IR (paraffin; CsBr plates): ν = 3383 w, 3323 w (NH); 2922 vs, 2853 vs, 2830 vs (paraffin); 1601 s δ(NH); 1497 s (phenyl); 1462 vs, 1377 m (paraffin); 1360 s, 1260 m, 1180 m, 1157 m, 1074 w, 1011 m, 935 m, 881 w, 831 vw, 808 m, 752 s ν(CCN), ν(CC₃), ν(CN), ν(NN), νₓ(CC₃) = 692 s, 557 w, 500 w, 482 m ν(InC), ν(InN), δ(CC₃) cm⁻¹, – 1H NMR (400 MHz, C₆D₆): δ = 7.01 (pseudo-t, 2 H, m-H of phenyl), 6.77 (pseudo-t, 1 H, p-H of phenyl), 6.21 (d, 2 H, o-H of phenyl), 4.87 (t, 3J₁H–H = 4.0 Hz, 1 H, NH), 3.49 (d, 3J₂H–H = 4.0 Hz, 2 H, NH₂), 1.37 (s, 27 H, In-t-Bu). – 13C(C₁H) NMR (100 MHz, C₆D₆): δ = 149.5 (ipso-C of phenyl), 130.1, 122.0 and 113.4 (o-, m- and p-C of phenyl), 34.3 (In(CMe₃)). In – C not detected. – MS (EI, 20 eV, 25 °C): m/z (%) = 286 (1) [In(t-Bu)₃]⁺, 229 (28) [In(t-Bu)₂]⁺, 108 (100) [H₂NHNH-Ph]⁺.

Crystal structure determinations

Single crystals were obtained by cooling of saturated solutions in n-hexane or n-pentane to −30 °C. Data collections were performed on a Bruker Smart Apex diffractometer employing graphite-monochromated MoKα radiation. The structures were solved by Direct Methods and refined with full-matrix least-squares calculations based on F² [29]. 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 2. The hydrazine ligand of compound 2 was disordered. The atoms were refined on split positions. Only very small crystals of 6 were obtained, thus, data collection was restricted to 2θ_max = 35°. Compound 7 crystallized with four independent molecules in the asymmetric unit, which possess quite similar structural parameters.

CCDC 663264 (1), 663265 (2), 663266 (3), 663267 (4), 663268 (5), 663269 (6), 663270 (7), 663271 (8), and 663272 (9) 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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