Solid- and solution-state structures of indium 'alkene analogues'

Michael S. Hill,*^a Peter B. Hitchcock^b and Ruti Pongtavornpinyo^a

Received 15th November 2006, Accepted 20th November 2006 First published as an Advance Article on the web 29th November 2006 DOI: 10.1039/b616747k

Although the nuclearity of In(I) 'carbenes' is dependent upon the steric demands of the supporting β -diketiminate ligand, it is shown by solution NMR diffusion (DOSY) methods that the In–In interactions observed in the solid-state are very weak and not retained in solution.

Lappert's report of the kinetically stabilised dimeric stannane diyl, 1, represented a watershed in our appreciation of the chemistry of the heavier p-block elements.1 Although now recognised as the first true heavy metal 'alkene analogue' (i.e. valence isoelectronic to a C=C double bond), the discovery that the Sn-Sn 'double bond' is weak and not retained in solution indicated that this analogy for principal quantum numbers >5 is tenuous at best and must be tempered by considerations embodied by the classical inert pair effect.¹ Recent research in our laboratory has concentrated upon the effects of varying the steric demands of indium diyls supported by anions derived by deprotonation of the N-aryl substituted iminoenamines, 2-5. Monomeric singlet indium diyls were isolated when $Ar = 2,6^{-i}Pr_2C_6H_3$ (e.g. 6),² while use of less sterically demanding N-mesityl subsituents permitted solid-state dimerisation and the formation of compound 7,3 which may be viewed as isoelectronic to the bis(stananne)diyls exemplified by 1. Further moderation of the steric demands of the Naryl substituents to 3,5-Me₂C₆H₃ resulted in the isolation of a remarkable linear catenated hexa-indium complex, 9, which displays behaviour consistent with a 'o-delocalised' manifold of molecular orbitals.⁴ The dimeric compound, 7, featured a long In-In interaction of 3.1967(4) Å in the solid state. Although instability to reductive decomposition restricted a thorough assessment of the solution molecularity of 7 by cryoscopy, our initial appraisal of the strength of the In-In interaction present in the solid state, in common with earlier analyses of oligomeric species containing either In(I)-In(I) or Ga(I)-Ga(I) contacts, signified that it is doubtful that anything other than transient In-In interactions persist in solution.3,5 In this report we detail a further In(I) complex that is similarly dimeric in the solid state. We also offer an experimental assessment of the molecularity of these species in solution from NMR-based diffusion measurements and consider the consequences of these data in relation to the nature of the M-M interactions in diyls of the heavier Group 13 elements.

Compound **8** was synthesised by a similar method to that reported for all our previous indium complexes,²⁻⁴ involving a simple metathesis reaction between the potassium β -diketiminate, [CH{(Me)CN-(2,6-Me₂C₆H₃)}₂K], and InI in THF. Extraction and crystallisation from hexane produced the analytically pure



compound, [CH{(Me)CN- $(2,6^{-i}Me_2C_6H_3)$]₂In] in reasonable (*ca.* 40% isolated) yield as pale orange/red crystals. The room temperature ¹H and ¹³C NMR spectra of the isolated material were very simple and indicated C_2 symmetry about the In centre.† A single crystal X-ray structural analysis (Fig. 1)‡ revealed that **8** dimerises in the solid-state in a similar manner to that observed in the *N*-mesityl analogue, compound **7**. The most notable contrast



Fig. 1 ORTEP diagram of **8** (50% probability ellipsoids). H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: In–N(1) 2.266(2), In–N(2) 2.270(2), In–In′ 3.3400(5), N(1)–C(1) 1.328(4), N(1)–C(6) 1.432(4), N(2)–C(3) 1.328(4), N(2)–C(14) 1.443(4), C(1)–C(2) 1.396(5), C(2)–C(3) 1.402(4); N(1)–In–N(2) 82.00(9), N(1)–In–In′ 109.72(7), N(2)–In–In′ 112.33(6), In–N(1)–C(1) 129.0(2), In–N(2)–C(3) 129.0(2), N(1)–C(1)–C(2) 124.3(3), C(1)–C(2)–C(3) 129.9(3), C(2)–C(3)–N(2) 124.2(3). Symmetry transformations used to generate equivalent atoms: '-x + 1, -y + 1, -z + 1.

^aDepartment of Chemistry, Imperial College London, Exhibition Rd, South Kensington, London, UK SW7 2AZ. E-mail: mike.hill@imperial.ac.uk; Fax: +44 (0)20 7594 5804; Tel: +44 (0)20 7594 5709 ^bSchool of Chemistry, University of Sussex, Falmer, Brighton, UK BN1 9QJ

to the structure of 7 is the conspicuous elongation of the In-In distance [3.3400(5) Å] in 8 despite what could be interpreted as a minor reduction in the steric protection of the In centres by replacement of the p-Me groups of the flanking N-aryl substituents with protons. This value is, in fact, in close agreement to the In-In separation determined by our DFT (B3LYP/LAN2DZ) calculations on the model complex [CH{(H)CNH}2In]2, 10 [3.388 Å], which we described as 'overestimated' in comparison to that of 7 in our previous communication.³ Independent of our research, an even longer In-In distance [3.428 Å] was calculated by Su et al. for the more realistic model species $[HC{(Me)CNPh}_2In]_2$, 11.6 Both calculations interpreted the In-In bonding in these complexes in a similar manner to that described for the rather more well precedented 'alkene analogues' of the heavier Group 14 elements via the formation of polarised donor-acceptor interactions between the metal centres, such as that depicted for the bis(stannane)diyl, 1. A complementary molecular orbital description ascribes increased non-bonding (or even antibonding) character to the b_u HOMO (via π/σ^* mixing, Fig. 2) with increasing principal quantum number of the valence orbitals of the Group 13 or 14 element. Both of these bonding models require somewhat localised interactions to be constructed from the diffuse atomic orbitals of the fifth quantum shell. Pyykkö has suggested that the M-M bonding within dimeric In(I) and Tl(I) species are better regarded as non-directional but attractive closed shell interactions analogous to those more commonly observed between gold(I) centres.^{7,8} On the basis of relativistic calculations the trans-bent geometries observed in the experimentally determined dimeric structures of $[C_5(CH_2Ph)_5M]$ (M = In, Tl) were reasoned to be a result of crystal packing forces.9 It seems likely, therefore, that this interpretation of the In-In bonding within 7 and 8 is equally, if not more, realistic.



Fig. 2 Possible π/σ^* mixing in 'heavy alkenes'.

While the demarcation between the different bonding models is unclear, it is evident from both the experimental and computational data that the In–In interactions within 7 and 8 are very weak. Although we proposed in our previous communication that it was highly unlikely that the In–In interactions within compound 7 (and in this communication, compound 8) persisted in solution,³ attempts to provide an experimental verification of this contention by cryoscopic methods were fruitless due to the solution instability of both complexes. An alternative means to determine the molecular volume and apparent hydrodynamic radii, $r_{\rm H}$, of molecular species has recently come to the fore through the application of NMR pulse gradient spin echo (PGSE) techniques to the direct measurement of molecular diffusion coefficients, *D*, in solution.¹⁰ PGSE data are easily acquired and may be presented as a 2D spectrum in which the chemical shift is displayed in the first dimension and the diffusion coefficient in the second one. These experiments are referred to as diffusion ordered spectroscopy (DOSY) and are independent of either concentration or even sample purity as long as the resonances of the species of interest are clearly defined. Indeed, such measurements have even been labelled 'NMR chromatograms' due to the ease with which specific resonances may be correlated by simple reference to their apparent diffusion coefficients.¹⁰ Once values of *D* have been determined for the species of interest, these may be related directly to the hydrodynamic radii *via* the Stokes–Einstein equation (eqn (1), where η = viscosity of the solvent at the temperature of the NMR experiment).

$$r_{\rm H} = \frac{kT}{6\pi\eta D} \tag{1}$$

The diffusion coefficients of the indium species, **6**, **7** and **8**, along with those of the iminoenamine precursors, **2–4** were determined in benzene solution at 298 K. Table 1 lists the experimentally determined values of *D* for each of the compounds together with the apparent hydrodynamic radii calculated using eqn (1). Also listed are radii (r_{mono} and r_{dimer}), estimated from the solid-state crystallographic data for both monomeric and, where appropriate, dimeric formulations of **6**, **7** and **8**. These latter values were calculated from the crystallographic coordinates through use of the 'sp volume' keyword of the Gaussian03 suite of programmes and an assumption that the tumbling molecules are 'spherical' (*i.e.* volume = $4/3\pi r^3$) with regard to their apparent radii in benzene solution.¹¹

Examination of the data in Table 1 shows that the the $r_{\rm H}$ values from the DOSY measurements show an acceptable agreement with those calculated for the mononuclear species, r_{mono} , in all three cases. Although the absolute values obtained from the solution measurements should be viewed with caution, it is clear that the trend of reducing radius (i.e increasing D) with decreasing N-aryl bulk of the supporting ligand environment may be confidently interpreted as the result of an analogous monomeric formulation of 6, 7 and 8 in C_6D_6 solution. This is further illustrated by the DOSY correlation spectrum in Fig. 3 resulting from measurements on a (1:1:1) three-component mixture of the compounds under study, which neatly emphasises the use of the PGSE technique as a form of 'NMR chromatography'. The values listed for the three ligand precursors, 2–4, show a similar trend of reducing $r_{\rm H}$, but are are actually slightly higher than the corresponding indium derivatives. This is possibly a result of the greater degree of freedom of the uncoordinated species.

Table 1 Diffusion coefficients and calculated radii of 6-8 and 2-4

	$D/10^{-10} \text{ m}^2 \text{s}^{-1}$	$r_{ m H}{}^a/{ m \AA}$	$r_{\rm mono}{}^b/{\rm \AA}$	$r_{\text{dimer}}{}^{b}/\text{\AA}$	
6	6.95	4.93	5.13	_	
7	7.58	4.49	4.96	6.04	
8	7.63	4.37	4.62	5.66	
2	6.50	5.23			
3	7.39	4.60			
4	7.67	4.43			

^{*a*} Calculated using eqn (1). ^{*b*} Calculated (Gaussian03) from crystallographic coordinates as detailed in text.



Fig. 3 DOSY spectrum of a 1:1:1 mixture of compounds 6 (red), 7 (blue) and 8 (black).



Fig. 4 ORTEP diagram of 12 (20% probability ellipsoids). H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: In(1)–O(1) 2.014(4), In(1)–O(3) 1.977(5), In(1)–N(1) 2.188(5), In(1)–N(2) 2.179(5), In(2)–O(1) 1.998(4), In(2)–O(2) 1.999(5), In(2)–N(3) 2.163(5), In(2)–N(4) 2.169(6), In(3)–O(2) 1.972(5), In(3)–O(3) 2.006(5), In(3)–N(5) 2.187(5), In(3)–N(6) 2.163(5); N(1)–In(1)–N(2) 87.9(2), O(1)–In(1)–O(3) 116.77(19), N(3)–In(2)–N(4) 87.8(2), O(1)–In(2)–O(2) 117.5(2), N(5)–In(3)–N(6) 87.7(2), O(2)–In(3)–O(3) 117.7(2).

Although we are continuing to explore the oxidative reaction chemistry of the In(I) compounds, **6–8**, the monomeric and 'carbene-like' formulation of all three species in hydrocarbon solution indicates that this reactivity will almost certainly exclude 'olefin-like' addition chemistry (*i.e.* with maintenance of an In– In interaction) for compounds **7** and **8**. Indeed, any divergence of reactivity of **6**, **7** or **8** with oxidising reagents is likely to be solely a result of kinetic factors and the differing steric demands of the supporting ligands. For example, a hexane solution of the *o*-xylyl substituted complex **8**, rapidly decolourises when exposed to air and deposits the trimeric indium oxide, **12**, (Fig. 4)‡ as the only reaction product. Although the outcome of a similar reaction of the more sterically hindered compound **6** has not yet yielded a definitive result, it is likely that the indium oxide will have a dimeric constitution by analogy to the known gallium oxide and sulfide species, $[HC{(Me)C(2,6-{}^{i}Pr_{2}C_{6}H_{3})}_{2}GaE]_{2}$ (E = O or S).¹²

We are continuing to sudy the reactivity of these, and related, well defined In(I) species.

We would like to thank the Royal Society for a University Research Fellowship (MSH) and Mr Peter Haycock for assistance with the diffusion NMR measurements.

Notes and references

† Selected analytical data; **8**: mp 175 °C. Elemental analysis: C₄₂H₃₀In₂N₄: calcd C 60.02, H 6.00, N 6.67; found C 60.12, H 6.00, N 6.57%; ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.58 (s, 6H, CMe), 2.11 (s, 12H, *o*-Me), 4.88 (s, 1H, CH), 6.95 (m, 2H, *p*-ArH), 7.08 (d, 4H, *m*-Ar). ¹³C{¹H} (100.6 MHz, C₆D₆) δ = 24.2 (*m*-Me), 28.4 (CMe), 102.9 (*γ*-CH), 129.4 (ArH), 133.0 (ArH), 133.9 (ArH), 142.3 (*i*-Ar), 153.4 (CN). **12**: Elemental analysis: C₆₃H₃₅In₃N₆O₃: calcd C 57.76, H 5.73, N 6.42; found C 57.78, H 6.68, N 6.36%; ¹H NMR (270 MHz, C₆D₆, 25 °C): δ = 1.54 (s, 6H, CMe), 2.13 (s, 12H, *o*-Me), 4.81 (s, 1H, CH), 6.97–7.08 (m, 6H, *m*,*p*-ArH).

‡ Crystal data: 173 K, Nonius Kappa CCD diffractometer, λ(Mo Ka) = 0.71073 Å. **8**: C₄₂H₃₀In₂N₄, M = 840.50, triclinic, $P\overline{1}$ (No. 2), a = 8.6989(5), b = 10.0246(6), c = 12.3181(7) Å, a = 67.338(3), $\beta = 82.783(3)$, $\gamma = 83.862(3)^\circ$, V = 981.38(10) Å³, Z = 1, $\mu = 1.21$ mm⁻¹, 7198 collected reflections, 3420 independent reflections [R(int) = 0.045], R indices [$I > 2\sigma(I)$] R1 = 0.033, wR2 = 0.073, [all data] R1 = 0.041, wR2 = 0.076. **12**: C₆₃H₇₅In₃N₆O₃, M = 1308.75, monoclinic, $P2_1/n$ (No. 14), a = 13.9231(3), b = 34.7614(10), c = 14.0230(3) Å, $\beta = 118.27(3)^\circ$, V = 5977.3(3) Å³, Z = 4, $\mu = 1.20$ mm⁻¹, 24282 collected reflections, 8154 independent reflections [R(int) = 0.049], R indices [$I > 2\sigma(I)$] R1 = 0.051, wR2 = 0.096, [all data] R1 = 0.078, wR1 = 0.106. CCDC reference numbers 625827 and 625828. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616747k

- 1 Review: P. P. Power, Chem. Rev., 1999, 99, 3463.
- 2 (a) M. S. Hill and P. B. Hitchcock, *Chem. Commun.*, 2004, 1818; (b) M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Dalton Trans.*, 2005, 1433.
- 3 M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Angew. Chem.*, 2005, 44, 1433.
- 4 M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Science*, 2006, **311**, 1904.
- 5 For example: (a) W. Uhl, A. Janschak, W. Saak, M. Kaupp and R. Wartchow, Organometallics, 1998, 17, 5009; (b) N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, Angew. Chem., Int. Ed., 2002, 41, 2842; (c) R. J. Wright, A. D. Phillips, N. J. Hardman and P. P. Power, J. Am. Chem. Soc., 2002, 124, 8538 and references therein.
- 6 C.-H. Chen, M.-L. Tsai and M.-D. Su, Organometallics, 2006, 25, 2766.
- 7 P. Pyykkö, Chem. Rev., 1997, 97, 597.
- 8 H. Schmidbaur, S. Cronje, B. Djordjevic and O. Schuster, *Chem. Phys.*, 2005, **311**, 151.
- 9 P. Pyykkö, M. Straka and T. Tamm, *Phys. Chem. Chem. Phys.*, 1999, 1, 3441.
- 10 P. S. Pregosin, P. G. Anil Kumar and I. Fernndez, *Chem. Rev.*, 2005, 105, 2977.
- 11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- 12 N. J. Hardman and P. P. Power, Inorg. Chem., 2001, 40, 2474.