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FULL PAPER

Bridged aminotroponiminate complexes of gallium and indium

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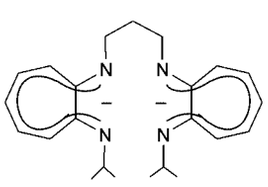
The reaction of the salt dipotassium 1,3-di[2-(isopropylamino)troponiminate]propane, $K_2[(^i Pr)TP]$, with MCl_3 (M = Ga, In) leads to complexes of composition $[\{(^i Pr)TP\}MCl]$ [M = Ga (**1**), In (**2**)]. The co-ordination polyhedron of **2** is best described in terms of a distorted chiral tetragonal pyramid in which the chlorine atom occupies the apex. The two seven-membered rings of the $[(^i Pr)TP]^{2-}$ ligand in **2** are twisted by about 19.9° with respect to each other. To study the reactivity of **2**, the derivatives $[\{(^i Pr)TP\}InMe]$, $[\{(^i Pr)TP\}InCH_2SiMe_3]$, and $[\{(^i Pr)TP\}InO^tBu]$ were synthesised.

Introduction

Aminotroponiminates ($[ATI]^-$) are bidentate, monoanionic ligands containing a 10 π-electron backbone. Like 1,4-diazabutadiene, $[ATI]^-$ forms five-membered metallacycles upon co-ordination to a metal atom. In contrast to 1,4-diazabutadiene $[ATI]^-$ is believed to be much more resistant to electrophiles and nucleophiles. The ligand system was introduced into co-ordination chemistry in the 1960's, mostly by researchers from DuPont. Between 1961 and 1970 a large number of Mn(II), Fe(II), Co(II), and Ni(II) complexes were prepared in order to study magnetic moments and NMR contact shifts, but only one Mn complex was characterised by single crystal X-ray methods. The early work was reviewed by Holm in 1971.[1]

Recent reports from our laboratory have described the preparation and characterisation of aminotroponiminates as cyclopentadienyl alternatives for group 3 and lanthanide elements,[2–4] while a similar approach on group 4 elements was reported by other groups.[5,6] We have shown that bis(aminotroponiminate)yttrium amides are active as catalysts for hydroamination/cyclization catalysis.[4] Since the aminotroponiminate ligand proved to be a formal substitute for cyclopentadienyl, we started to prepare mono-bridged aminotroponiminates as alternatives for *ansa* metallocenes.[7] It was shown that the tris(methylene)-bridged ligand 1,3-di[2-(isopropylamino)troponiminate]propane, $[(^i Pr)TP]^{2-}$ (**A**),† is able to co-ordinate in a



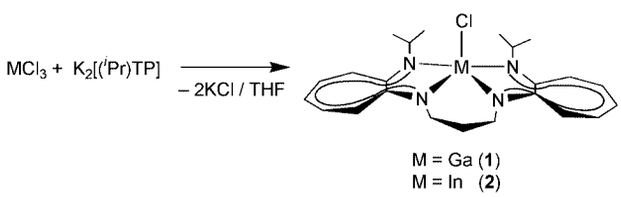
A

chelating or metal bridging mode to lanthanum.[7] Both kinds of co-ordination have been observed previously for *ansa* metallocenes of the lanthanides.[8–11] Depending on the size of the ion radius of the lanthanide atom, products of composition $[\{(^i Pr)TP\}LnCl(THF)]_2$ (Ln = La, Nd) or $[\{(^i Pr)TP\}LnCl]_2$ (Ln = Er, Yb, Lu) were obtained in which the co-ordination number is either seven (La, Nd) or six (Er, Yb, Lu).[12,13] Since we were interested in studying the co-ordination behaviour of $[(^i Pr)TP]^{2-}$ with metal ions smaller in size than lutetium in oxidation state +3, we focused our attention on group 13 metals. Herein we report on the reaction of $K_2[(^i Pr)TP]$ with gallium and indium trichloride which leads to products of composition $[\{(^i Pr)TP\}MCl]$ (M = Ga, In). In order to study the reactivity of $[\{(^i Pr)TP\}InCl]$, some selected derivatives were synthesised by substitution of the chlorine atom of $[\{(^i Pr)TP\}InCl]$.

† $H_2[(^i Pr)TP]$ = Trimethylenedinitrilobis(2-isopropylaminocyclohepta-2,4,6-triene).

Results and discussion

In a straightforward synthesis, the complexes $[\{(^i Pr)TP\}MCl]$ [M = Ga (**1**), In (**2**)] can be obtained by transmetallation of $K_2[(^i Pr)TP]$ with the metal trichlorides in a 1:1 molar ratio in THF at room temperature. The reaction affords the corresponding complexes as yellow powders in high yield (Scheme 1). Compounds **1** and **2** have been characterised by standard



Scheme 1

analytical/spectroscopic techniques. On recrystallisation from pentane–THF (3:1), centimetre size single crystals of **2** were obtained. The solid state structure was established by single crystal X-ray diffraction (Fig. 1). Compound **2** crystallises in the monoclinic space group $P2_1/n$, having four molecules in the unit cell. The structure reveals a five-fold co-ordination sphere of the ligands around the indium atom. Four co-ordination sites are occupied by the chelating $[(^i Pr)TP]^{2-}$ ligand. The co-ordination polyhedron is best described in terms of a distorted tetragonal pyramid with the chlorine atom at the apex. The two seven-membered rings of the $[(^i Pr)TP]^{2-}$ ligand in **2** are twisted by about 19.9° with respect to each other. As a result of the twisting, **2** has no mirror plane and thus is a chiral molecule. A comparison of the structure of **2** with the non-bridged bis(aminotroponiminato) complexes of gallium and indium, $[(Me)_2ATI]_2MCl$ (M = Ga, In),[14] {$[(Me)_2ATI]$ = *N*-methyl-2-(methylamino)troponiminate} which adopt a trigonal bipyramidal geometry, shows the influence of the tris(methylene) bridge between the two aminotroponiminate moieties of the $[(^i Pr)TP]^{2-}$ ligand. The structural parameters of

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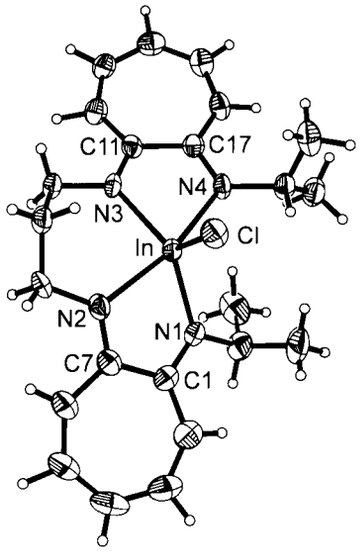


Fig. 1 Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass a 50% probability. Selected bond distances (pm) and angles (°): In–N1 217.4(4), In–N2 217.7(4), In–N3 214.8(4), In–N4 218.9(4), In–Cl 243.5(1); N1–In–N2 73.92(14), N1–In–N3 135.97(15), N1–In–N4 110.57(14), N2–In–N3 89.66(15), N2–In–N4 160.74(15), N3–In–N4 74.12(15), N1–In–Cl 110.00(11), N2–In–Cl 99.01(10), N3–In–Cl 112.83(10), N4–In–Cl 96.87(10).

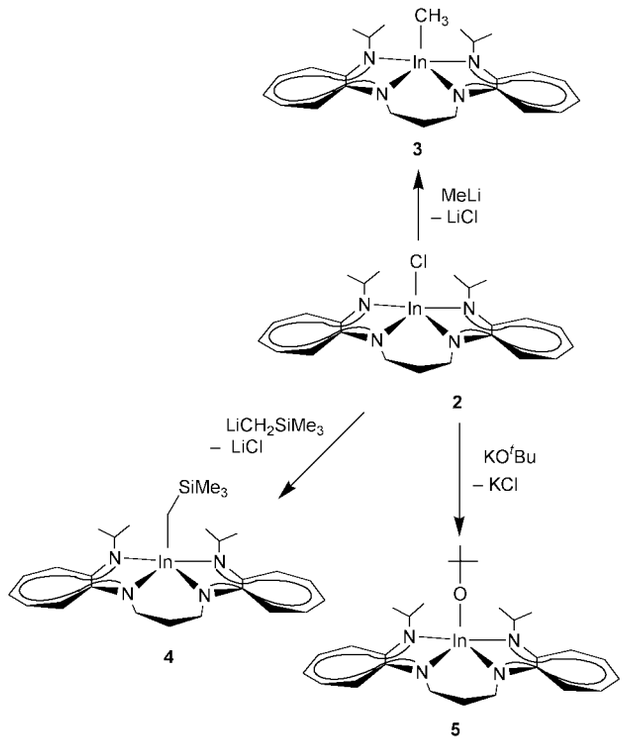
2 can be compared to the corresponding values of other indium adducts. The In–Cl bond distance [243.5(1) pm] is similar to those in $[CyNC(^tBu)NCy]_2InCl$ [240.5(1) pm] (Cy = cyclohexyl)[15] and $[(Me)_2ATI]_2InCl$ [241.74(9) pm].[14] The In–N bond lengths [av. 217.2(4) pm] are shorter than those in $[CyNC(^tBu)NCy]_2InCl$ (av. 221.5 pm)[15] but longer than those in $[(Me)_2ATI]_2InCl$ (av. 215.8 pm).[14] As expected, the angles inside the $[ATI]^-$-moiety, N1–In–N2 [73.92(14)°] and N3–In–N4 [74.12(15)°], are significantly smaller than the angles between the moieties N2–In–N3 [89.66(15)°] and N1–In–N4 [110.57(14)°]. The N–In–Cl angles span a broad range from 96.87(10) to 112.83(10)° [av. 104.86(10)°], which indicates the asymmetric co-ordination of the $[(^iPr)TP]^{2-}$ ligand around the indium atom.

Due to the lack of a mirror plane through the isopropyl groups the ^1H and ^{13}C NMR spectra of **1** and **2** show splitting of the isopropyl CH_3 signals [^1H NMR: δ 1.25 and 1.58 (**1**); δ 1.42 and 1.46 (**2**)]. In contrast to $[(Me)_2ATI]_2MCl$ (M = Ga, In),[14] no fluxional behaviour of the complexes is observed in solution. The ^1H NMR signals of the isopropyl CH of **1** (δ 4.38) and **2** (δ 4.26) are well resolved into a septet but show a marked downfield shift compared to that of the free ligand $H_2[(^iPr)TP]$ (δ 3.55).[7] Besides the NMR investigations, both **1** and **2** were characterised by EI mass spectroscopy. For both compounds, strong molecular ion peaks, as well as their characteristic fragmentation patterns, were observed.

Derivatives of 2

To study the reactivity of **2**, some selected derivatives were synthesised by substitution of the chlorine atom. A general overview of the reactions is given in Scheme 2.

Transmetallation of **2** with slightly more than one equivalent of MeLi in toluene gives $[\{(^iPr)TP\}InMe]$ (**3**) as a yellow powder. In the ^1H NMR spectrum of **3**, a characteristic signal due to the In–CH_3 group is observed at δ 0.23. Compared to Me_3In (δ 1.56), this In–CH_3 signal is significantly upfield shifted.[16] On the other hand, methyl indium compounds with a saturated co-ordination sphere, such as $[MeInCl_2{\cdot}SSbMe_3]$ (δ 0.35) or $[Me_2InCl{\cdot}SSbMe_3]$ (δ 0.00), show similar chemical shifts.[17] In an analogous manner to the synthesis of **3**, the reaction of **2** with the sterically demanding alkylating reagent $LiCH_2SiMe_3$ leads to the alkyl complex $[\{(^iPr)TP\}InCH_2SiMe_3]$ (**4**) in fairly good yields. In the ^1H NMR spectrum of **4**, the signal due to the In–CH_2 group is seen at δ −0.12.



Scheme 2

As observed for **1** and **2**, the ^1H and ^{13}C NMR spectra of both alkyl complexes **3** and **4** show splitting of the isopropyl CH_3 signals. The signals are observed at δ 1.21 and 1.34 for **3** and δ 1.21 and 1.40 for **4**. In contrast to $[\{(^iPr)TP\}LaCH(SiMe_3)_2]$, no dynamic behaviour of the pentacoordinate complexes **3** and **4** is observed.[7] As expected, replacement of the chlorine atom at the indium centre by an alkyl group also has an influence on the chemical shifts of the ^1H and ^{13}C NMR signals of **3** and **4**. Hence, the signals due to the isopropyl CH group of **3** (δ 4.01) and **4** (δ 4.04) show an upfield shift compared to **2** (δ 4.26).

For further investigation of the reactivity of **2**, an alkoxy complex was synthesised. The *tert*-butoxy complex $[\{(^iPr)TP\}InO^tBu]$ (**5**) is obtained by transmetallation of **2** and KO^tBu in THF at room temperature (Scheme 2). The ^1H NMR spectrum of **5** shows only one sharp resonance for the ^{t}Bu group (δ 1.54) which indicates rigid co-ordination of the ^{t}BuO group to the indium atom. Once again, splitting of the isopropyl CH_3 signals of **5** is observed in the NMR spectra [δ 1.34 and 1.49 (^1H NMR), δ 22.2 and 23.2 (^{13}C NMR)]. Besides the NMR investigations, all derivatives of **2** (**3**–**5**) were characterised by EI mass spectroscopy. For **3**–**5**, the molecular ions, as well as their characteristic fragmentation patterns, were observed.

Summary

In summary, it has been shown that the reaction of $K_2[(^iPr)TP]$ with MCl_3 (M = Ga, In) leads to **1** and **2**. The co-ordination polyhedron of **2** is best described in terms of a distorted chiral tetragonal pyramid in which the chlorine atom occupies the apex. As seen in the solid state structure of **2**, the distortion of the co-ordination polyhedron is caused by the two seven-membered rings of the ligand being twisted by almost 20° with respect to each other. Due to the lack of a mirror plane through the isopropyl groups, the NMR spectra of **1** and **2** show splitting of the isopropyl CH_3 signals. In order to study the reactivity of **2**, the derivatives **3**–**5** were synthesised.

Experimental

General

Experimental conditions have been reported previously.[7] $GaCl_3$, $InCl_3$, MeLi, $LiCH_2SiMe_3$, and K^{t}OBu were obtained from Aldrich Inc. K_2[(^{i}Pr)TP] was prepared according to literature procedures.[7]

[{(^{i}Pr)TP}MCl] (M = Ga, In)

THF (10 mL) was condensed at −196 °C onto a mixture of 1.0 mmol of MCl_3 and 440 mg (1.0 mmol) of K_2[(^{i}Pr)TP] and the suspension was stirred for 18 h at room temperature. The solvent was then evaporated *in vacuo* and toluene (10 mL) condensed onto the mixture. Then, the solution was filtered and the solvent removed from the toluene extract. The remaining solid was washed with pentane (10 mL) and dried *in vacuo*. Finally, the product was recrystallised from pentane–THF (3 : 1).

M = Ga (1). Yield 310 mg (66%). Anal. calcd for $C_{23}H_{30}ClGaN_4$ (M_w 467.69): C, 59.07; H, 6.47; N, 11.98; found C, 58.88; H, 6.23; N, 12.23%. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 1.25 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 1.58 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 2.74 (m, 2 H, NCH_2CH_2), 2.89 (m, 2 H, NCH_2), 3.35 (m, 2 H, NCH_2), 4.38 [sept, 4 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 6.22 [d, 2 H, H_{ring}, J(H,H) = 9.6 Hz], 6.28 [t, 2 H, H_{ring}, J(H,H) = 9.0 Hz], 6.80 (m, 6 H, H_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 21.0 [$(CH_3)_2CH$], 21.4 [$(CH_3)_2CH$], 28.8 (NCH_2), 48.8 (NCH_2CH_2), 49.8 [$(CH_3)_2CH$], 113.5 (C_{ring}), 116.3 (C_{ring}), 119.5 (C_{ring}), 135.4 (C_{ring}), 136.4 (C_{ring}), 158.8 (C_{ring}), 159.0 (C_{ring}). EI-MS (70 eV) *m*/*z* (%): 466 ([*M* − H]$^+$, rel. int. 6), 423 ([*M* − ^{i}Pr]$^+$, 25), 163 ([$C_{10}H_{15}N_2$]$^+$, 100).

M = In (2). Yield 360 mg (70%). IR (KBr/cm^{-1}): 2965 (m), 2926 (m), 1594 (s), 1422 (s), 1356 (s), 1275 (s), 1233 (s), 721 (s). Anal. calcd for $C_{23}H_{30}ClInN_4$ (M_w 512.79): C, 53.87; H, 5.90; N, 10.93; found C, 53.27; H, 5.93; N, 10.33%. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 1.42 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.8 Hz], 1.46 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.8 Hz], 2.67 (m, 2 H, NCH_2CH_2), 2.92 (m, 2 H, NCH_2), 3.24 (m, 2 H, NCH_2), 4.26 [sept, 4 H, $(CH_3)_2CH$, J(H,H) = 6.8 Hz], 6.27 [d, 2 H, H_{ring}, J(H,H) = 11.32 Hz], 6.33 [t, 2 H, H_{ring}, J(H,H) = 9.0 Hz], 6.58 [d, 2 H, H_{ring}, J(H,H) = 11.6 Hz], 6.88 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 22.50 [$(CH_3)_2CH$], 22.70 [$(CH_3)_2CH$], 31.5 (NCH_2), 51.4 (NCH_2CH_2), 51.6 [$(CH_3)_2CH$], 114.2 (C_{ring}), 116.1 (C_{ring}), 119.3 (C_{ring}), 135.5 (C_{ring}), 136.0 (C_{ring}), 159.6 (C_{ring}), 159.8 (C_{ring}). EI-MS (70 eV) *m*/*z* (%): 512 ([*M*]$^+$, rel. int. 73), 469 ([*M* − ^{i}Pr]$^+$, 67), 131 ([$C_8H_7N_2$]$^+$, 100).

[{(^{i}Pr)TP}InMe] (3)

0.55 mL (0.88 mmol) of a 1.6 M MeLi solution in ether was added to a solution of 410 mg (0.8 mmol) of **2** in 25 mL of THF. The solution was stirred for 18 h at room temperature. The solvent was then evaporated *in vacuo* and toluene (10 mL) added to the mixture. Then, the solution was filtered and the solvent was removed from the toluene extract. The remaining solid was washed with pentane (10 mL) and dried *in vacuo*.

Yield 210 mg (43%). Anal. calcd for $C_{24}H_{33}InN_4$ (M_w 492.37): C, 58.55; H, 6.76; N, 11.38; found C, 58.01; H, 6.29; N, 11.18%. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.23 (s, 3 H, $InCH_3$), 1.21 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz], 1.34 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 2.85 (m, 2 H, NCH_2CH_2), 2.92 (m, 2 H, NCH_2), 3.25 (m, 2 H, NCH_2), 4.01 [sept, 4 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 6.15–6.27 (m, 8 H, H_{ring}), 6.58 (d, 2 H, H_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 0.2 ($InCH_3$), 22.4 [$(CH_3)_2CH$], 23.1 [$(CH_3)_2CH$], 31.8 (NCH_2), 50.6 (NCH_2CH_2), 51.5 [$(CH_3)_2CH$], 112.9 (C_{ring}), 115.3 (C_{ring}), 117.1 (C_{ring}), 135.0 (C_{ring}), 135.7 (C_{ring}), 160.8 (C_{ring}), 161.3 (C_{ring}). EI-MS (70 eV) *m*/*z* (%): 493 ([*M* + H]$^+$, rel. int. 12), 477 ([*M* − (CH_3)]$^+$, 67), 292 ([(^{i}Pr)TP]$^+$, 20), 163 ([$C_{10}H_{15}N_2$]$^+$, 100).

[{(^{i}Pr)TP}InCH$_2$SiMe$_3$] (4)

THF (10 mL) was condensed at −196 °C onto a mixture of 570 mg (1.1 mmol) of **2** and 115 mg (1.2 mmol) of $LiCH_2SiMe_3$ and the solution was stirred overnight at room temperature. The solvent was then evaporated *in vacuo* and pentane (10 mL) condensed onto the mixture. Finally, the solution was filtered and the solvent was removed from the pentane extract.

Yield 360 mg (64%). Anal. calcd for $C_{27}H_{41}InN_4Si$ (M_w 564.55): C, 57.44; H, 7.32; N, 9.92; found C, 55.80; H, 6.98; N, 9.80%. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ −0.12 (s, 2 H, $InCH_2$), 0.10 [s, 9 H, $Si(CH_3)_3$], 1.21 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz], 1.40 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.8 Hz], 2.26 (m, 2 H, NCH_2CH_2), 2.96 (m, 2 H, NCH_2), 3.27 (m, 2 H, NCH_2), 4.04 [sept, 4 H, $(CH_3)_2CH$, J(H,H) = 7.0 Hz], 6.12–6.23 (m, 4 H, H_{ring}), 6.60 (d, 2 H, H_{ring}), 6.68–6.92 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 3.14 [$Si(CH_3)_3$], 4.14 ($InCH_2$), 22.0 [$(CH_3)_2CH$], 23.1 [$(CH_3)_2CH$], 31.7 (NCH_2), 50.7 (NCH_2CH_2), 51.6 [$(CH_3)_2CH$], 113.0 (C_{ring}), 115.5 (C_{ring}), 117.2 (C_{ring}), 135.0 (C_{ring}), 135.8 (C_{ring}), 160.9 (C_{ring}), 161.1 (C_{ring}). ^{29}Si NMR (C_6D_6, 49.7 MHz, 25 °C): δ 2.4. EI-MS (70 eV) *m*/*z* (%): 564 ([*M*]$^+$, rel. int. 6), 549 ([*M* − CH_3]$^+$, 2), 521 ([*M* − ^{i}Pr]$^+$, 25), 477 ([*M* − $CH_2Si(CH_3)_3$]$^+$, 100).

[{(^{i}Pr)TP}InO^{t}Bu] (5)

THF (10 mL) was condensed at −196 °C onto a mixture of 360 mg (0.7 mmol) of **2** and 79 mg (0.7 mmol) of KO^{t}Bu and the solution was stirred overnight at room temperature. The solvent was then evaporated *in vacuo* and toluene (10 mL) condensed onto the mixture. Then, the solution was filtered and the solvent was removed from the toluene extract. The remaining solid was washed with pentane (10 mL) and dried *in vacuo*.

Yield 310 mg (56%). Anal. calcd for $C_{27}H_{39}InN_4O$ (M_w 550.45): C, 58.91; H, 7.14; N, 10.18; found C, 58.49; H, 6.79; N, 9.16%. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 1.34 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz], 1.49 [d, 6 H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz], 1.54 [s, 9 H, $(CH_3)_3C$], 2.56 (m, 2 H, NCH_2CH_2), 2.91 (m, 2 H, NCH_2), 3.28 (m, 2 H, NCH_2), 4.13 [sept, 4 H, $(CH_3)_2CH$, J(H,H) = 6.7 Hz], 6.25 (m, 4 H, H_{ring}), 6.70 [d, 2 H, H_{ring}, J(H,H) = 11.3 Hz], 6.82–6.96 (m, 4 H, H_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz, 25 °C): δ 22.2 [$(CH_3)_2CH$], 23.2 [$(CH_3)_2CH$], 31.5 (NCH_2), 35.7 [$(CH_3)_3C$], 51.2 (NCH_2CH_2), 51.5 [$(CH_3)_2CH$], 70.5 [$(CH_3)_3C$], 113.6 (C_{ring}), 115.8 (C_{ring}), 118.3 (C_{ring}), 135.4 (C_{ring}), 136.0 (C_{ring}), 160.0 (C_{ring}), 160.2 (C_{ring}). EI-MS (70 eV) *m*/*z* (%): 550 ([*M*]$^+$, rel. int. 0.2), 505 ([*M* − $(CH_3)_3$]$^+$, 0.5), 477 ([$C_{13}H_{18}N_2$]$^+$, 100), 364 ([(^{i}Pr)TP]$^+$, 20).

X-Ray crystallographic study of 2

Crystals of $C_{23}H_{30}ClInN_4$ were grown from a pentane–THF (3 : 1) solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the −70 °C cold stream of an STOE STADI IV diffractometer (Mo-Kα radiation). Subsequent computations were carried out on a SGI Power Challenge.

Data collection and refinement: SHELXS-86,[18] SHELXL-93;[19] monoclinic, space group $P2_1/n$ (no. 14); lattice constants a = 978.9(3), b = 1928.7(3), c = 1188.5(3) pm, β = 97.26(3)°, V = 2225.9(9) 10^6 pm^3, Z = 4; μ(Mo-Kα) = 1.199 mm^{-1}; $2\theta_{max}$ = 45.00; 2893 (R_{int} = 0.0868) independent reflections measured, of which 2423 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.666 and −0.593 e Å^{-3}; 338 parameters (all non hydrogen atoms were calculated anisotropically; the positions of the H atoms were calculated for idealised positions) $R1$ = 0.0323; $wR2$ = 0.0835.

CCDC reference number 186/1867.

See http://www.rsc.org/suppdata/dt/a9/a909773b for crystallographic files in .cif format.

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