Reversible complexation of isocyanides by the distannyne Ar′SnSnAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2)_2$)†

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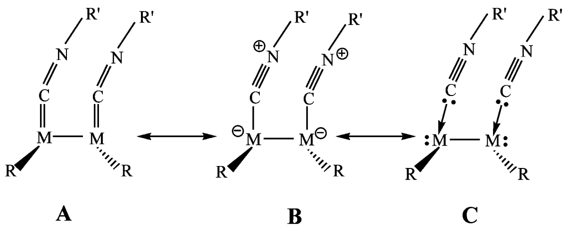
The reaction of the distannyne Ar′SnSnAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2)_2$) with *tert*-butyl or mesityl isocyanide afforded the bis-adducts Ar′SnSnAr′$(CNBu^t)_2$ or Ar′SnSnAr′$(CNMes)_2$ in which the isonitriles are reversibly bound under ambient conditions.

Several heavier group 14 element analogues of ketenimines (which can also be viewed as isonitrile adducts of the heavier element carbene congeners) have been isolated with the use of bulky substituents.[1] Their chemistry has been shown to differ considerably from that of their carbon analogues. For example, the reactions of isonitriles with alkynes generally afford cyclopropenimine products derived from cycloadditions.[2,3] In contrast, the treatment of digermyne Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2)_2$) with isonitriles afforded 1 : 1 or 2 : 1 isonitrile adducts in which one or both of the group 14 element atoms are complexed as in Ar′GeGeAr′$(CNBu^t)$ or Ar′GeGeAr′$(CNMes)_2$ (Mes = C_6H_2-2,4,6-Me_3).[4] The structural details of the latter species—strongly pyramidal germanium coordination, short C–N multiple bonds and Ge–C(isonitrile) distances consistent with single bonds—suggest that its bonding is most accurately represented by structure C in Scheme 1.

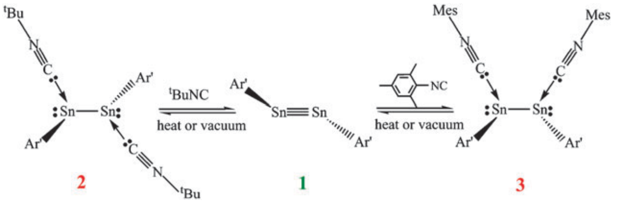
A similar reaction between Me_3SiNC and the disilyne RSiSiR (R = $Si^iPr\{CH(SiMe_3)_2\}_2$) was reported by Sekiguchi and co-workers to afford the 2 : 1 bis-adduct RSiSiR$(CNSiMe_3)_2$ which was proposed to have the silaketenimine structure A with a significant zwitterionic contribution from B due to its somewhat short Si–C (isonitrile) bond and pyramidalization of the coordination geometry at the Si atoms.[5] Herein we report the reactions of the distannyne Ar′SnSnAr′ **1** with ^tBuNC and MesNC which yield 2 : 1 adducts Ar′SnSnAr′$(CNBu^t)_2$ **2** and Ar′SnSnAr′$(CNMes)_2$ **3** exclusively. The most striking feature of the formation of **2** and **3** is that the reaction is reversible under ambient conditions and has similarities to the reversible complexation of ethylene by distannynes near room temperature.[6]



Scheme 1 Resonance forms bis(isonitrile) complexes of RMMR species (M = Si, Ge, Sn, Pb; R = bulky ligand; R′ = Bu^t, Mes, $SiMe_3$).

Complex **2**‡ was prepared by the dropwise addition of excess Bu^tNC to a concentrated toluene solution of **1**. This afforded a deep red solution which, upon cooling to −18 °C, gave **2** as very dark red crystals in 70% yield. In a similar way the reaction of MesNC with **1** gave dark red crystals of **3** in 67% yield (Scheme 2). Both **2** and **3** are stable in the solid state but dissociate to **1** and the corresponding isocyanides when redissolved in hydrocarbon solvents. No 1 : 1 complexes could be detected by NMR spectroscopy.

When red crystals of **3** are dissolved in hexane at room temperature, a green solution is obtained whose electronic spectrum displays two absorptions at 410 and 597 nm which are characteristic of the $\pi \rightarrow n_+$ and $n_- \rightarrow n_+$ transitions of **1**[7] indicating that **3** is mainly dissociated to **1** and MesNC. Cooling the solution to *ca.* −40 °C regenerated the red color characteristic of **3** (Fig. 1). The UV-vis spectrum of the −40 °C solution afforded an absorption at 514 nm. Warming the solution to room temperature restored the absorptions at 410 and 597 nm with disappearance of the feature at 514 nm



Scheme 2 Reactions of Ar′SnSnAr′ with Bu^tNC or MesNC.

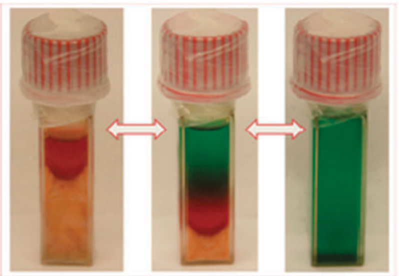


Fig. 1 Annealing solution of **3** at *ca.* −40 °C (red, left) which upon warming to 25 °C (green, right) indicated dissociation to **1** and free MesNC.

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† Electronic supplementary information (ESI) available: Crystallographic data for **2** and **3** (CIF), determination of association energy of **2** and **3** by variable temperature ^1H NMR and variable temperature behavior of the UV-vis spectrum illustrating the dissociation of **3** to **1** and free MesNC. CCDC 748927, 748928. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b919828h

(see ESI†). Complex **2** displays similar UV-vis spectral characteristics to those of **3**. The IR spectrum of **2** displays bands at 2162 and 2175 cm^{-1} which are shifted to higher frequencies than the free ligand (Bu^tNC, 2134 cm^{-1}). This trend has also been observed in other metal isocyanide complexes.[8–10] The IR spectrum of **3** displays a strong broad C–N stretching band at 2278 cm^{-1} which is unusually high for a transition metal isocyanide complex[8–10] (*cf.* MesNC, 2118 cm^{-1}). The ^{119}Sn NMR spectra of **2** and **3** display signals at 181 and 381 ppm respectively. These shifts lie upfield and downfield of the 335.1 ppm from Ar′SnSnAr′ in the solid state.[11] The reasons for the different spectroscopic properties of **2** and **3** are unclear at present.

The crystal structures§ of **2** and **3** determined by X-ray crystallography are shown in Fig. 2 and 3, where it can be seen that each tin is complexed by a RNC: donor (R = Bu^t, Mes). As a result, the tins are pyramidally coordinated with inter-ligand angular sums at Sn1 = 310.3° and Sn2 = 305.8° for **2** and Sn1 = 285.3° and Sn2 = 281.7° for **3**. This indicates that there is a non-bonded electron pair at each tin. The flatter geometry in **2** is consistent with the more crowding nature of the Bu^tNC ligand, which may also be responsible for the fact that the angles subtended by the isonitrile ligands with respect to the tin–tin bond averages more than 20° greater in **2**. The C–N–C angle in the complexed isocyanide ligands is *ca.* 170° for **2** and 175° for **3**. The average Sn–C distances to the Bu^tNC and MesNC ligands, *ca.* 2.29 Å, are very similar and are *ca.* 0.05 Å longer than the 2.24 Å seen for the Sn–C(ipso) bonds. The Sn–Sn bond lengths in **2** and **3** are 2.9282(6) and 3.0412(3) Å, respectively, which are at the upper end of the reported Sn–Sn single bond range.[12] The N–C bond distances within the isocyanide donors (1.159 Å for **2** and **3**) are typical for the N–C triple bonds.[13] There are bending angles of 154° for **2** and 157° for **3** at the ligating carbons of each isonitrile ligand. These crystal data thus support the bonding model **C** shown in Scheme 1. The main difference between the structures of **2** and **3** can be attributed to the fact that in **3** MesNC has a flat, two-dimensional shape so that the mesityl rings can be oriented parallel to each other. The mesityl rings are partially eclipsed since the two MesNC molecules complex on the same side of the molecule with an acute torsion angle (C61Sn1Sn2C71) of *ca.* 71° between the Sn–C(isocyanide) vectors. The mesityl ring planes are separated by only *ca.* 4.0 Å which is consistent with weak π-interactions. The torsion angle (C1Sn1Sn2C31) between the two large Ar′ substituents is also decreased from 180° in the precursor **1** to 81.9° in **3**. Conversely, in **2**, the large size of Bu^tNC ligands is reflected in the fact that each one coordinates to the tin at different sides of Sn–Sn bond. The torsion angle between the two isonitriles (C61Sn1Sn2C66 = 131.02(2)°) is much wider than the corresponding angle (*ca.* 71°) in **3**. In addition the torsion angle C1Sn1Sn2C31 (*ca.* 158°) is much wider than the 81.9° in **3**. The greater steric congestion lowers torsion angles between the two MesNC and the two Ar′ groups in **3**, which may be responsible for the fact that the Sn–Sn distance is *ca.* 0.1 longer than it is in **2**.

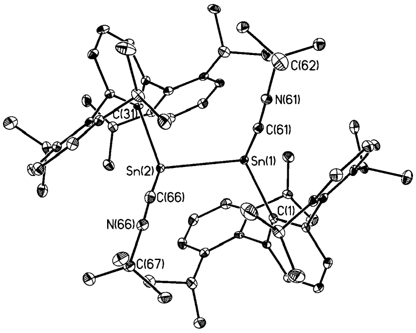

Fig. 2 Crystal structure of **2**. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Sn1–Sn2 2.9282(6) Å, Sn1–C1 2.240(4) Å, Sn1–C61 2.294(5) Å, Sn2–C31 2.244(4) Å, Sn2–C66 2.309(5) Å, C61–N61 1.160(5) Å, C66–N66, 1.157(6) Å; C1–Sn1–C61 100.07(14)°, C1–Sn1–Sn2 110.29(10)°, C61–Sn1–Sn2 99.96(11)°, C31–Sn2–Sn1 104.35(10)°, C31–Sn2–C66 100.29(15)°, C66–Sn2–Sn1 101.13(10)°, Sn1–C61–N61 154.8(4)°, C61–N61–C62 171.5(4)°, Sn2–C66–N66 154.6(4)°, C66–N66–C67 168.4(4)°.

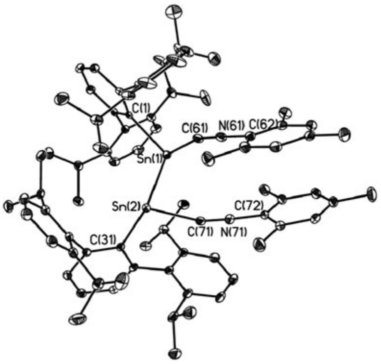

Fig. 3 Crystal structure of **3**. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Sn1–Sn2 3.0412(3) Å, Sn1–C1 2.244(3) Å, Sn1–C61 2.294(3) Å, Sn2–C31 2.234(3) Å, Sn2–C71 2.284(3) Å, C61–N61 1.158(4) Å, C71–N71 1.160(4) Å; C1–Sn1–C61 99.04(10)°, C1–Sn1–Sn2 107.93(7)°, C61–Sn1–Sn2 78.34(7)°, C31–Sn2–C71 98.97(11)°, C31–Sn2–Sn1 106.68(7)°, C71–Sn2–Sn1 76.03(8)°, Sn1–C61–N61 159.7(3)°, C61–N61–C62 178.2(3)°, Sn2–C71–N71 155.9(3)°, C71–N71–C72 171.9(3)°.

van't Hoff analysis of variable temperature ^1H NMR spectrum affords reaction enthalpy $\Delta H_{assn} = -25(3)$ kJ mol^{-1} for **2** and $\Delta H_{assn} = -127(4)$ kJ mol^{-1} for **3** (see ESI†) and indicates relatively weak isonitrile coordination. The free energy ΔG_{assn} is *ca.* −17(3) kJ mol^{-1} for **2** and −4.3(3) kJ mol^{-1} for **3** which indicates that the reaction is strongly affected by the entropic factor $T\Delta S$. Coordination occurs *via* the empty 5p orbital perpendicular to the tin coordination plane. The ready availability of the 5p orbital at each tin is supported by the calculations of Takagi and Nagase,[14,15] who showed that the energy between the single bonded forms of Ar′SnSnAr′ which contains an essentially empty 5p orbital and a non-bonded electron pair at each tin and a multiple bonded form Ar′SnSnAr′ is only *ca.* 5 kcal mol^{-1}(Fig. 4).

In related work reversible reactions of isonitrile with mononuclear silylene or stannylene species, which are heavier element carbene analogues, are known. For the silylenes, it was shown that either silylene–Lewis base complex[16] or dialkylsilaketenimine product[17] was obtained depending on the isonitrile employed. The association–dissociation equilibrium was qualitatively shown by NMR spectroscopy but no

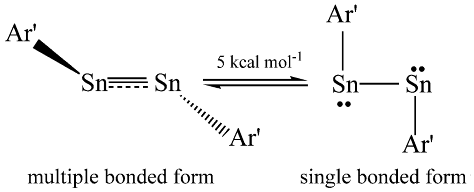

Fig. 4 Calculated energy difference between single and multiple bonded isomers of Ar′SnSnAr′.[14,15]

quantitatively measured association energies were determined however. For a stannylene, a fully characterized reversible complex of isocyanide with stannylene was reported by Grűtzmacher *et al.* in which the association energy ($\Delta H_{\mathrm{assn}} = \sim -29.6$ kJ mol^{-1}) and 0.16 Å longer distance of Sn–C(isonitrile) than Sn–C(ipso) indicated quite weak interaction between the stannylene and isocyanide.[18]

In summary, distannyne **1** reacts reversibly with isonitriles Bu^{t}NC and MesNC to afford 2 : 1 bis-adducts **2** and **3** exclusively. The bonding occurs mainly by the carbon lone pair Lewis base complexation *via* the 5p orbital at each tin. The crystal data and variable temperature UV-vis spectrum suggested that the weak interaction between the Sn and isocyanide due to the steric effect might be the main contributor to the reversible process.

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Notes and references

‡ All manipulations were carried out under anaerobic and anhydrous conditions. **2**: to a solution of Ar′SnSnAr′ **1** (0.3 g, 0.29 mmol) in toluene (10 ml) was added excess Bu^{t}NC (0.1 ml, 0.89 mmol) at ambient temperature. The color of the solution changed immediately from deep green to dark red. Stirring was maintained for 1 h to ensure complete conversion. The solution was cooled to *ca.* −18 °C for one day, after which X-ray quality crystals were obtained as dark red blocks (0.24 g, 70%). Mp: 156–157 °C. The dark red crystals afforded a deep green colored solution when they were redissolved in hexane or toluene. To obtain the electronic spectrum, a cooled hexane solution of **2** (9.18×10^{-6} mol L^{-1}) was prepared on which the UV-vis spectrum was immediately obtained. $\lambda_{\max}$: nm (ε in mol^{-1} L cm^{-1}) = 422 (300). For NMR studies, a deep green C_7D_8 solution of **1** was prepared in a J. Young NMR tube to which excess Bu^{t}NC was added. This resulted in a dark red solution and was then exposed to ultrasonic frequencies for 5 minutes to ensure reaction completion. At 22 °C, ^{1}H NMR (C_7D_8): δ 1.01 (excess neutral $(\mathrm{C}H_3)_3\mathrm{CNC}$), 1.06 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.32 (s, 9H, coordinated $(\mathrm{C}H_3)_3\mathrm{CNC}$), 1.34 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 3.04 (septets, 4H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{C}H(\mathrm{CH}_3)_2$), 6.92–7.21(Ar–H). ^{13}C{^{1}H} NMR (C_7D_8): 24.2 (complex $(\mathrm{CH}_3)_3C\text{–NC}$), 24.3 ($\mathrm{CH}(C\mathrm{H}_3)_2$), 25.6 (complexed $(C\mathrm{H}_3)_3\text{C–NC}$), 26.5 ($\mathrm{CH}(C\mathrm{H}_3)_2$), 27.1 ($C\mathrm{H}(\mathrm{CH}_3)_2$), 31.5 (excess $(\mathrm{CH}_3)_3C\text{–NC}$), 31.7 (excess $(C\mathrm{H}_3)_3\text{C–NC}$), 47.8 (complexed $(\mathrm{CH}_3)_3\text{C–N}C$), 54.3 (excess $(\mathrm{CH}_3)_3\text{C–N}C$)), 124.0, 124.3, 128–129 (overlap with C_7D_8), 147.7, 156.6 (Ar–C). Signal of *i*-C_6H_3 was not observed. ^{119}Sn{^{1}H}: 181. ν_{NC}(cm^{-1}): 2175, 2162. **3**: to a solution of Ar′SnSnAr′ **1** (0.3 g, 0.29 mmol) in toluene (10 ml) was added excess MesNC (0.1 g, 0.69 mmol) at ambient temperature. The color of the solution changed immediately from deep green to dark red. Stirring was maintained for 1 h to ensure complete conversion. The solution was cooled to *ca.* −18 °C for one day, after which X-ray quality crystals were obtained as dark red blocks (0.26 g, 67%). Mp: 182–185 °C. The dark red crystals afforded a deep green colored solution when they were redissolved in hexane or toluene. To obtain the electronic spectrum, a cooled hexane solution of **3** (2.23×10^{-6} mol L^{-1}) was prepared on which the UV-vis spectrum was immediately obtained. $\lambda_{\max}$: nm (ε in mol^{-1} L cm^{-1}) = 502 (5400). For NMR studies, a deep green C_7D_8 solution of **1** was prepared in a J. Young NMR tube to which excess MesNC was added to result in a dark red solution and was then exposed to ultrasonic frequencies for 5 minutes to ensure the reaction completion. At 22 °C, ^{1}H NMR (C_7D_8): δ 1.12 (d, 6H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.17 (d, 6H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.28 (d, 6H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.50 (d, 6H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.87 (*o*-CH_3 on the complexed MesNC), 1.92 (*o*-CH_3 on the neutral MesNC), 2.06 (*p*-CH_3 on the complexed MesNC), 2.17 (*p*-CH_3 on the neutral MesNC), 2.89 (septets, 1H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{C}H(\mathrm{CH}_3)_2$), 3.14 (septets, 2H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{C}H(\mathrm{CH}_3)_2$), 3.22 (septets, 1H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{C}H(\mathrm{CH}_3)_2$), 6.36 (neutral MesNC), 7.06 (complexed MesNC), 6.89–7.31(Ar–H). ^{13}C{^{1}H} NMR (C_7D_8): 18.7 (neutral MesNC), 20.8 (neutral MesNC), 24.3 ($\mathrm{CH}(C\mathrm{H}_3)_2$), 24.5 (complex MesNC), 26.5 ($\mathrm{CH}(C\mathrm{H}_3)_2$), 30.8 (complexed MesNC), 31.1 ($C\mathrm{H}(\mathrm{CH}_3)_2$), 122.9, 123.7, 124.4, 128.5, 146.9, 1482 (Ar–C). Signal of *i*-C_6H_3 was not observed, 134.7, 137.4, 138.6, 170.2 (neutral MesNC). ^{119}Sn{^{1}H}: 381. ν_{NC}(cm^{-1}): 2278 (br).

§ Crystal data for **2** at T = 90(2) K with MoKα (λ = 0.71073 Å): $C_{70}H_{92}N_2Sn_2(2.5C_7H_8)$, M = 1429.17, monoclinic, space group $P2_1/c$, a = 19.763(4) Å, b = 16.802(4) Å, c = 25.620(5) Å, β = 113.081(3)°, V = 7827(3) Å^3, Z = 4, μ = 0.682 mm^{-1}, R_{int} = 0.0678, R_1 = 0.0495 for 11 397 ($I > 2\sigma(I)$) reflections, wR_2 = 0.1180 (all data). CCDC 748928. Crystal data for **3** at T = 90(2) K with MoKα (λ = 0.71073 Å): $C_{80}H_{96}N_2Sn_2(2C_7H_8)$, M = 1507.28, monoclinic, space group C/c, a = 14.1189(9) Å, b = 22.0924(13) Å, c = 25.6881(16) Å, β = 91.1690(10)°, V = 8011.0(9) Å^3, Z = 4, μ = 0.670 mm^{-1}, R_{int} = 0.0400, R_1 = 0.0312 for 16 462 ($I > 2\sigma(I)$) reflections, wR_2 = 0.0740 (all data). CCDC 748927.

1 J. Escudié, H. Ranaivonjatovo and L. Rigon, *Chem. Rev.*, 2000, **100**, 3639.
2 T. R. Oakes, H. G. David and F. J. Nagel, *J. Am. Chem. Soc.*, 1969, **91**, 4761.
3 H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 409.
4 G. H. Spikes and P. P. Power, *Chem. Commun.*, 2007, 85.
5 K. Takeuchi, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2008, **130**, 16848.
6 Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger and P. P. Power, *Science*, 2009, **325**, 1668.
7 A. D. Phillips, R. J. Wright, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2002, **124**, 5930.
8 K. Klinkhammer, *Polyhedron*, 2002, **21**, 587.
9 M. J. Robertson and R. J. Angelici, *Langmuir*, 1994, **10**, 1488.
10 J. I. Henderson, S. Feng, T. Bein and C. P. Kubiak, *Langmuir*, 2000, **16**, 6183.
11 G. H. Spikes, J. R. Giuliani, M. P. Augustine, I. Nowik, R. H. Herber and P. P. Power, *Inorg. Chem.*, 2006, **45**, 9132.
12 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon, Oxford, 5th edn, 1984, p. 1279.
13 J. A. Green and P. T. Hoffmann, *Isonitrile Chemistry*, in *Org. Chem.*, ed. I. Ugi, Academic Press, New York, 1971, vol. 20, p. 1.
14 N. Takagi and S. Nagase, *Organometallics*, 2007, **26**, 469.
15 N. Takagi and S. Nagase, *Organometallics*, 2007, **26**, 3627.
16 N. Takeda, H. Suzuki, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, 1997, **119**, 1456.
17 T. Abe, T. Iwamoto, C. Kabuto and M. Kira, *J. Am. Chem. Soc.*, 2006, **128**, 4228.
18 H. Grűtzmacher, S. Freitag, R. Herbst-Irmer and G. S. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 437.