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Synthesis, characterisation and theoretical studies of amidinato-indium(I) and thallium(I) complexes: isomers of neutral group 13 metal(I) carbene analogues

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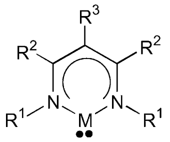
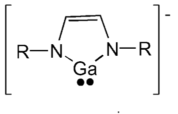
The synthesis and characterisation of the monomeric amidinato-indium(I) and thallium(I) complexes, [M(Piso)]·PisoH, M = In or Tl, Piso$^-$ = [ArNC(Bu^t)NAr]$^-$, Ar = $C_6H_3Pr^i_2$-2,6, are reported. These complexes, in which the metal centre is chelated by the amidinate ligand in an N,η^3-arene-fashion, can be considered as isomers of four-membered group 13 metal(I) carbene analogues. Theoretical studies have compared the relative energies of both isomeric forms of a model complex, [In{PhNC(H)NPh}].

The rapidly emerging importance of five-membered N-heterocyclic carbenes (NHCs),:C{N(R)C(R′)}$_2$, cannot be understated. Since they were first isolated in 1991, numerous reports of their complexation to the majority of the p-, d- and f-block metals have come forward.[1] Much of the interest in NHCs has derived from their special electronic properties which have led to many of their transition metal complexes exhibiting catalytic activity in a number of synthetic processes.[1b] Not surprisingly, studies of heavier p-block element analogues of these heterocycles have followed. In group 13, these include the neutral, monomeric six-membered β-diketiminato-metal(I) complexes, **1**,[2] the coordination and other chemistry of which has begun to be examined.[3] In addition, two direct valence iso-electronic analogues of NHCs, namely the anions, **2**, have been reported by our group[4] and that of Schmidbaur.[5] Like NHCs, one of these, **2**, R = $C_6H_3Pr^i_2$-2,6, has been shown to be very nucleophilic and capable of stabilising p- and d-block metal fragments which are normally thermally labile and/or contain the metal in a low oxidation state.[3]

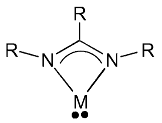
Considering the success had with these five and six-membered heterocycles, it seemed appropriate to attempt the preparation of neutral, four membered group 13 metal(I) heterocycles, **3**, and to subsequently develop their chemistry. Such a goal is especially timely, as the first example of a four-membered NHC has been very recently reported, and its use as a ligand in an olefin metathesis catalyst described.[6] Although the steric protection afforded the metal centre by the N-substituents in **3** is likely to be less than in **1** or **2**, the fact that N,N-chelating amidinate ligands have been shown to stabilise normally thermally labile group 13 metal(III) fragments (*e.g.* indium hydrides[7]), lent hope to our cause. Initial efforts in this direction have led, unexpectedly, to two monomeric N,arene-chelated isomers of **3**, the synthesis, characterisation and theoretical study of which are reported herein.



R^1 = $C_6H_3Pr^i_2$-2,6; R^2 = Me; R^3 = H
M = Al **1a**, Ga **1b**, In **1c** or Tl **1d**
R^1 = $C_6H_3Pr^i_2$-2,6; R^2 = CF_3; R^3 = H
M = In **1e**
R^1 = $C_6H_3Pr^i_2$-2,6; R^2 = H; R^3 = Ph
M = Tl **1f**
R^1 = $SiMe_3$; R^2 = Ph; R^3 = H
M = Tl **1g**

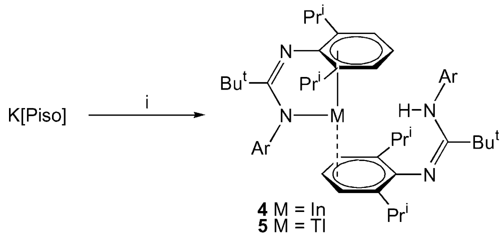


2 R = $C_6H_3Pr^i_2$-2,6
or Bu^t



3 M = group 13 metal
R = alkyl or aryl

The reaction of the potassium amidinate, K[Piso], Piso$^-$ = [ArNC(Bu^t)NAr]$^-$, Ar = $C_6H_3Pr^i_2$-2,6, with either InCl or TlBr in a 1 : 1 stoichiometry led to the amidinato-metal(I) complexes, **4** and **5**, in low to moderate yields (*ca.* 30%) after recrystallisation from hexane (Scheme 1). It is believed that the PisoH of crystallisation in these complexes arises from the partial decomposition of [M(Piso)], M = In or Tl, *via* metal deposition and solvent hydrogen abstraction. Similar decomposition processes have been suggested for examples of the β-diketiminato complexes, **1**.[2] Although the partial decomposition of [M(Piso)] can be avoided in these reactions, we have not yet been able to crystallise [M(Piso)] free of PisoH. As a result, higher yields of **4** and **5** were achieved with the 1 : 1 : 1 reactions of the metal halide, K[Piso] and PisoH. Hexane solutions of both **4** and **5** decompose, depositing metal, upon standing at 25 °C overnight, but the complexes display differing thermal stabilities in the solid state (**4** decomp. 150–155 °C, **5** decomp. 50–52 °C).



4 M = In
5 M = Tl

Scheme 1 *Reagents and conditions*: i, InCl or TlBr, PisoH, THF.

The solution state ^{1}H NMR spectra† of **4** and **5** are complicated but similar to each other. It is, however, clear that the weak interaction between the PisoH and [M(Piso)] fragments seen in the solid state is not retained in solution. The reasoning behind this conclusion is that the ^{1}H NMR spectra of the complexes dissolved in D_8-toluene exhibit the characteristic pattern for free PisoH, which is known to exist as a number of isomers in solution[8] and not solely as its *Z-anti*-isomer, as it does in the structures of **4** and **5**. In addition, there is little change in the appearance of the spectra over the temperature range 298–213 K, which suggests that there is no significant fluxional interaction of the fragments in solution. From the available NMR data we cannot be sure if the [M(Piso)] fragments of **4** and **5** retain their solid state structure in solution, or if they are in equilibrium with their heterocyclic form, *cf.* **3**. However, considering the likely high barrier to conversion between the two forms (*vide infra*) and the fact that **4** and **5** can be recrystallised unchanged from hexane/toluene solutions, it is probable that their N,arene-amidinate chelated structures persist in solution.

Compounds **4** and **5** are isomorphous‡ and thus only the molecular structure for **4** is depicted in Fig. 1. Both complexes are monomeric with the localised amidinate ligand chelating the metal in an η^1-N,η^3-arene fashion, rather than acting as a delocalised N,N-chelating ligand. It is noteworthy that a formamidinate anion, $[\mathrm{ArNC(H)NAr}]^-$ (Fiso$^-$), which is closely related to Piso$^-$ has recently been reported to act as a similar N,arene-chelating ligand in its potassium complex, $[\mathrm{K(THF)_3(Fiso)}]$.[9] The fact that **5** is monomeric is of interest, as recent work on thallium(I) amides has revealed their propensity to aggregate through intermolecular Tl–Tl and/or Tl–arene interactions,[10] *e.g.* as in $[\{\mathrm{TlN(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)}\}_4]$.[11] Saying that, monomeric thallium amides are accessible if bulky amide substituents are employed. Examples here include the two-coordinate systems, **1d,f** and **g**,[2d,e] and the essentially one-coordinate complex, $[\mathrm{TlN(Me)\{C_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\text{-}2,6\}}]$.[12]

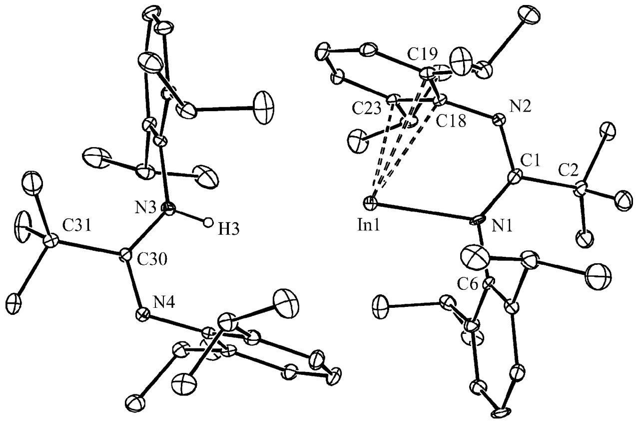


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.329(5), N(1)–C(1) 1.379(8), C(1)–N(2) 1.286(7), N(2)–C(18) 1.406(6), In(1)–C(18) 2.822(6), In(1)–C(19) 2.968(6), In(1)–C(23) 3.038(6), N(3)–C(30) 1.387(8), N(4)–C(30) 1.269(7), In(1)–N(1)–C(1) 126.3(4), N(1)–C(1)–N(2) 122.2(5), C(1)–N(2)–C(18) 119.9(5). Selected bond lengths (Å) and angles (°) for **5**: Tl(1)–N(1) 2.445(7), N(1)–C(1) 1.366(11), C(1)–N(2) 1.299(10), N(2)–C(18) 1.412(8), Tl(1)–C(18) 2.882(7), Tl(1)–C(19) 3.015(7), Tl(1)–C(23) 3.087(7), N(3)–C(30) 1.352(10), N(4)–C(30) 1.283(10), Tl(1)–N(1)–C(1) 125.6(5), N(1)–C(1)–N(2) 122.9(7), C(1)–N(2)–C(18) 120.4(6).

The Tl–N distance in **5** is in the normal range for thallium(I) amides,[13] though because of a strong dependence of Tl–N bond lengths on steric and electronic effects, this range is wide. In contrast, there are very few examples of indium(I) amides to compare to **4**, but its In–N separation is not dissimilar to those of **1c** [2.272 Å avge.][2c] and **1e** [2.361 Å avge.].[2d] In both **4** and **5** one arene substituent is approximately η^3-coordinated to the metal centre with M-arene least squares plane distances of 2.734(3) Å and 2.786(4) Å, respectively. The latter distance is within the normal range for intramolecular arene–Tl(I) interactions.[10] To the best of our knowledge there are no structurally characterised examples of intramolecular In–arene interactions in indium(I) amide complexes to compare with **4**, however, reported interactions between arenes and the $\mathrm{In^+}$ ion appear to be of a similar distance, *e.g.* 2.83 and 2.89 Å in $[\mathrm{In(\eta^6\text{-}mesitylene)_2}]^+$.[14] Although the arene substituent attached to N(4) in both structures appears to be orientated correctly with respect to the metal centres to act as a π-donor ligand, the large distances from the metal to the least squares plane of that substituent [**4** 3.978(4) Å and **5** 3.830(6) Å] suggest that any intermolecular M–arene interactions must be weak. In addition, the large separations between the amidine proton, H(3), and the metal centres [**4** 3.684(4) Å, **5** 3.583(5) Å] are probably not indicative of any unconventional hydrogen bonding interaction between the metal lone pair and N–H fragments.

In order to estimate the strength of the solid state interaction between the PisoH and [In(Piso)] molecules in **4**, DFT calculations were carried out on the model complex, $[\mathrm{In\{PhNC(H)NPh\}]\cdot\{PhN(H)C(H)NPh\}}$.[15] Starting from symmetrised (C_s) and "cut-down" coordinates taken from the X-ray crystal structure of **4**, the model complex converged with an optimised geometry similar to that observed in the solid state structure of the indium complex. The magnitude of the binding energy between the two molecular fragments was found to be very weak (7.20 kJ mol^{-1}), as expected.

We were also interested in examining the difference in energy between the isomers of **4** in which the amidinate ligand chelates the In centre in either an N,N- or N,arene-fashion. To this end, the geometries of both isomers of the model complex, $[\mathrm{In\{PhNC(H)NPh\}}]$ **6**, were optimised using the same DFT method as above. Graphical representations of these isomers, and relevant geometrical parameters, are depicted in Fig. 2. Isomer **6b** converged with a similar geometry to the [In(Piso)] fragment of **4**, taking into account the steric differences between the theoretical and experimental molecules. Isomer **6a** converged with a delocalised amidinate backbone and an essentially planar $\mathrm{InN_2C}$ four-membered ring. Not surprisingly, the In–N bond lengths of **6a** are significantly longer than that in **6b**. More surprising is the fact that **6a** is more stable than **6b** by 37.9 kJ mol^{-1}, despite the apparent strain of its four-membered ring. The barrier to conversion between these isomeric forms was found to be significant at 85.0 kJ mol^{-1}. An NBO charge analysis of isomer **6b** revealed the In–N bond to be largely ionic (In charge +0.778) and the lone pair at the indium centre to be essentially of s-character ($5s^{1.92}$ $5p^{0.30}$). In combination with the aforementioned M · · · H separations, these observations count against any significant M · · · H–N hydrogen bonding in **4** and **5**.

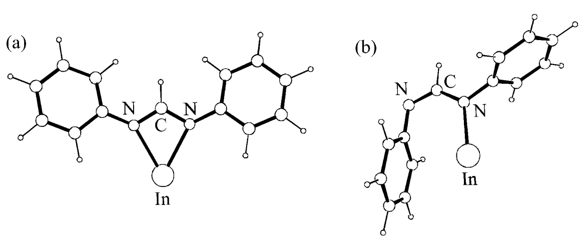


Fig. 2 Calculated and fully optimised geometries of (a) the N,N-amidinate chelating and (b) N,arene-amidinate chelating isomers of $[\mathrm{In\{PhNC(H)NPh\}}]$ **6**. Selected bond lengths (Å) and angles (°) for (a): In–N 2.397 (avge.), N–C(amid.) 1.321 (avge.), N–In–N 56.02, In–N–C(amid.) 93.43 (avge.), N–C–N 116.95; (b): In–N 2.281, N–C(amid.) 1.351, N=C(amid.) 1.295, In–phenyl plane 2.850, N–C–N 127.02, In–N–C(amid.) 125.26.

In conclusion, the synthesis and characterisation of monomeric amidinato-indium(I) and thallium(I) complexes has been reported. The former represents a rare example of an indium(I)–amide, and both can be considered as isomeric forms of four-membered group 13 metal(I) carbene analogues. Theoretical studies have suggested that the heterocyclic isomer of the indium amide, **4**, should be stable and perhaps interconvertible with its experimentally observed form. Our further efforts to stabilise four-membered group 13 metal(I) carbene analogues will be documented in a forthcoming publication.

Acknowledgements

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Notes and references

† *Synthesis and selected data for* **4**: A solution of K[Piso] (0.64 g, 1.40 mmol, prepared from the reaction of PisoH[8] and KN(SiMe$_3$)$_2$) and PisoH (0.59 g, 1.40 mmol) in THF (30 mL) was added over 5 min to a suspension of InCl (0.20 g, 1.32 mmol) in THF (20 mL) at −90 °C. The reaction mixture was warmed to 0 °C overnight in the absence of light, whereupon it was filtered and volatiles removed from the filtrate *in vacuo*. Extraction of the residue into hexane (30 mL) and concentration to *ca.* 6 mL afforded pale yellow crystals of **4** after placement at −30 °C overnight. Yield: 0.92 g (72 %); Mp 150–155 °C (dec.); ^{1}H NMR (400 MHz, C$_7$D$_8$, 298 K): δ 0.72–1.55 (overlapping unresolved multiplets, 48 H, CH(C*H*$_3$)$_2$), 1.27 (br. s, 9 H, Bu^t), 1.41 (s, 9 H, Bu^t), 3.02–3.45 (overlapping septets, 8 H, C*H*(CH$_3$)$_2$), 5.15 and 5.31 (2 br. s, 1 H, NH from PisoH isomers), 6.70–7.25 (overlapping m, 12 H, ArH); MS/APCI m/z (%): 533 (InPiso − H$^+$, 8), 422 (PisoH$_2^+$, 100); IR ν/cm^{-1} (Nujol): 3324(m) (NH), 1653(m), 1616(m), 1456(s), 1388(m), 1210(m), 932(m), 800(m), 767(m); accurate mass MS/EI calc. for [In(Piso)] C$_{29}$H$_{43}$N$_2$In: 534.2460, found: 534.2459; **5**: A similar procedure as was used to prepare **4** gave compound **5** as pale yellow crystals. (74%); Mp 50–52 °C (dec.); ^{1}H NMR (400 MHz, C$_7$D$_8$, 298 K): δ 0.78–1.43 (overlapping unresolved multiplets, 48 H, CH(C*H*$_3$)$_2$), 1.27 (br. s, 9 H, Bu^t), 1.47 (s, 9 H, Bu^t), 3.04–3.47 (overlapping septets, 8 H, C*H*(CH$_3$)$_2$), 5.13 and 5.31 (2 br. s, 1 H, NH from PisoH isomers), 6.65–7.26 (overlapping m, 12 H, ArH); MS/APCI m/z (%): 422 (PisoH$_2^+$, 100); IR ν/cm^{-1} (Nujol): 3331(m) (NH), 1651(m), 1614(m), 1455(s), 1376(m), 1211(m), 930(m), 801(m), 760(m). The ^{13}C{^{1}H} NMR spectra of both compounds displayed many broad, overlapping signals which could not be confidently assigned.

‡ *Crystal data* for **4**: C$_{58}$H$_{87}$InN$_4$ M = 955.14 triclinic, space group $P1$, a = 10.436(2), b = 10.670(2), c = 14.277(3) Å, α = 102.258(10), β = 109.421(10), γ = 105.790(10)o, V = 1360.1(5) Å^3, Z = 1, D_c = 1.166 g cm^{-3}, F(000) = 512, μ(Mo-Kα) = 0.473 mm^{-1}, 150(2) K, 10385 unique reflections [R(int) 0.0630], R (on F) 0.0529, wR (on F^2) 0.1261 ($I > 2\sigma I$); **5**: C$_{58}$H$_{87}$TlN$_4$ M = 1044.69 triclinic, space group $P1$, a = 10.398(2), b = 10.654(2), c = 14.201(3) Å, α = 102.53(3), β = 108.39(3), γ = 105.77(3), V = 1355.5(5) Å^3, Z = 1, D_c = 1.280 g cm^{-3}, F(000) = 544, μ(Mo-Kα) = 3.017 mm^{-1}, 120(2) K, 10072 unique reflections [R(int) 0.0928], R (on F) 0.0525, wR (on F^2) 0.1353 ($I > 2\sigma I$). During the course of refinement it was found that the metal atoms in both structures were disordered over two sites. This disorder was successfully modelled. CCDC reference numbers 272677 and 272648. See http://dx.doi.org/10.1039/b507242e for crystallographic data in CIF or other electronic format.

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