

Dimerization of Indanediyl Fragments: An Alkene Analogue for Group 13?*

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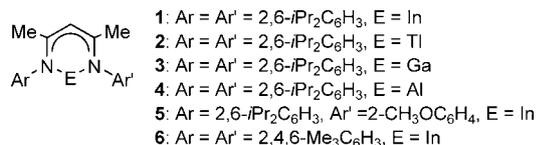
The occasionally vexed question of the potential for homo-nuclear multiple bonding between the heavier elements of Groups 13 and 14 continues to provoke intense interest.^[1] For the wide-ranging family of Group 14 derivatives in this category, a lineage that culminated in the recent synthesis of the long-sought silicon alkyne analogue, 1,1,4,4-tetrakis[bis-(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilyne,^[2] may be traced directly to the seminal discovery of the dimeric stannanediyl $[[[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Sn}]_2]$ by Lappert and co-workers.^[3] All possible alkene and alkyne analogues based on a link between two Group 14 centers have since been prepared.^[4] The structures of these R_2EER_2 and REER (E = Group 14 element) complexes substantiate an incremental decrease in the strength of any π -bonded component on transition from the respective planar D_{2h} and linear $D_{\infty h}$ structures. More pronounced *trans*-bent (C_{2h}) configurations (defined by the out-of-plane angle δ) are observed as the group is descended, alongside an increasing tendency of the R_2EER_2 species to dissociate to monomeric forms in solution. These observations have been attributed to the increasing stability of the lone pair of electrons in the *ns* orbital with increasing atomic number and the formation of polarized donor–acceptor interactions between the metal centers. A complementary molecular-orbital description ascribes increased nonbonding (or even antibonding) character to the b_u highest unoccupied molecular orbital (HOMO), through σ^* mixing, with increasing principal quantum number of the valence orbitals of E.^[1,4]

Similar questions of multiple bond order in respect to Group 13 species have been especially problematic. The claim by Robinson and co-workers^[5] of a triple-bond interaction between the Ga centers of the reduced species $[\text{Na}_2(\text{GaC}_6\text{H}_32,6\text{-trip})_2]$ (trip = 2,4,6-*i*Pr₃C₆H₂) provoked vigorous debate,^[5–13] while the subsequent work of Power and co-workers has highlighted as many contrasts as similarities within complexes maintaining contacts between formally low-valent heavier Group 13 and 14 elements.^[14–16]

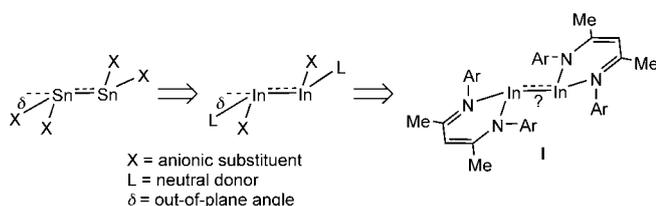
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Our entry point was provided by the syntheses of the monovalent indium and thallium β -diketiminate derivatives **1** and **2**, respectively.^[17] These compounds exist as well-sepa-

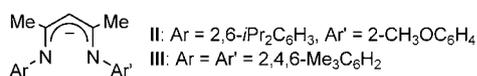


rated singlet “carbene analogues” and are isostructural to the previously reported gallium and aluminum complexes, **3** and **4**, respectively.^[18,19] It has been observed that variation of the overall steric demands of the bulky terphenyl ligands in combination with a low-valent gallium or indium center results in either monomeric or metal–metal-bonded species, the nuclearity of which is dictated by the size and topology of the stabilizing ligand system.^[16,20] Although investigations by us suggested that an ability to isolate the two-coordinate species **1–4** was chiefly a product of the kinetic stability imparted by the bulky *N*-aryl 2,6-diisopropylphenyl (dipp) substituents,^[17–19] we reasoned that use of substituents with decreased steric demands would similarly promote the formation of compounds with higher nuclearity. A particularly appealing target was the dimeric species, illustrated as the localized enamideimine form **I**, which may be considered as essentially isoelectronic to the stannanediyl discovered by Lappert and co-workers and other dimeric stannanediyls (Scheme 1).



Scheme 1. Generalized Sn=Sn and In=In complexes and target dimeric species **I**.

Known anions **II** and **III** were selected to provide an incremental decrease in the steric demands of the supporting ligand environment.^[21] The appropriate β -imino amine pre-



cursor was used in a synthetic route identical to that employed in the synthesis of **1**, providing facile access to In^I derivatives supported by **II** and **III**. Although the THF reaction solutions were somewhat photo- and thermally sensitive to depositing indium metal, rapid workup and crystallization in the dark from hexane at 5 °C provided yellow crystals of the desired In^I derivatives **5** and **6**. In common with the behavior of **1**, both compounds begin to decompose immediately on dis-

solution in aromatic solvents. Prompt acquisition of ¹H and ¹³C NMR spectra in [D₆]benzene, however, enabled collection of data that were consistent with C_s- and C₂-symmetric structures for **5** and **6**, respectively. This solution lability to reductive decomposition has thus far restricted a thorough assessment of the nature of these species in solution. However, our appraisal of the strength of the In–In interactions present in the solid state (see below) and the analysis of Power and co-workers of the unique neutral Group 13 dimers [(2,6-dippC₆H₃M)₂] (M = Ga, In)^[14,16] indicate that it is unlikely that anything other than transient In–In interactions persist in solution.^[22]

Although crystalline samples of both complexes may be successfully manipulated for crystallographic purposes, both compounds darken because of the separation of metallic indium over the course of several days, even when stored at low temperature under N₂ and in the dark. These difficulties notwithstanding, the molecular structures of both compounds were determined by single-crystal X-ray diffraction studies. Although the data for **5** were of a poor quality, the structure, in common with our previously reported indium complexes bearing dipp substituents at both nitrogen donor centers, was unambiguously monomeric and contained no short In–In interactions (Figure 1). It is apparent that the presence of a single dipp group is sufficient to prevent any well-defined intermolecular contact.

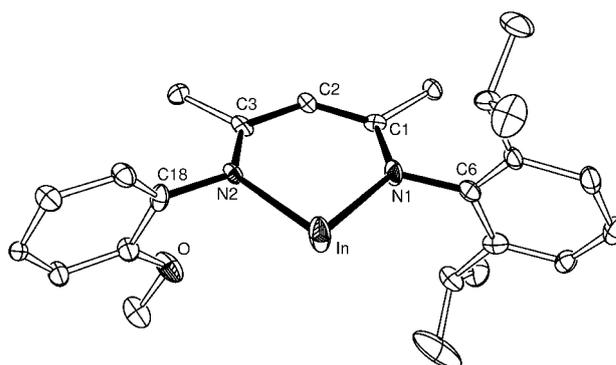


Figure 1. Structure of **5** (ORTEP plot, ellipsoids are set at 20% probability; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: In–N1 2.277(10), In–N2 2.257(9), N1–C1 1.339(16), N1–C6 1.461(18), N2–C3 1.318(15), N2–C18 1.453(15), C1–C2 1.389(18), C2–C3 1.414(17); N1–In–N2 82.6(4), In–N1–C1 128.0(8), In–N2–C3 129.0(7), N1–C1–C2 125.1(10), C1–C2–C3 129.5(13), C2–C3–N2 125.3(12).

Further X-ray analysis of **6** provided high-quality data and revealed that replacement of both of the dipp substituents of **1** by mesityl permits dimerization through the formation of a direct In–In bond. The centrosymmetric dimer possesses approximate C_{2h} symmetry with a mutual *trans*-bent orientation of the N-chelated ligands (Figure 2). It is notable, therefore, that **6** provides the first example of a neutral dimeric Group 13 species that is formally isoelectronic to the historically significant bis(stannane)diyls. The space-filling models shown in Figure 3 emphasize the efficient encapsulation of the In–In bond axis provided by the *N*-mesityl substituents of the chelate ligands within the dimeric arrange-

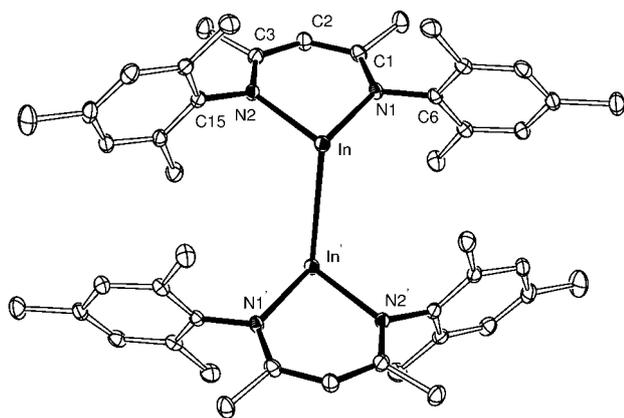


Figure 2. Structure of **6** (ORTEP plot, ellipsoids are set at 25% probability; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: In–N1 2.262(2), In–N2 2.256(2), In–In' 3.1967(4), N1–C1 1.336(3), N1–C6 1.435(3), N2–C3 1.327(3), N2–C15 1.435(3), C1–C2 1.394(4), C2–C3 1.397(4); N1–In–N2 83.15(8), N1–In–In' 110.65(6), N2–In–In' 107.88(6), In–N1–C1 127.68(19), In–N2–C3 128.73(19), N1–C1–C2 125.1(3), C1–C2–C3 130.2(3), C2–C3–N2 124.4(3).

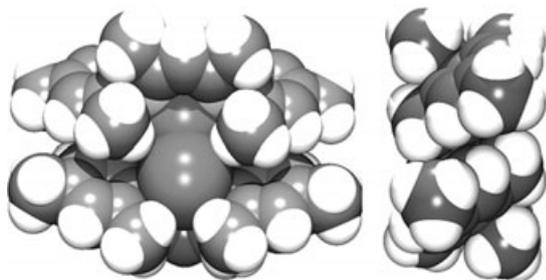


Figure 3. Space-filling (POVRAY) illustrations of **6** showing the kinetic protection of the In–In bond.

ment. The In–In distance in **6** (3.1967(4) Å) is significantly longer than that observed in the dimeric terphenyl derivative [(2,6-dippC₆H₃In)₂] (2.9786(5) Å).^[16] Irrespective of the precise details of the bonding, this elongation can be interpreted in a straightforward manner as a consequence of the increased overall coordination number of the individual indium centers in **6** (three compared to two). This view is given further credence by the observation that the only other known In^I dimer features pentahapto coordination with a pentabenzylcyclopentadienyl anion and a very weak In⋯In interaction of 3.631(2) Å.^[23] The In–In distance in **6** also lies well above the range established for typical In–In single bonds, such as those within the β-diketiminato disproportionation product [{"HC[CMeN(dipp)]₂InCl]₂] (2.8343(7) Å) and the three-coordinate indium centers of [{"(2,4,6-*i*Pr₃C₆H₂)₂In]₂] (2.775(2) Å), both of which feature formally divalent indium.^[24,25] The β-diketiminato chelate structure is effectively planar (root-mean-square deviation of the In–N1–C1–C2–C3–N2 plane: 0.03 Å) with the result that the *trans*-bent configuration may be accurately defined by the In'–In–C2 angle of 113.02°. This represents an out-of-plane angle of 66.98° and indicates that dimerization occurs with a significantly greater degree of pyramidalization (with respect to a

planar alkene-like *D*_{2h} structure) than that observed in the majority of homoleptic stannylenes of the general formula R₂SnSnR₂ (typically δ = 30–45°).^[1]

Dimerization has little effect on the local environment around the indium center provided by the chelated β-diketiminato ligand. The N1–In–N2 angle (83.15(8)°) is similar to the angles observed in the mononuclear compounds **1** and **5** (81.12(10) and 82.6(4)°, respectively), whereas the In–N1 and In–N2 bond lengths (2.262(2) and 2.256(2) Å, respectively) are actually the shortest observed for any indium(i) β-diketiminato chelate.^[17] This latter, somewhat counterintuitive, feature occurs despite the increased coordination number of the indium centers and may be an illustration of the decreased steric demands of the chelated ligands and intrasubstituent repulsion.

We undertook DFT calculations on the dimeric model complex [{"In[N(H)C(H)]₂CH]₂] by using the B3LYP DFT and LANL2DZ pseudo potentials (and basis set) implemented in Gaussian 03.^[26] The bond lengths and angles with regard to the two indium-containing fragments of the fully optimized structures are, in general, within 2% of the experimentally determined parameters. The In–In distance for the model system is, however, somewhat overestimated at 3.388 Å, as is the degree of *trans* bending indicated by the out-of-plane angle of 77.69°. The calculated molecular orbitals of this model compound do, however, reveal a qualitative insight into the In–In bonding present within **6** and provide a cogent comparison to bonding models developed for related Group 13 and 14 species. The frontier molecular-orbital diagram is presented in Figure 4 and illustrates that the

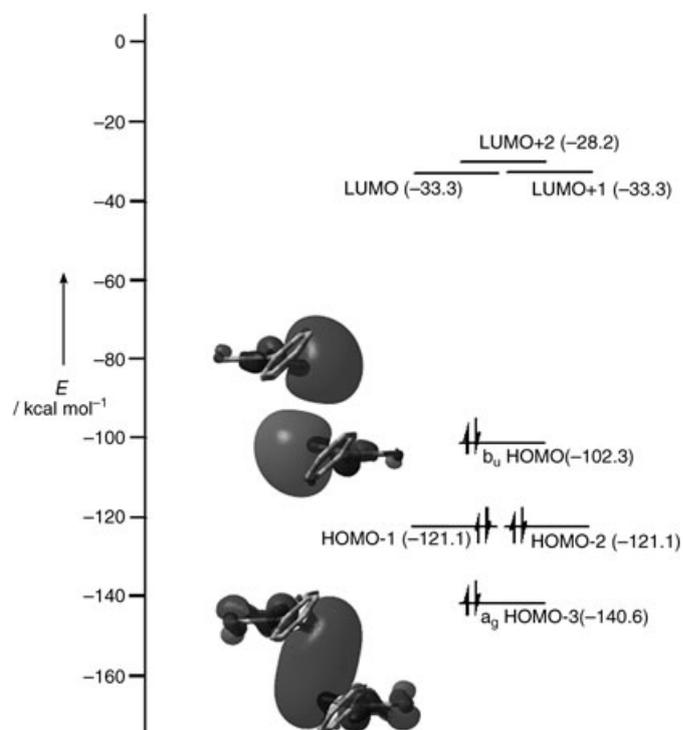


Figure 4. Calculated (B3LYP/LANDZ) frontier molecular-orbital diagram for [{"In[N(H)C(H)]₂CH]₂] illustrating the b_u HOMO and a_g HOMO-3. LUMO = lowest unoccupied molecular orbital.

HOMO is a b_u orbital that is nonbonding with regard to In–In contact. The degenerate HOMO-1 and -2 provide a level of π overlap between the indium centers and the nitrogen donor atoms of the chelated ligands. The HOMO-3 is an In–In σ -bonding orbital of A_g symmetry. This a_g orbital thus provides the primary bonding interaction between the metal centers. This view of the metal–metal bonding within **6** is qualitatively similar to that which has been evinced for alkene analogues of the heavier Group 14 elements and some multiply bonded gallium species.^[1,9–13,27] The b_u HOMO in these cases has been variously interpreted as a “slipped” π bond or as possessing lone-pair or even antibonding character. Experimental and theoretical studies of heavier Group 14 R_2EER_2 species indicate that, despite increased lone-pair character with increased atomic mass of E, the π -bonding b_u HOMO acts to provide a minor augmentation of the overall bonding interaction between the metal centers.^[1] A similar rationale has been applied to the recently completed series of REER derivatives.^[4] The data presented herein and the somewhat limited literature precedents highlight some notable contrasts within Group 13. The experimental data indicate that In–In bonding with π character within **6** is feeble at best, or indeed destructive. A further calculation based on the separation of $\{[In\{(N(H)C(H)_2)CH\}_2]\}$ into two singlet indanediyl fragments provided a bond-dissociation energy of only 2 kcal mol⁻¹. This extremely low value is commensurate with values calculated (ca. 3 kcal mol⁻¹) for the separation of the two $\{InH\}$ fragments of $[In_2H_2]$ and suggests that the notion of “multiple bonding” within molecules such as **6** is fallacious if the only expectation is an augmentation of the overall bond strength.^[28] The weakness of the Ga–Ga bonding within the neutral complex $\{[(2,6-dipp)_2C_6H_3Ga]_2\}$ was similarly attributed to the large energy difference between the lone pair on the singlet Ga' center and the p orbitals.^[14] This situation is likely to be exacerbated in the current case by N–In π interactions within the planar β -diketiminato chelates and indicates that the “multiple bonding” present within **6** actually represents an overall bond order of less than unity. This view of the HOMO within homonuclear bonding in Group 13 elements has been emphasized previously by calculations carried out on the hypothetical cationic species $[MeGaGaMe]^+$.^[11] In this case, removal of an electron from the b_u HOMO of $[MeGaGaMe]$ caused a decrease of approximately 0.2 Å in the computed Ga–Ga bond length. Preliminary calculations on the $\{[In\{(N(H)C(H)_2)CH\}_2]^+\}$ species indicated a similar and pronounced contraction of the In–In bond length to approximately 3 Å and highlighted the fact that the b_u HOMO may also possess antibonding character. Experiments to assess the validity of this hypothesis and further studies on the reactivity of these unusual species are in progress.

Experimental Section

5: Precooled THF (20 mL) was added at -78°C to a rapidly stirred mixture of **II**-H (0.45 g, 1.25 mmol), InI (0.30 g, 1.25 mmol), and $KN(SiMe_3)_2$ (0.24 g, 1.25 mmol) in the absence of light. The reaction mixture was stirred for 3 h and allowed to warm to room temperature to produce a gray slurry. Volatiles were removed and the gray solid

residue extracted with hexane (25 mL). Filtration, concentration to approximately 10 mL, and storage at 5°C afforded bright yellow crystals suitable for X-ray analysis (0.29 g, 49%). Elemental analysis calcd (%) for $C_{24}H_{31}InN_2O$: C 60.26, H 6.55, N 5.86; found: C 62.26, H 5.47, N 5.42 (partially decomposed in transit); 1H NMR (270 MHz, $[D_6]benzene$, 25°C): $\delta = 1.14$ (d, 6H, $^3J_{HH} = 6.9$ Hz; $CH(CH_3)_2$), 1.21 (d, 6H, $^3J_{HH} = 6.9$ Hz; $CH(CH_3)_2$), 1.75 (s, 3H; CCH_3), 1.90 (s, 3H; CCH_3), 3.20 (m, 2H, $^3J_{HH} = 6.9$ Hz; $CH(CH_3)_2$), 3.25 (s, 3H; OCH_3), 5.06 (s, 1H; CH), 6.50 (d, 1H; ArH), 6.88–6.96 (m, 2H; ArH), 7.15–7.16 ppm (m, 4H; ArH); $^{13}C\{^1H\}$ NMR (125.8 MHz, $[D_6]benzene$): $\delta = 23.8$ ($CH(CH_3)_2$), 25.7 (CCH_3), 28.2 ($CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 55.1 (OCH_3), 98.7 (γ -CH), 111.8, 121.3, 123.3, 123.9, 124.5, 125.2, 125.5, 125.8, 126.7, (ArH) 142.3 (o -C(dipp)), 145.2 (i -C(dipp)), 155.6 (i -Ar-2- OCH_3), 163.6 (CN), 163.9 ppm (CN).

6: This compound was made by the same general method employing **III**-H (0.69 g, 2.07 mmol), InI (0.50 g, 2.07 mmol), and $KN(SiMe_3)_2$ (0.42 g, 2.10 mmol) to afford pale yellow rectangular crystals suitable for X-ray analysis (0.42 g, 45%). Elemental analysis (%) calcd for $C_{46}H_{58}In_2N_4$: C 61.62, H 6.53, N 6.25; found: C 61.68, H 6.47, N 6.18; 1H NMR (500 MHz, $[D_6]benzene$, 25°C): $\delta = 1.59$ (s, 6H; CCH_3), 2.03 (s, 12H; o - CH_3), 2.12 (s, 6H; p - CH_3), 4.92 (s, 1H; CH), 6.76 ppm (s, 4H; m - ArH); $^{13}C\{^1H\}$ NMR (125.8 MHz, $[D_6]benzene$): $\delta = 19.3$ (o - CH_3), 20.9 (p - CH_3), 23.6 (CCH_3), 98.2 (γ -CH), 129.5 (m - ArH), 133.4 (p - Ar), 137.4 (o - Ar), 146.0 (i - Ar), 163.4 ppm (CN).

Data for the X-ray structural analyses of **5** and **6** were collected on a KappaCCD diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å), solved by direct methods (SHELXS-97), and refined against all F^2 using SHELXL-97) with non-hydrogen atoms anisotropic and hydrogen atoms in riding mode. An absorption correction (MULTISCAN) was applied. For **5**, the diffraction was weak and limited in extent. Crystallographic data for **5** ($C_{24}H_{31}InN_2O$) at 173(2) K: $M_r = 478.33$, crystal dimensions $0.25 \times 0.10 \times 0.05$ mm³, orthorhombic, space group $P2_12_12$ (no. 18), $a = 11.6183(8)$, $b = 22.8982(14)$, $c = 8.7686(6)$ Å, $V = 2332.8(3)$ Å³, $Z = 4$, $\rho_{calcd} = 1.36$ Mg m⁻³, $\mu = 1.03$ mm⁻¹; of 10481 reflections measured ($3.41 < \theta < 23.26^\circ$), 3304 were independent ($R_{int} = 0.067$); $wR2 = 0.253$ (all data), $R1 = 0.100$ (for 2765 reflections with $I > 2\sigma(I)$), 254 parameters, GOF = 1.114. Crystallographic data for **6** ($C_{46}H_{58}In_2N_4$) at 173(2) K: $M_r = 896.6$, crystal dimensions $0.10 \times 0.10 \times 0.05$ mm³, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.6847(3)$, $b = 9.9683(3)$, $c = 13.5822(5)$ Å, $\alpha = 71.003(2)$, $\beta = 82.758(2)$, $\gamma = 81.907(2)^\circ$, $V = 1096.67(6)$ Å³, $Z = 1$, $\rho_{calcd} = 1.36$ Mg m⁻³, $\mu = 1.09$ mm⁻¹; of 17033 reflections measured ($3.54 < \theta < 26.06^\circ$), 4316 were independent ($R_{int} = 0.053$); $wR2 = 0.072$ (all data), $R1 = 0.031$ (for 3783 reflections with $I > 2\sigma(I)$), 241 parameters, GOF = 1.031. CCDC-264672 and -264673 (**5** and **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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