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Reaction of $\{HC(CMeNAr)_2\}Li (Ar = 2,6-i-Pr_2C_6H_3)$ with indium monochloride to yield the In–In bonded dimer $[\{HC(CMeNAr)_2\}InCl]_2$ and the hydroxide $[\{HC(CMeNAr)_2\}InCl(\mu-OH)]_2$

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Abstract

The reaction of the sterically encumbered lithium β -diketiminate {HC(CMeNAr)_2}Li (Ar = 2,6-*i*-Pr_2C₆H₃) with InCl in THF at approximately -78 °C yielded In metal and [{HC(CMeNAr)_2}InCl]_2 (1) as well as minor amounts of the hydroxide [{HC(CMeNAr)_2}In(Cl)(μ -OH)]_2, **2**. The compounds **1** and **2** were characterized by ¹H, ¹³C NMR, IR spectroscopy and X-ray crystallography. The centrosymmetric structure of **1** features an In–In bond that is 2.8343(7) Å long which is well within the known range of In–In single bond distances. The metal β -diketiminate ring (i.e. C₃N₂In) is folded along the N···N vector and features an out of plane deviation by the indium of 0.8953 Å and a dihedral angle between the C₃N₂ and InN₂ arrays of 145.8°. This can be attributed to steric effects of the Ar groups on the β -diketiminiate ligand. The structure of the hydroxide derivative **2** is a dimer in which the indiums are bridged by hydroxides to afford a planar In₂O₂ core with an average In–O distance of 2.13(2) Å. Attempted reduction of the dihalide compounds {HC(CMeNAr)₂}InX₂ (X = Cl, I) with sodium or potassium led to the formation of metallic indium and the free β -aminoimine (Ar)NC(Me₂)CHC(Me₂)N(Ar)H rather than the desired In(I) species, {HC(CMeNAr)₂}In:. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recent years have witnessed an impressive revival of interest in bidentate, β -diketiminate ligands which have been known for more than four decades [1]. Much of the recent work has focused on more sterically encumbered derivatives that feature bulky substituents at the nitrogens. These ligands have proved to be very useful in a variety of rôles including the stabilization of low coordinate, low valent main Group 13 metal complexes [2–4]. Through the use of the ligand [HC(CMeNAr)₂]⁻ (Ar = 2,6-*i*-Pr₂C₆H₃) the unusual, two-coordinate, monomeric M(I) species [HC(CMeNAr)₂]M: (M = Al [3], Ga [4]), which are analogous to carbenes, have been stabilized. The corresponding In(I) species are un-

known, although there is widespread interest in In(I) compounds as evidenced by the growing number of organometallic [5-7] and related derivatives [7,8] of In(I) that have been synthesized. Almost all of the organoindium(I) compounds are associated in the solid state. However, the trispyrazolylborate complexes $HB(pz)_{3}In$ (pz = 3-phenylpyrazolyl [7], 3,5-di-tertbutylpyrazolyl [8a], 3-tert-butylpyrazolyl [8b], 3,5- $(CF_3)_2$ -pyrazolyl [8b,8c]), in which the In atom is coordinated by three N donors, are monomeric in the solid state. There is only one example of a monomeric, organometallic In(I) species in the literature and this species involves the bulky *m*-terphenyl group $-C_6H_3$ -2,6-Trip₂ (Trip = $-C_6H_2$ -2,4,6-*i*-Pr₃) [9]. This ligand shows a steric resemblance to the bulkyl β-diketiminate $[HC(CMeNAr)_2]^-$ (Ar = 2,6-*i*-Pr₂C₆H₃) [10]. Due to the very rich chemistry already displayed by the monomeric M(I) species $[HC(CMeNAr)_2]M$: (M = AI), Ga) [11–14] it is of interest to synthesize the In ana-

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logue and explore its chemistry. We now report that the reaction of $\{HC(CMeNAr)_2\}Li$ with InCl leads not to the expected monomeric $\{HC(CMeNAr)_2\}In$ analogue but to disproportionation reactions that yield the unexpected In–In bonded species $[\{HC(CMeNAr)_2\}InCl]_2$ (1) and the hydroxo complex $[\{HC(CMeNAr)_2\}InCl(\mu-OH)]_2$ (2).

2. Experimental

2.1. Synthesis

2.1.1. General procedures

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N₂ or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na–K alloy and degassed three times before use. The compound {HC(CMeNAr)₂}H (Ar = C_6H_3 -2,6-*i*-Pr₂) was prepared as previously described [10]. InCl (99.99%) was purchased commercially and used as received.

2.2. $[{HC(CMeNAr)_2}InCl]_2$ (1) and $[{HC(CMeNAr)_2}InCl(\mu-OH]_2$ (2)

A solution of $\{HC(CMeNAr)_2\}Li$ in THF (generated by reaction of 1.06 g of $\{HC(CMeNAr)_2\}H$ and 1.6 ml of 1.6 M *n*-BuLi in 20 ml of THF with cooling in an ice bath) was added dropwise to a suspension of InCl (0.42 g, 2.79 mol) in THF (30 ml) with rapid stirring and cooling in a dry ice acetone bath. The reaction mixture was stirred for 2 h and then allowed to come to approximately -10 °C (ice–NaCl bath). After stirring for an additional 1 h the solvents were removed under reduced pressure. The solid residue was extracted with

Table 1Data collection parameters for 1 and 2

| | 1.hexane | 2 ·2PhMe |
|--|----------------|--|
| Formula | C64H96Cl2In2N4 | C ₇₂ H ₁₀₀ Cl ₂ In ₂ N ₄ O ₂ |
| Formula weight | 1222.98 | 1354.13 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_{1}/c$ | $P2_{1}/c$ |
| β (°) | 102.051(2) | 101.440(2) |
| a (Å) | 13.5411(10) | 13.6314(17) |
| b (Å) | 13.3095(10) | 13.6336(17) |
| c (Å) | 17.2363(13) | 18.915(2) |
| $V(Å^3)$ | 3038.0(4) | 3445.3(7) |
| Z | 2 | 2 |
| μ (Mo K α) (mm ⁻¹) | 0.888 | 0.792 |
| T (K) | 90(2) | 90(2) |
| R_1 | 0.0650 | 0.0260 |
| wR_2 | 0.1117 | 0.0648 |

 $R_1 = \Sigma ||F_0| - |F_c|| / |F_0|$. $wR_2 = [\Sigma \omega (F_0^2 - F_c^2)^2 \Sigma [\omega (F_0^2)]^{1/2}$.

cold hexane (40 ml, ca. -10 °C). The solution was allowed to come to ambient temperature where the dark precipitate which had formed (indium metal and lithium chloride) was allowed to settle. The amber supernatant solution was then filtered through celite. Concentration under reduced pressure produced a low yield of large colorless needles which were collected after ca. 8 h in a ca. 4 °C refrigerator. These were identified as the hydroxide derivative 2. Yield: 0.05 g, 0.037 mmol, 15%, melting point (decomposition) m.p. (dec.) > 100 °C. ¹H NMR (400 MHz, C_6D_6): δ 7.2–7.1 (m, 12H, Ph), 4.63 (s, 2H, γ-CH), 3.31 (sept, 8H, J = 6.8 Hz, CHMe₂), 1.48 (s, 12H, Me), 1.25 (d, 24H, J = 6.8 Hz, CHMe₂), 1.10 (d, 24H, J = 6.8 Hz, CHMe₂), 0.93 (s, broad, 2H, OH); ¹³C NMR (C₆D₆): δ (ppm) = 159.2 (CN), 142.7, 141.3, 125.8, 123.6 (Ph), 94.2 $(\gamma$ -C), 28.6 (CHMe₂), 24.4 (CHMe₂), 23.4 $(CHMe_2)$, 20.7 (Me); IR (Nujol): v (cm⁻¹) = 3660 (vOH). The supernatant solution was decanted and concentrated under reduced pressure to incipient crystallization (ca. 30 ml). Storage for 30 h in a ca. 4 °C refrigerator yielded the product 1 as colorless crystals. Yield: 0.23 g, 0.20 mmol, 16%, m.p. 155-157 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.2–7.0 (m, 12H, Ph), 4.73 (s, 2H, γ -CH), 3.33 (sept, 8H, J = 6.8 Hz, CHMe₂), 1.58 (s, 12H, Me), 1.35 (d, 24H, J = 6.8 Hz, CHMe₂), 1.21 (d, 24H, J = 6.8 Hz, CHMe₂); ¹³C NMR (C₆D₆): δ (ppm) = 171.8 (CN), 144.5, 138.0, 124.8 (Ph), 98.1 (γ -C), 28.3 (CHMe₂), 25.8 (CHMe₂), 25.2 (CHMe₂), 24.6 (Me).

The attempted reduction of the dihalides $\{HC(CMeNAr)_2\}InX_2$ (X = Cl, I) with finely divided potassium in toluene resulted in the precipitation of In metal at room temperature (r.t.).

2.3. X-ray data collection

X-ray quality crystals of 1 or 2 were removed from the Schlenk tube and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the cold temperature N₂-stream as previously described [15]. The data were collected near 90 K using a Bruker SMART 1000 diffractometer and Mo K α ($\lambda = 0.71073$ Å) radiation. The SHELXTL version 5.03 program package was used for the structure solutions and refinements [16]. Absorption corrections were applied using the SADABS program [17]. The structures were solved by direct methods and refined by full matrix, least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program package. Some details of the data collection and refinement are given in Table 1. Selected bond distances and angles for 1 and 2 are provided in Table 2.

Table 2 Selected bond lengths (\AA) and angles (°) for 1 and 2

| 1 | | 2 | |
|--------------------|------------|-------------------|------------|
| Bond lengths | | | |
| In(1)-N(1) | 2.169(4) | In(1)-N(1) | 2.1654(12) |
| In(1)-N(2) | 2.172(4) | In(1)–N(2) | 2.1874(12) |
| In(1)-Cl(1) | 2.4142(14) | In(1)-Cl(1) | 2.3876(4) |
| In(1)-In(1A) | 2.8342(7) | In(1)–O(1) | 2.1148(11) |
| N(1)-C(1) | 1.335(7) | In(1)–O(1A) | 2.1534(11) |
| N(2)-C(3) | 1.347(7) | N(1)–C(1) | 1.3343(19) |
| C(1)–C(2) | 1.389(7) | N(2)–C(3) | 1.3325(19) |
| C(2)–C(3) | 1.392(7) | C(1)–C(2) | 1.407(2) |
| | | C(2)–C(3) | 1.401(2) |
| Bond angles | | | |
| N(1)-In(1)-N(2) | 87.85(16) | N(1)-In(1)-N(2) | 87.26(5) |
| N(1)-In(1)-Cl(1) | 99.39(12) | N(1)-In(1)-Cl(1) | 106.12(4) |
| N(2)-In(1)-Cl(1) | 99.81(11) | N(2)-In(1)-Cl(2) | 103.91(3) |
| N(1)-In(1)-In(1A) | 126.60(11) | O(1)–In(1)–O(1A) | 71.47(5) |
| N(2)-In(1)-In(1A) | 126.75(11) | O(1)-In(1)-N(1) | 145.70(5) |
| Cl(1)-In(1)-In(1A) | 110.59(4) | O(1)-In(1)-N(2) | 94.48(5) |
| N(1)-C(1)-C(2) | 125.8(3) | In(1)–O(1)–In(1A) | 108.53(5) |
| C(1)-C(2)-C(3) | 128.5(5) | N(1)-C(1)-C(2) | 124.66(13) |
| C(2)-C(3)-N(2) | 125.9(5) | C(1)-C(2)-C(3) | 129.27(14) |
| | | C(2)-C(3)-N(2) | 124.72(14) |

3. Discussion

3.1. Synthesis

The compounds 1 and 2 were both obtained by the addition of {HC(CMeNAr)₂}Li, generated in THF, to a suspension of InCl in THF with cooling in an approximately -78 °C dry ice acetone bath. None of the expected product {HC(CMeNAr)₂}In: was isolated from the reaction under these conditions. This was to some extent surprising since the aluminum(I) and gallium(I) analogues of this putative indium species were already known [3,4]. Furthermore, the one coordinate indium derivative of the $-C_6H_3$ -2,6-Trip₂ (Trip = C_6H_2 -2,4,6-i-Pr₃) group, which bears a close steric resemblance to the $\{HC(CMeNAr)_2\}$ ligand, was already characterized [9]. Moreover 2,6-Trip₂H₃C₆In: was synthesized by the direct reaction of the lithiated terphenyl ligand with InCl in THF under almost identical conditions to those described in this paper. In view of the fact that indium metal, lithium chloride and free ligand were produced during the course of the attempted synthesis of {HC(CMeNAr)₂}In:, it seems probable that disproportionation and ligand redistribution reactions occur to give the observed product 1 in 16% yield. Small amounts of the hydroxo-bridged species 2 were also obtained in much lower yield. The latter species is probably the result of moisture contamination and it is possible to carry out the reaction to generate negligible amounts of 2 by using extremely strict anaerobic and anhydrous procedures. In spite of the unanticipated nature of the product 1, it has been recently reported [18] that the reaction of the aza alkyl lithium compound PhC{(Me₃Si)₂C}{N(SiMe₃)}Li with InBr afforded the In–In bonded dimer [PhC{C(SiMe₃)₂}{N-(SiMe₃)₂}InBr]₂. This reaction is significant in that the uninegative, bidentate nature of this ligand is related to the β -diketiminate {HC(CMeNAr)₂}⁻. Other examples of disproportionation reactions of various lithium amide ligands with indium(I) halides to afford In–In bonded products are also known [19,20].

3.2. Structures

The structure of 1 is illustrated in Fig. 1. Selected bond distances and angles are provided in Table 2. The structure possesses a center of symmetry at the midpoint of the In-In bond. The indiums are four-coordinate with a very distorted tetrahedral geometry at the metals. The In–In distance is 2.8334(7) Å which may be regarded as a typical one since it falls in the middle of the currently known range (2.696(2) - 2.922(1) Å [21,22])for neutral molecular In-In singly bonded species. The In-N distances, av. 2.171(2) Å, are marginally longer than the 2.111(3)-2.147(1) Å range observed in the $\{HC(CMeNAr)_2\}InX_2$ (X = Cl or I) [2], but they are shorter than the average distance of 2.197(4) Å in {HC(CMeNAr)₂}InMe₂ [2]. The variation in these distances illustrates the influence of coligands on the effective ionic radius of indium. More electronegative co-ligands contract the radius, whereas more electropositive ligands expand it; hence the longer In-N distances in $\{HC(CMeNAr)_2\}$ InMe₂. The C₃N₂ ring fragment of the β-diketiminate ligand has planar geometry and the C-C and C-N distances are symmetric indicating delocalization of the negative charge. However, the C₃N₂In ring is folded along the N···N vector such that there is a dihedral angle of 145.8° between the InN_2 and C_3N_2 planes. The indium atom lies 0.895 Å from the extended C_3N_2 plane. This folding is similar to that reported in $\{HC(CMeNAr)_2\}$ InMe₂ but it is higher than that seen in the halide derivatives. Another feature



Fig. 1. Thermal ellipsoid plot (30%) of 1. H atoms are not shown.



Fig. 2. Thermal ellipsoid plot (30%) of 2. H atoms are not shown.

of the structure of **1** is the narrow N–In–N angle and this is similar to those reported for the halide and methyl derivatives [2] which all have N–In–N angles that are less than 90°. The In–Cl bond length is 2.4142(14) Å which is very similar to the 2.4174(9) Å in the tropoiminate complex $(Me_2ATI)_2InCl$ [23] and slightly longer than the average of 2.396(3) Å in {HC(CMeNAr)₂}InCl₂ [2] although the accuracy of the latter distance is reduced by the presence of bromine contaminant.

The structure of the hydroxide bridged dimer 2 is illustrated in Fig. 2. Like 1, it is centrosymmetric with a crystallographically required planarity for the In_2O_2 core in this case. The core has diamond geometry with a difference of approximately 18° between the ring angles at indium and oxygen. The two In-O distances differ slightly and have an average value of 2.13(2) Å which is not significantly different from the average of 2.14(1) Å observed in bis(3-(2-pyridyl)pyrazolyl-1yl)methane stabilized complex of the dimer {ClIn(µ- OH_{2} [24] or the average of 2.164(2) Å observed for $[{(Me_3Si)_2CH}_2In(\mu-OH)]_2$ [25]. The In–N bond lengths in 2 are essentially indistinguishable from those observed in 1 in spite of the increase in coordination number of the metal from four to five. As in 1, the C₃N₂In ring is folded along the N···N vector. A dihedral angle of 150° is observed between the C₃N₂ and InN₂ planes and the indium lies 0.800 Å from the extended C₃N plane. The N-In-N angle is also less than 90° and within 0.6° of the value reported for 1.

4. Conclusions

The attempted synthesis of $\{HC(CMeNAr)\}$ In: has led to the disproportionation or hydrolysis products **1** or **2**. The reasons for the apparent lack of stability $\{HC(CMeNAr)_2\}$ In: are not obvious, especially since the sterically related species 2,6-Trip₂H₃C₆In: [9] is known to be stable. The existence of this compound and the aluminum and gallium species $\{HC(CMeNAr)\}M: (M = Al [3] \text{ or } Ga [4])$ strongly suggest that $\{HC(CMeNAr)\}In:$ should be obtainable under different reaction conditions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 169219 and 169220 for compounds 1 and 2. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

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