Preparation, Characterization, and Reactivity of the **Stable Indium Trihydride Complex** [InH₃{CN(Mes)C₂H₂N(Mes)}]

Colin D. Abernethy, Marcus L. Cole, and Cameron Jones*

Department of Chemistry, University of Wales, Cardiff, P.O. Box 912, Park Place, Cardiff, CF10 3TB, U.K.

Received June 13, 2000

Reaction of either $LiInH_4$ or $[InH_3(NMe_3)]$ with the Arduengo-type carbene :CN(Mes)- $C_2H_2N(Mes)$, Mes = $C_6H_2Me_3$ -2,4,6, affords the indium trihydride complex [InH₃{CN(Mes)- $C_{2}H_{2}N(Mes)$]. This compound displays a remarkable thermal stability (dec 115 °C). In solution the products of decomposition depend on the solvent used. In toluene decomposition results in liberation of the free carbene and deposition of indium metal, and in tetrahydrofuran in the presence of indium metal hydrogen transfer occurs to give H₂CN(Mes)C₂H₂N-(Mes) and indium metal, while in dichloromethane, chloride abstraction occurs from the solvent to yield $[InCl_3{CN(Mes)C_2H_2N(Mes)}]$. A number of related compounds have also been prepared and their structures and properties investigated. These include [GaH₃{CN- $(Mes)C_2H_2N(Mes)$], which is the most stable gallium trihydride yet reported, and the indium hydride halide complex $[InH_2Cl{CN(Mes)C_2H_2N(Mes)}]$.

Introduction

The chemistry of both aluminum and gallium hydride compounds has been studied extensively.¹ In particular, Lewis base complexes of aluminum and gallium trihydride have found a variety of practical applications, which include their use as chemical vapor deposition precursors for thin films of the group 13 metal or semiconducting materials,^{2,3} as well as reagents for hydrogenation in organic synthesis.⁴ Considering this, we believe that indium trihydride complexes have the potential to find a similar range of applications. Unfortunately, however, there is a paucity of structurally characterized compounds containing indium hydride bonds.⁵ which is due both to the weakness of the In-H bond as well as to kinetically facile decomposition pathways, which are thought to proceed via associative mechanisms involving In-H-In bridges.⁶ In order for the field of indium hydride chemistry to be developed and its potential applications realized, further examples of these species need to be synthesized and their general reactivity, stability, and decomposition pathways understood.

During the past two years our group has reported the first examples of indium trihydride complexes [InH₃- $\{CN(Pr^{i})C_{2}Me_{2}N(Pr^{i})\}], 1,^{7,8} \text{ and } [InH_{3}(PCy_{3})] (Cy =$

(2) Simmonds, M. G.; Gladfelter, W. L. In *The Chemistry of Metal CVD*; Kodas, T., Hampden-Smith, M., Eds.; VCH: Weinheim, 1994.
(3) Kidder, J. N.; Yun, H. K.; Rogers, J. W.; Pearsall, T. P. *Chem.*

cyclohexyl), $\mathbf{2}$, ^{9,10} in which the InH₃ moiety is stabilized by coordination to either a highly nucleophilic "Arduengo-type" carbene or a bulky tertiary phosphine ligand, respectively. Compound 1 is unstable in solution above -20 °C and decomposes in the solid state above -5 °C,⁷ while **2** exhibits a greater thermal stability, decomposing slowly at 25 °C in solution and at 50 °C in the solid state.9

We are interested in synthesizing indium trihydride complexes of even greater thermal stability in order to investigate the chemical reactivity of these species. The remarkable thermal stability exhibited by the aluminum trihydride complex of the sterically demanding Arduengo-type carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, **3**, viz., [AlH₃{CN(Mes)C₂H₂N(Mes)}] $(Mes = C_6H_2Me_3-2,4,6), 4 (mp 246 °C, decomposition)$ temperature not stated),¹¹ compared with other AlH₃ complexes, which decompose at much lower temperatures, e.g., [AlH₃(NMe₃)] (mp 78 °C, decomposition ca. 100 °C),¹² suggested that the indium-containing analogue [InH₃{CN(Mes)C₂H₂N(Mes)}], 5, would also prove to have an exceptional thermal stability. Herein, we report the synthesis and characterization of 5 and describe its reactivity and decomposition under certain conditions. We also report several related complexes incorporating 3: the indium trideuteride complex [InD₃- $\{CN(Mes)C_2H_2N(Mes)\}$, **5a**; the mixed indium hydride chloride complex $[InH_2Cl{CN(Mes)C_2H_2N(Mes)}]$, 6; the

^{*} Corresponding author. Tel: (+44) (029) 2087 4060. Fax: (+44) (029) 2087 4030. E-mail: jonesca6@cardiff.ac.uk.

⁽¹⁾ Gardiner, M. G.; Raston, C. L. Coord. Chem. Rev. 1997, 166, 1, and references therein.

⁽⁴⁾ Raston, C. L.; Siu A. F. H.; Tranter C. J.; Young, D. J.

Tetrahedron Lett. 1994, 35, 5915.

⁽⁵⁾ Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Smithies N. A. Organometallics 1998, 17, 3108.

⁽⁶⁾ Downs, A. J.; Pulham, C. R. Chem. Soc. Rev. 1994, 175.

⁽⁷⁾ Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Smithies, N. A. Chem. Commun. 1998, 869.

⁽⁸⁾ Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; (9) Hibbs, D. E.; Jones, C.; Smithies, N. A. Chem. Commun. 1999, (9) Hibbs, D. E.; Jones, C.; Smithies, N. A. Chem. Commun. 1999,

^{185.}

⁽¹⁰⁾ Cole, M. L.; Hibbs, D. E.; Jones, C.; Smithies, N. A. J. Chem. Soc., Dalton Trans. 2000, 545.
(11) Arduengo, A. J., III; Dias H. V. R.; Calabrese, J. C.; Davidson, J. J. Am. Chem. Soc. 1992, 114, 9724.
(12) Purf I. V. Hautherman, M. E. J. Am. Chem. Soc. 1960, 82 2141.

⁽¹²⁾ Ruff, J. K.; Hawthorne, M. F. J. Am. Chem. Soc. 1960, 82, 2141.

indium trichloride complex $[InCl_3{CN(Mes)C_2H_2N-(Mes)}]$, 7; and the gallium trihydride complex $[GaH_3-{CN(Mes)C_2H_2N(Mes)}]$, 8.

Experimental Section

General Information. All manipulations were carried out under anaerobic conditions using standard Schlenk glassware and vacuum line techniques. Paraffin and ether solvents were distilled from Na/K alloy and purged with nitrogen prior to use. Dichloromethane was distilled from CaH_2 prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded with a Bruker DPX400 and calibrated against the residual ¹H or ¹³C resonances of the solvents used. Infrared spectra were recorded as either Nujol mulls or as solutions in toluene using a Perkin-Elmer 1725-X Fourier transform instrument. Mass spectra were obtained with a VG Fisons Platform II instrument under APCI conditions. Elemental analyses were performed by the Warwick University Microanalytical Service. Melting points were determined in sealed glass capillaries under argon and are not corrected.

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene,¹³ LiInH₄,¹⁴ and [InH₃(NMe₃)]⁷ were prepared according to the published procedures. LiInD₄ was prepared by a slight modification of a published procedure.¹⁴ InBr₃ was sublimed in vacuo, and NMe₃·HCl and quinuclidine·HCl were dried in vacuo at 100 °C prior to use. All other reagents were used as received from commercial sources.

Preparation of [InH₃{CN(Mes)C₂H₂N(Mes)}], 5. (a) Reaction of 3 with LiInH₄. A solution of 3 (1.60 g, 5.26 mmol) in 50 mL of diethyl ether was added dropwise to a solution of LiInH₄ (0.66 g, 5.26 mmol) in 100 mL of diethyl ether at -78°C. The resulting hazy pale yellow solution was allowed to warm to room temperature and stirred for a further 2 h. The diethyl ether was removed in vacuo, and toluene (80 mL) was added. The mixture was filtered and the volume of the filtrate reduced to 30 mL in vacuo. Pale yellow crystals of [InH₃{CN- $(Mes)C_2H_2N(Mes)$ formed on standing for 24 h at -35 °C, yield 1.90 g (86%). Mp: 115 °C (dec). Anal. for C₂₁H₂₇N₂In: calcd C, 59.73; H 6.44, N 6.64. Found: C 59.39, H 6.39, N 6.46. MS APCI: m/z(%) 421 [{M - H}⁺, 33], 305 [{M - InH₂}⁺, 100]. IR (Nujol) ν /cm⁻¹: 1650 (s, br, In–H str); (toluene solution) 1640 cm⁻¹ (s, br, In–H str). ¹H NMR (400 MHz, C₆D₆, 298 K): δ 2.29 [s, 12 H, o-CH₃], 2.38 [s, 6 H, p-CH₃], 5.2 [s (br), 3H, In-H₃], 6.35 [s, 2 H, NCH], 7.05 [s, 4 H, Ar-H]. ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 16.3 [s, *o*-*C*H₃], 19.7 [s, *p*-*C*H₃], 121.4 [s, NCC], 124.2 [s, m-CH], 129.8 [s, p-CCH3], 133.2 [s, *o*-*C*CH₃], 138.5 [s, *ipso*-*c*], In–*C* not observed.

(b) Reaction of 3 with [InH₃(NMe₃)]. A solution of 3 (1.60 g, 5.26 mmol) in 50 mL of diethyl ether was added dropwise to a solution of [InH₃(NMe₃)] (0.93 g, 5.26 mmol) in 100 mL of diethyl ether at -78 °C. The resulting pale yellow solution was worked up as above. Yield: 1.2 g (54%).

Preparation of [InD₃{CN(Mes)C₂H₂N(Mes)}], 5a. Compound **5a** was prepared by reacting LiInD₄ (0.66 g, 5.26 mmol) with **3** (1.60 g, 5.26 mmol) in an identical fashion to the preparation of **5**, yield 1.61 g (75%). Mp: 114 °C (dec). MS APCI: m/z(%) 423 [{M – D}⁺, 15], 306 [{M – InD₂}⁺, 100]. IR (Nujol) ν/cm^{-1} : 1180 (s, br, In–D str). ¹H NMR (400 MHz, C₆D₆, 298 K): δ 2.27 [s, 12 H, o-CH₃], 2.38 [s, 6 H, p-CH₃], 6.30 [s, 2 H, NCH], 7.03 [s, 4 H, Ar–H]. ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 16.3 [s, o-CH₃], 19.7 [s, p-CH₃], 121.0 [s, NCC], 124.0 [s, m-CH], 130.1 [s, p-CCH₃], 133.6 [s, o-CCH₃], 137.2 [s, *ipso-c*]. In–*C* not observed.

Thermal Decomposition of a Toluene Solution of [InH₃{CN(Mes)C₂H₂N(Mes)]. A solution of 5 (0.35 g, 0.83 mmol) in toluene (100 mL) was heated to 100 °C for 2.5 h,

(13) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. Am. Chem. Soc. 1991, 113, 361.

(14) Wiberg, E.; Schmidt, M. Z. Naturforch., Teil B 1957, 12, 54.

after which time indium metal deposited from solution. The resulting suspension was filtered, and the solvent was removed from the filtrate in vacuo. An ¹H NMR spectrum (C_6D_6) showed the residue to be : $CN(Mes)C_2H_2N(Mes)$, **3**.

Indium Metal Catalyzed Decomposition of a Tetrahydrofuran Solution of [InH₃{CN(Mes)C₂H₂N(Mes)}]. Indium powder (0.02 g, 0.17 mmol) dried in vacuo was added to a stable clear light yellow solution of 5 (0.25 g, 0.59 mmol) in THF (50 mL) at 25 °C. The resulting gray suspension was stirred for 16 h, whereupon it was filtered to yield a yellow solution. Volatiles were removed in vacuo to yield H₂CN(Mes)-C₂H₂N(Mes), 9, as an off-white solid (0.17 g, 94%), mp 48 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 2.29 [s, 6H, *p*-CH₃], 2.54 [s, 12H, o-CH₃], 5.12 [s, 2H, CH₂], 5.66 [s, 2H, C₂H₂], 6.94 [s, 4H, Ar-H]. ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 19.5 [s, o-CH₃], 21.4 [s, p-CH₃], 74.5 [s, CH₂], 117.6 [s, C₂H₂], 130.5 [s, *m*-*C*H], 135.8 [s, *p*-*C*CH₃], 137.9 [s, *o*-*C*CH₃], 140.5 [s, *ipso*-*C*]. MS APCI: *m*/*z* (%) 307 [MH⁺, 100]. IR (Nujol) *v*/cm⁻¹: 1409 (m), 1312 (m), 1286 (m), 979 (m), 871 (m), 851 (m), 784 (m). Anal. for C21H26N2: calcd C 82.31, H 8.55, N 9.14. Found: C 81.85. H 8.61. N 8.49.

Decomposition of a Dichloromethane Solution of [InH₃{CN(Mes)C₂H₂N(Mes)}]. A solution of [InH₃{CN(Mes)- $C_2H_2N(Mes)$] (0.43 g, 1.02 mmol) in dichloromethane (15 mL) at 0 °C was slowly warmed to room temperature. Upon warming, gas evolution was observed, the clear yellow solution was stirred for a further 7 days and filtered, and volatiles were removed from the filtrate in vacuo to yield a white residue. This was recrystallized from diethyl ether/dichloromethane to give [InCl₃{CN(Mes)C₂H₂N(Mes)}], 7, as hexagonal rods (0.36 g, 67%), dec 191 °C. ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 2.13 [s, 12H, o-CH₃], 2.39 [s, 6H, p-CH₃], 7.13 [s, 4H, Ar-H], 7.40 [s, 2H, C_2H_2]. ¹³C NMR (100.6 MHz, CD_2Cl_2 , 298 K): δ 15.9 [s, o-CH₃], 19.5 [s, p-CH₃], 124.5 [s, C₂H₂], 128.2 [s, m-CH], 133.8 [s, o-CCH₃], 133.9 [s, p-CCH₃], 139.9 [s, ipso-C]. MS APCI: m/z (%) 305 [{MH - InCl₃}⁺, 22], 490 [{M - Cl}⁺, 100]. IR (Nujol) v/cm⁻¹: 1301 (m), 1260 (m), 1230 (m), 1020 (m), 799 (m). Anal. for C₂₁H₂₄N₂Cl₃: calcd C 48.01, H 4.57, N 5.33, Cl 20.24. Found: C 47.78, H 4.57, N 5.20.

Preparation of [GaH₃{CN(Mes)C₂H₂N(Mes)}], 8. A solution of 3 (0.86 g, 2.82 mmol) in diethyl ether (20 mL) was slowly added to a solution of LiGaH4 (2.82 mmol) in diethyl ether (70 mL) at -78 °C. The resulting hazy light yellow solution was warmed to room temperature and stirred for 1 h, whereupon a colorless product precipitated from solution. This was isolated via filtration and dried in vacuo. Extraction with THF (30 mL) and placement at -35 °C overnight yielded airstable [GaH₃{CN(Mes)C₂H₂N(Mes)}] as colorless blocks (0.94 g, 89%), dec 214 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 2.15 [s, 12H, o-CH₃], 2.20 [s, 6H, p-CH₃], 3.96 [br s, 3H, Ga-H], 6.16 [s, 2H, C₂H₂], 6.86 [s, 4H, Ar-H]. ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 17.9 [s, *o*-*C*H₃], 21.3 [s, *p*-*C*H₃], 122.4 [s, *C*₂H₂], 129.6 [s, m-CH], 135.2 [s, o-CCH₃], 136.1 [s, p-CCH₃], 139.6 [s, *ipso-C*]. MS APCI: *m*/*z* (%) 305 [{MH – GaH₃}⁺, 19], 375 $[{M - H}^+, 100];$ IR (Nujol) v/cm⁻¹: 1780 (s, br, Ga-H str). (Analyses for $[GaH_3{CN(Mes)C_2H_2N(Mes)}]$ were found to be consistently 2-3% high in carbon. NMR studies on the bulk material suggest contamination with a small amount of an unknown material, which proved difficult to remove.)

Preparation of [InH₂Cl{CN(Mes)C₂H₂N(Mes)}], 6. (a) Reaction of [InH₂Cl(NMe₃)_n] with :CN(Mes)C₂H₂N(Mes). A slurry of NMe₃·HCl (0.25 g, 2.62 mmol) in diethyl ether (15 mL) was slowly added to a solution of LiInH₄ (1.41 mmol) in diethyl ether (35 mL) at -78 °C. The resulting opaque colorless solution was warmed to -50 °C and stirred for 2.5 h, whereupon all the solid had reacted to yield a colorless clear solution of [InH₂Cl(NMe₃)_n]. Further reaction with an ethereal (20 mL) slurry of :CN(Mes)C₂H₂N(Mes) (0.43 g, 1.41 mmol) at -50 °C formed a white precipitate. The reaction mixture was warmed to -20 °C and stirred for a further 2 h, whereupon the precipitate was isolated by filtration. Extraction with

 Table 1. Summary of Crystallographic Data for

 Complexes 5, 6, and 7

	5	6	7
formula	C ₂₁ H ₂₇ N ₂ In	C21H26N2ClIn	C ₂₁ H ₂₄ N ₂ Cl ₃ In
$M_{\rm r}$	422.27	456.71	525.59
<i>a</i> , Å	30.579(6)	8.783(4)	16.468(2)
<i>b</i> , Å	32.414(6)	14.569(5)	16.543(2)
<i>c</i> , Å	8.477(2)	16.260(5)	17.220(3)
α, deg	90	83.94(2)	90
β , deg	90	83.60(4)	90
γ , deg	90	89.75(3)	90
V, Å ³	8402.3(30)	2056.0(13)	4691.3(11)
cryst syst	orthorhombic	triclinic	orthorhombic
space group	Fdd2	$P\overline{1}$	$Pca2_1$
λ, Å	0.71073	0.71073	0.71073
Т, К	150(2)	150(2)	150(2)
Z	16	4	8
size	$0.5\times0.2\times0.1$	0.3 imes 0.2 imes 0.2	$0.4\times0.4\times0.3$
color	pale yellow	colorless	colorless
μ , cm ⁻¹	11.29	12.85	13.57
F(000)	3456	928	2112
no. of reflns collected	8669	7949	7005
no. of unique reflns	3967	7421	7001
no. of params varied	223	463	500
$R\{I > 2\sigma(I)\}$	0.0412	0.0538	0.0333
$R_{\rm w}$ {all data}	0.1133	0.1465	0.1039
	C21 C3	$- \Re^{C2}$ \Re^{C10} (5)	



Figure 1. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): In(1)-C(1) 2.253(5), N(1)-C(1) 1.353-(6), N(1)-C(2) 1.390(6), N(2)-C(1) 1.353(6), N(2)-C(3) 1.399(6), C(2)-C(3) 1.328(8), C(1)-N(1)-C(2) 110.7(4), N(1)-C(1)-N(2) 104.5(4), C(1)-N(2)-C(3) 110.9(4), N(1)-C(2)-C(3) 107.5(4), N(2)-C(3) -C(2) 106.3(4).

toluene (30 mL) at -10 °C and cooling to -35 °C overnight afforded [InH₂Cl{CN(Mes)C₂H₂N(Mes)}] as colorless prisms (0.36 g, 65%), dec 119 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 2.13 [s, 12H, *o*-CH₃], 2.17 [s, 6H, *p*-CH₃], 6.09 [s, 2H, C₂H₂], 6.25 [br s, 2H, In-H], 6.84 [s, 4H, Ar-H]. ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 17.8 [s, *o*-CH₃], 21.1 [s, *p*-CH₃], 122.9 [s, C₂H₂], 129.6 [s, *m*-CH], 135.0 [s, *p*-CCH₃], 134.9 [s, *o*-CCH₃], 140.1 [s, *ipso*-C]. MS APCI: *m*/*z* (%) 305 [{MH - ClInH₂}+, 100], 458 [MH⁺, 28]. IR (Nujol) *v*/cm⁻¹: 1737 (s, br, In-H str). A reproducible microanalysis could not be obtained for **6**, presumably due to contamination of the bulk crystalline material with small quantities of **5** or [InCl₂H{CN(Mes)C₂H₂N-(Mes)}].

(b) Reaction of Quinuclidine·HCl with [InH₃{CN(Mes)-C₂H₂N(Mes)]. Solid quinuclidine·HCl (0.09 g, 0.61 mmol) was added to a stirred solution of $[InH_3{CN(Mes)C_2H_2N(Mes)}]$ (0.25 g, 0.59 mmol) in diethyl ether (70 mL) at -20 °C. The resulting white slurry was stirred for 1 h, whereupon the solid had reacted to yield a light yellow solution. This was filtered, and the filtrate was concentrated in vacuo at -10 °C and placed at -35 °C overnight to yield $[InH_2Cl{CN(Mes)C_2H_2N-(Mes)}]$ as colorless prisms (0.13 g, 50%), which analyzed as above.

X-ray Crystal Structure Determinations. Crystals of **5**, **6**, and **7** that were suitable for single-crystal X-ray diffraction were mounted in silicone oil. All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer.



Figure 2. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): In(1)-C(1) 2.244(6), In(1)-Cl(1) 2.356(2), N(1)-C(1) 1.346(8), N(1)-C(2) 1.376(8), N(2)-C(1) 1.351(8), N(2)-C(3) 1.380(8), C(2)-C(3) 1.349(9), C(1)-In-(1)-Cl(1) 101.71(16), N(1)-C(1)-N(2) 104.5(5), C(1)-N(2)-C(3) 110.8(5), N(1)-C(2)-C(3) 106.1(5), N(2)-C(3)-C(2) 106.9(6).

The structures were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX97)¹⁵ using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions (riding model) except the hydride ligands of **5**. Empirical absorption corrections were carried out by the DIFABS method.¹⁶ Crystal data and details of data collections and refinement are given in Table 1. Both compounds **5** and **6** crystallized with two crystallographically independent molecules in the asymmetric unit. In each case, there are no significant geometric differences between the independent molecules, so the molecular structures of only one are shown in Figure 1 and Figure 2.

Results and Discussion

Treatment of an ethereal solution of either LiInH₄ or [InH₃(NMe₃)] with 1 equiv of the Arduengo-type carbene 3 at -78 °C resulted in the formation of the indium trihydride complex [InH₃{CN(Mes)C₂H₂N(Mes)}], 5, in high yield after recrystallization from toluene (Scheme 1). The ¹H NMR spectrum of **5** in C_6D_6 showed the presence of the carbene moiety as well as a broad resonance at δ 5.2 ppm assigned to the three hydride ligands attached to the indium center. The chemical shift of this resonance compares well to the indium hydride resonances reported for [InH₃{CN(Prⁱ)C₂Me₂N- (Pr^{i})], **1**, δ 5.58 ppm,⁷ and $[InH_{3}(PCy_{3})]$ (Cy = cyclohexyl), **2**, δ 5.61 ppm.^{9,10} The broadness of the indium hydride resonance in the spectrum of 5 is due to the high quadrupole moment of the indium center (¹¹⁵In 95%, I = 9/2, ¹¹³In 5%, I = 9/2)¹⁷ to which the hydrides are attached. This also accounts for the absence of a resonance for the indium-coordinated carbene center, C(1), in its ¹³C NMR spectrum. The IR spectra of 5 display characteristic strong, broad absorptions centered

⁽¹⁵⁾ Sheldrick, G. M. SHELX97; University of Göttingen, 1997.

⁽¹⁶⁾ Walker, N. P. C.; Stuart, D. Acta Crystallogr. Sect. A 1983, 39, 158.

⁽¹⁷⁾ Downs, A. J. In *Chemistry of Aluminium, Gallium and Thallium*; Downs, A. J., Ed.; Blackie Academic: Glasgow, 1993; Chapter 1.



at 1650 cm⁻¹ (Nujol) or 1640 cm⁻¹ (toluene solution), both of which were assigned to the stretching modes of its In–H bonds. The observed frequencies are close to those described for **1**, 1640 cm⁻¹,^{7,8} and **2**, 1661 cm⁻¹.⁹ It is believed that, as with most Lewis base adducts of AlH₃ or GaH₃,¹ single In–H stretching absorptions were observed due to effective overlap of the expected stretching bands.

For purpose of comparison the indium trideuteride complex $[InD_3{CN(Mes)C_2H_2N(Mes)}]$, **5a**, was prepared by a method analogous to that of **5**. Its ¹H NMR and ¹³C NMR spectra are almost identical with those of **5** with the exception that no hydride resonance is seen in the ¹H NMR spectrum of **5a**. As expected, there was a significant shift to lower frequency (1180 cm⁻¹) for the In–D stretch of **5a** in its infrared spectrum compared with the In–H stretch of **5**. The magnitude of this shift is consistent with the difference in the reduced masses of the two atom pairs (i.e., InD and InH).

An X-ray crystal structure analysis of **5** was carried out (Figure 1). Unfortunately, none of the hydride ligands could be located from the difference maps, but the In-C(1) distance, 2.253(5) Å, compares well to that reported, 2.260(6) Å, for the closely related compound, **1**. In addition, the bond lengths and angles within the carbene heterocycle are similar to those reported for the aluminum-containing analogue, **4**.¹¹ As expected, the N-C(carbene)-N angle of 104.5° is typical for Arduengo-type carbenes coordinated to metal centers and lies between the normal value for free imidazol-2ylidenes (ca. 102°) and imadazolium cations (ca. 108°).¹¹ The molecule is monomeric and does not display any intermolecular interactions in the solid state. It is noteworthy that compound **5a** is isostructural and isomorphous to **5**.

The most remarkable feature of complex **5** is its surprisingly high thermal stability. In the solid state it is stable under an inert atmosphere up to 115 °C. Interestingly, the stability of **5** in solution is dependent on the solvent. Toluene solutions of **5** are stable at room temperature for periods in excess of three months. However, on heating in toluene at 100 °C decomposition occurs after 2.5 h via loss of the carbene ligand and deposition of indium metal. Similarly, Lewis base loss is the primary decomposition process for complexes of AlH₃ and GaH₃¹⁸ and the indium trihydride complex **2**.¹⁰

It was observed that when a toluene solution of **5** was heated at 100 °C, no decomposition of the complex occurred until traces of indium metal appeared in suspension. As soon as this occurred, the decomposition process went to completion within 2 minutes. This suggests that the decomposition was catalyzed by indium metal. To test this hypothesis, indium metal powder was added to a toluene solution of **5** at room temperature. After 12 h an NMR spectrum of the soluble material showed that **5** had decomposed and that only the free carbene, **3**, was present. In contrast, when

⁽¹⁸⁾ Jones, C.; Koutsantonis, G. A.; Raston, C. L. Polyhedron 1993, 12, 1829.

indium metal powder was added to a stable solution of **5** in tetrahydrofuran under identical conditions, decomposition occurred overnight and the only tetrahydrofuran-soluble decomposition product was found to be $H_2CN(Mes)C_2H_2N(Mes)$, **9**. This suggests that in tetrahydrofuran hydrogen transfer occurs from the indium center to the carbenic carbon of the ligand. This hypothesis was confirmed by decomposing a THF solution of **5a** in a similar way to afford $D_2CN(Mes)C_2H_2N(Mes)$. Complex **5** is also unstable at room temperature when dissolved in dichloromethane. Chloride abstraction from the solvent takes place at 25 °C to form [InCl₃-{CN(Mes)C_2H_2N(Mes)}], **7**, in moderate (67%) yield.

A photolytic decomposition of **5** was also attempted in order to gain further insight into the different decomposition pathways displayed by **5**. After 12 h of ultraviolet irradiation of a toluene solution of **5**, indium metal was deposited and a ¹H NMR spectrum revealed that a complex mixture of products had been formed. No further workup was attempted.

The remarkable thermal stability of 5, both in solution and the solid state, may be explained by a combination of the large steric bulk and high nucleophilicity of 3. With respect to the latter, Nolan et al. have demonstrated that 3 binds to metals with a greater M-L bond enthalpy than tricyclohexylphosphine and other similar tertiary phosphines.¹⁹ Therefore, the greater stability of 5 with respect to 2 is not surprising. Compound 5 also has a significantly enhanced thermal stability relative to that of the closely related indane complex 1 (dec ca. -5 °C). This cannot be due to differences in the nucleophilicities of the carbene ligands, as these are similar. Instead, the lower stability of 1 is due to it decomposing via a different pathway, which is believed to involve metalation of the isopropyl carbene substituents by the InH₃ moiety with a concomitant loss of H₂. Compound 5 does not decompose via a related metalation of the ortho methyl groups of its mesityl substituents, perhaps for steric reasons, but instead its primary thermal decomposition process is ligand loss or dihydroimidazole formation, depending on the conditions employed. Interestingly, metalation of the methyl substituents of 3 has recently been observed in a Rh(I) complex, though in this case the process was presumably more facile due to it being an oxidative insertion reaction.²⁰

To gain further insights into the stabilities of $[MH_3-{CN(Mes)C_2H_2N(Mes)}]$ compounds, we decided to synthesize the gallium-containing analogue $[GaH_3\{CN-(Mes)C_2H_2N(Mes)\}]$, **8**. To this end, the free carbene, **3**, was reacted with an equimolar amount of LiGaH₄ in diethyl ether. The product **8** was formed in 89% yield and characterized by ¹H and ¹³C NMR together with APCI MS and IR spectroscopy. The ¹H NMR spectrum (C₆D₆) showed a broad resonance at 3.96 ppm, which was assigned to the three hydride ligands of the GaH₃ unit and can be compared with the hydride resonance (4.48 ppm) seen for $[GaH_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}]$,**10**. A resonance (139.6 ppm) assigned to the carbenic carbon of **8** was also observed in the ¹³C NMR spectrum, which is in the region expected for a carbenic carbon of a metal-

coordinated Arduengo-type carbene. Complex **8** is stable in air and is the most thermally stable (dec 214 °C) GaH₃ complex yet reported. Its thermal stability can be compared with that of **10**, which decomposes at 180 °C.⁸ Unfortunately, single crystals of suitable quality for X-ray diffraction could not be obtained.

Despite the ease of formation of bis-carbene complexes of indium trihalides, no evidence of bis-carbene complexes of indium trihydrides has been observed.⁷ It has been suggested that this is due to the lower Lewis acidity of InH_3 with respect to InX_3 (X = Cl, Br).⁸ Bisphosphine complexes of indium trihydride have, however, recently been reported.¹⁰ To attempt the formation of a bis-carbene indium trihydride complex, the Arduengo-type carbene :CN(Me)C₂Me₂N(Me), 11, was reacted with an equimolar amount of 5 in toluene at room temperature. After 4 h indium metal was deposited and a ¹H NMR spectrum showed that the only products remaining in solution were 3 and 11. This result suggests that instead of a five-coordinate complex forming, carbene exchange took place at the indium center to form $[InH_3{CN(Me)C_2Me_2N(Me)}]$, which then decomposes under the experimental conditions employed. The thermal instability of this less sterically protected InH₃ complex has been previously reported.²¹

To extend the synthetic utility of stable indium hydride complexes, we wished to synthesize the mixed indium hydride halide complexes $[InH_{(3-x)}Cl_x\{CN-(Mes)C_2H_2N(Mes)\}]$ (x = 1 or 2), which would enable us to carry out further chemistry at the indium centers via metathesis reactions. The reaction of $[InH_2Cl(NMe_3)_n]$ with an equimolar amount of **3** yielded $[InH_2Cl\{CN-(Mes)C_2H_2N(Mes)\}]$, **6**, in 65% yield. It was also produced in 50% yield by the reaction of quinuclidine·HCl with **5**. In this instance the quinuclidine·HCl acted as a source of Cl⁻, and **6** was produced with the elimination of hydrogen. Attempts were made to prepare a pure sample of $[InHCl_2\{CN(Mes)C_2H_2N(Mes)\}]$ by similar procedures, but all met with failure.

Complex 6 was characterized by ¹H and ¹³C NMR and IR spectroscopy together with an X-ray crystal structure analysis. A broad resonance due to the two hydride ligands attached to the indium center occurred at δ 6.25 ppm in the ¹H NMR spectrum of **6**. The downfield shift of this resonance compared with that of the hydride ligands of 5 is probably due to the influence of the electronegative chloride ligand also bound to the indium center. The presence of the chloride ligand also serves to strengthen the In-H bonds in the complex by a negative inductive effect, as evidenced by their IR stretching modes. These are centered at 1737 cm⁻¹, which is at a considerably higher frequency than for the corresponding In-H stretching modes for 5. It is noteworthy that uncoordinated InH₂Cl has recently been prepared and isolated in a solid argon matrix, and its properties have been studies.²²

The X-ray crystal structure of **6** (Figure 2) revealed that this compound, like **5**, is monomeric in the solid state without any intermolecular contacts. This is also consistent with the structures of **7** (Figure 3) and the

⁽¹⁹⁾ Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. Organometallics 1999, 18, 2370.

⁽²⁰⁾ Huang, J.; Stevens, E. D.; Nolan, S. P. Organometallics 2000, 19, 1194.

⁽²¹⁾ Smithies, N. A. Ph.D. Thesis, Cardiff University, 1999.
(22) Himmel, H.-J.; Downs, A. J.; Greene, T. M. J. Am. Chem. Soc.
2000, 122, 922.



Figure 3. Molecular structure of 7. Selected bond lengths (Å) and angles (deg): In(1)-C(1) 2.200(7), In(1)-Cl(1) 2.355(2), In(1)-Cl(2) 2.349(2), In(1)-Cl(3) 2.353(2), N(1)-C(1) 1.336(8), N(1)-C(2) 1.366(9), N(2)-C(1) 1.334(7), N(2)-C(3) 1.372(8), C(2)-C(3) 1.329(10), C(1)-In(1)-Cl(1) 108.7(2), C(1)-In(1)-Cl(2) 112.09(15), C(1)-In(1)-Cl(3) 111.45(15), Cl(1)-In(1)-Cl(2) 107.35(7), Cl(1)-In(1)-Cl(3) 111.45(15), Cl(2)-In(1)-Cl(3) 107.63(7), N(1)-C(1)-N(2) 106.7(6), C(1)-N(2)-C(3) 109.7(5), N(1)-C(2)-C(3) 108.1(6), N(2)-C(3)-C(2) 106.5(6).

related indium bromide complex $[InBr_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}]^{23}$ The In-C(1) distances in **6**, 2.244(6) Å, and **7**, 2.200(7) Å, compare well to those observed in **5**, 2.253-(5) Å, and $[InBr_3\{CN(Pr^i)C_2Me_2N(Pr^i)\}]$, 2.199(5) Å.

(23) Black, S. J.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Malik,
 K. M. A.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* 1997, 4313.
 (24) Abernethy, C. D.; Cole, M. L.; Davies, A. J.; Jones, C. *Tetra*-

Unsurprisingly, the In–Cl distance in **6**, 2.356(2) Å, is very close to the average In–Cl distance observed in **7**, 2.352 Å. In **7** the geometry at In(1) is close to tetrahedral (av C(1)–In(1)–Cl angle – 110.7°), while in **6** it appears to be distorted, as the C(1)–In(1)–Cl(1) angle is 101.71-(16)°.

Conclusion

The indium hydride complex $[InH_3\{CN(Mes)C_2H_2N-(Mes)\}]$, **5**, has been synthesized in high yield and possesses exceptional thermal stability. The decomposition of this compound has been studied under a variety of conditions and occurs via different pathways depending on the conditions employed. The related complexes $[GaH_3\{CN(Mes)C_2H_2N(Mes)\}]$, **8**; $[InH_2Cl\{CN(Mes)-C_2H_2N(Mes)\}]$, **6**; and $[InCl_3\{CN(Mes)C_2H_2N(Mes)\}]$, **7**, have also been prepared and their structures and properties compared to those of **5**. We are currently investigating the reactivity of **5** and related compounds toward a variety of organic²⁴ and inorganic²⁵ substrates.

Acknowledgment. We gratefully acknowledge the financial support of the Engineering and Physical Sciences Research Council (Postdoctoral Fellowship for C.D.A. and Studentship for M.L.C.).

Supporting Information Available: Full crystallographic data for compounds **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004951

hedron Lett., in press. (25) Abernethy, C. D.; Cole, M. L.; Jones, C. Manuscript in preparation.