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A mononuclear indium(I) carbene analogue

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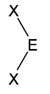
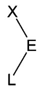
The 'one pot' reaction between $K[N(SiMe_3)_2]$, InI and the β-diimine ligand precursor $[H(NDippCMe)_2CH]$ (Dipp = $C_6H_3Pr^i_2$-2,6) gave $[In\{(NDippCMe)_2CH\}]$ 1, the first example of a two-coordinate, neutral, In(I) singlet 'carbene analogue'.

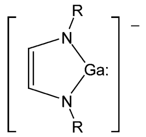
The search for Group 13 and 14 species that are formally analogous to singlet carbenes has gathered pace in recent years.[1] Monomeric derivatives, **I** (X = anionic substituent; E = C, Si, Ge, Sn or Pb), are known for the Group 14 elements,[2] isoelectronic Group 13 species, **II** (X = anionic substituent; L = neutral donor; E = B, Al, Ga, In, Tl) are rare. Schmidbaur and Jones have reported the heterocyclic anions **III** and **IV**, both of which contain gallium in a formal +1 oxidation state,[3,4] and Roesky and Power have described syntheses of the neutral six electron aluminium(I) and gallium(I) β-diketiminato derivatives **V** and **VI**.[5,6] It is reasoned that the doubly occupied HOMO of all four compounds is mainly an aluminium or gallium sp orbital. The availability of this lone pair has been shown in coordination and reaction chemistry.[7] In view of the increasing stability of the univalent state as Group 13 is descended,[8] it is surprising that indium complexes analogous to **III–VI** have not been reported. The In(I) halides are readily available and a number of In(I) σ-alkyl and σ-aryl derivatives have been synthesised from them by treatment with organolithium reagents.[9,10] Although an attempted synthesis of the indium analogue (**1**) of **V** and **VI** resulted in disproportionation to indium(III), indium(II) and indium(0) products, Power has suggested that this compound should be obtainable under the correct conditions.[11] After our successful syntheses of β-diketiminato compounds of Group 2 elements from the potassium compound and the alkaline earth iodides,[12] we attempted to synthesise the elusive In(I) derivative **1** by a similar procedure.



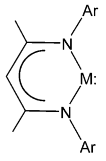
I



II



III, R = ^tBu;
IV, R = $C_6H_3Pr^i_2$-2,6



V, M = Al;
VI, M = Ga
1, M = In
Ar = $C_6H_3Pr^i_2$-2,6

$[In\{(NDippCMe)_2CH\}]$ (Dipp = $C_6H_3Pr^i_2$-2,6) (**1**) was obtained by a simple 'one pot' reaction of equimolar quantities of $K[N(SiMe_3)_2]$, InI and $H(NDippCMe)_2CH$ in THF at −78 °C.†Some disproportionation was evident from the deposition of indium metal as the solution was warmed to room temperature, but extraction with hexane and crystallisation gave compound **1** in reasonable (36% unoptimised) yield as pale yellow, thermally stable crystals. We have not yet identified further products from this reaction, although it is likely that mixtures of iodoindium(II) and iodoindium(III) compounds are produced.[11] Compound **1** is photolabile but stable in hexane solution and in the solid state if stored in the absence of light. In aromatic solvents however decomposition, accompanied by the deposition of elemental indium, occurs over a 48 hour period even in the dark. Compound **1** has been characterised by ^1H and ^{13}C NMR spectroscopy, elemental analysis and a single crystal X-ray structure determination.‡The spectroscopic and analytical data were consistent with the X-ray structure obtained from single crystals grown at room temperature from hexane solution. Compound **1** is monoclinic ($P2_1/n$) and isostructural with the Al(I) and Ga(I) derivatives **V** and **VI**.[5,6] The molecular structure, illustrated in Fig. 1, comprises well separated monomers with a V-shaped two-coordinate geometry at indium. The In–N(1)–C(1)–C(2)–C(3)–N(2) heterocycle is effectively planar (rms deviation of least squares plane = 0.0067 Å). The In–N bond lengths [2.268(3), 2.276(3) Å] are longer than those in previously reported In(III) derivatives bearing the same ligand (*e.g.* $[In\{(NDippCMe)_2CH\}X_2]$: X = I; 2.121(2), 2.147(1), X = Me; 2.190(1), 2.204(1) Å)[13] and the In(II) complex $[In\{(NDippCMe)_2CH\}Cl]_2$ (2.169(4), 2.172(4) Å)[11] which contains a direct In–In bond, but shorter than those in monomeric In(I) tris(pyrazolyl)borates [*e.g.* tris(3,5-di-*tert*-butylpyrazolyl)hydroboratoindium(I), average *ca.* 2.49 Å][14c] which contain an additional In–N interaction.[14] The N(1)–M–N(2) angle [81.12(10)°] in **1** is more acute than those in the Al(I) [89.86(8)°] and Ga(I) [87.53(5)°] derivatives, and the remaining endocylic angles in the chelate ligand are significantly wider than those observed in **V** and **VI**. As a result, the indium centre of **1** protrudes from the cavity provided by the ligand to a greater extent than the aluminium or gallium cations in **V** or **VI**. The isolation of **1** vindicates Power's surmise regarding the probable stability of this compound and shows that the In(I) centre is indeed stabilised towards disproportionation by the β-diketiminato ligand. It is unclear why **1** can be obtained from the potassium β-diketiminate and InI but not from the lithium β-diketiminate and InCl. It appears that the outcome of the metathesis is determined by the properties of intermediates produced *during* the reaction rather than by the stability of the In(I) carbene analogue. In the work described by Power it seems that these intermediates gave predominantly disproportionation products.[11]

Compound **1** is the first example of a neutral monovalent indium 'carbene analogue'. In(I) species are isoelectronic with the stannylenes, the most intensively studied Group 14 carbenoid species. Experiments to delineate the coordination and reaction chemistry of **1** will be reported in future publications.

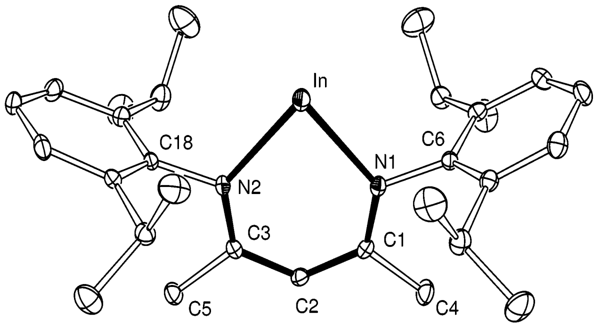


Fig. 1 Thermal ellipsoid plot (30%) of **1**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): In–N(1) 2.268(3), In(1)–N(2) 2.276(3), N(1)–C(1) 1.324(4), N(1)–C(6) 1.445(4), N(2)–C(3) 1.323(4), N(2)–C(18) 1.439(4), C(1)–C(2) 1.398(4), C(2)–C(3) 1.403(4), N(1)–In–N(2) 81.12(10), In–N(1)–C(1) 130.3(2), In–N(2)–C(3) 130.3(2), N(1)–C(1)–C(2) 124.6(3), C(1)–C(2)–C(3) 129.5(3), C(2)–C(3)–N(2) 124.2(3).

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Notes and references

† THF (50 mL) was added to a mixture of InI (1.00 g, 4.14 mmol), $K[N(SiMe_3)_2]$ (0.83 g, 4.14 mmol) and $[H(NDippCMe)_2CH]$ (1.73 g, 4.14 mmol) at −78 °C. Warming to room temperature in the absence of light produced a grey slurry. Volatiles were removed and the solid residue extracted with hexane (30 mL). Filtration and concentration of the filtrate produced compound **1** as pale yellow crystals suitable for X-ray diffraction analysis (0.80 g, 36%). Anal. Calc.(found) for $C_{29}H_{41}InN_2$: C 65.41 (65.72); H 7.78 (7.83); N 5.26 (5.15)%. Mp 203–205 °C (dec). ^{1}H NMR (270 MHz, toluene-d$_8$) δ 1.15 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.23 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 1.72 (s, 6H, C*Me*), 3.19 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$), 5.00 (s, 1H, C*H*), 7.14 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR (67.94 MHz, toluene-d$_8$) δ 23.8 (CH*Me*$_2$), 24.3 (C*Me*), 25.7 (CH*Me*$_2$), 28.3 (*C*HMe$_2$), 98.1 (γ-*C*H), 123.9 [*m*-*C*(Dipp)], 125.5 [*p*-*C*(Dipp)], 142.1 [*o*-*C*(Dipp)], 144.9 [*i*-*C*(Dipp)], 163.8 (*C*N).

‡ *Crystal data* at 173(2) K for **1** with Mo-Kα radiation (λ = 0.71073 Å): $C_{29}H_{41}InN_2$, M = 532.46, monoclinic, $P2_1/n$ (No. 14), a = 12.5576(4), b = 16.0978(7), c = 14.1307(5) Å, β = 105.421(2)°, V = 2753.68(18) Å^3, Z = 4, D_c = 1.28 g cm^{-3}, μ = 0.88 mm^{-1}, $R1$ = 0.038 for 3674 [$I > 2\sigma(I)$] data; $wR2$ = 0.099 for all data. Data collection Kappa CCD. Refinement using SHELXL-97. CCDC 238162. See http://www.rsc.org/suppdata/cc/b4/b406017b/ for crystallographic data in .cif format.

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