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## The structures of ring-expanded NHC supported copper(i) triphenylstannyls and their phenyl transfer reactivity towards heterocumulenes†

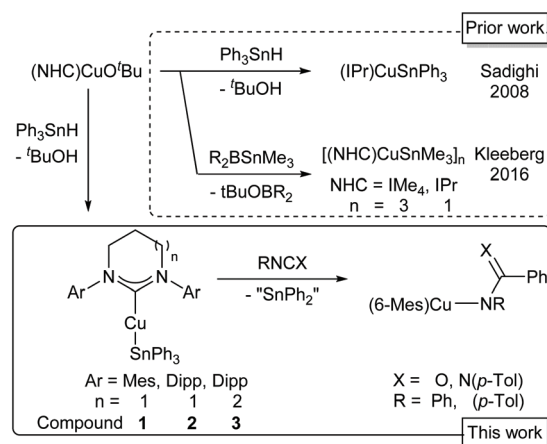
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Three ring-expanded N-heterocyclic carbene-supported copper(i) triphenylstannyls have been synthesised by the reaction of (RE-NHC)CuO<sup>t</sup>Bu with triphenylstannane (RE-NHC = 6-Mes, 6-Dipp, 7-Dipp). The compounds were characterised by NMR spectroscopy and X-ray crystallography. Reaction of (6-Mes)CuSnPh<sub>3</sub> with di-*p*-tolyl carbodiimide, phenyl isocyanate and phenylisothiocyanate gives access to a copper(i) benzamidinate, benzamide and benzothiamide respectively via phenyl transfer from the triphenylstannyl anion with concomitant formation of (Ph<sub>2</sub>Sn)<sub>*n*</sub>. Attempts to exploit this reactivity under a catalytic regime were hindered by rapid copper(i)-catalysed dimerisation of Ph<sub>3</sub>SnH to Ph<sub>4</sub>Sn, various perphenylated tin oligomers, H<sub>2</sub> and a metallic material thought to be Sn(0). Mechanistic insight was provided by reaction monitoring via NMR spectroscopy and mass spectrometry.

Organostannanes have found widespread use in a range of organic synthetic procedures, most notably Stille-type cross-couplings where carbon–tin bonds are useful C-nucleophilic synthons.<sup>1,2</sup> To facilitate the synthesis of such species, a plethora of stannyl transfer reagents have been developed. Of these, organostannyl anions constitute a particularly attractive class of reagents owing to the net umpolung elaboration represented by the C–X to C–Sn transformation when combined with transition-metal catalysed cross-coupling. Group 1 organostannyl anions have received extensive attention,<sup>3–8</sup> and reports have begun to elucidate the organostannyl-transfer potential of alkaline earth–tin bonds.<sup>9–12</sup> For example, Hill and co-workers reported the formation of a structurally unprecedented stannaamidinate formed by the insertion of diisopropyl carbodiimide into a Ca–Sn bond.<sup>10</sup>

Homodehydrocoupling of stannanes is a useful route to di- and oligotin compounds. Alongside methods applying electro-

chemistry<sup>13</sup> and organic hydrogen acceptors,<sup>14</sup> a number of d-block catalysed couplings have been described,<sup>15–18</sup> and some key metal–stannyl intermediates have been characterised.<sup>16</sup> Structural characterisation of organostannyl-coinage metal complexes, however, is limited to a very small number of N-heterocyclic carbene (NHC) supported copper(i) complexes<sup>19,20</sup> alongside a single phosphine supported gold(i) system.<sup>21</sup> Sadighi and co-workers reported the first structurally authenticated copper stannyl, synthesising (IPr)CuSnPh<sub>3</sub> (IPr = 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene) by the deprotonation of Ph<sub>3</sub>SnH by (IPr)CuX (X = H, O<sup>t</sup>Bu).<sup>19</sup> Kleeberg and co-workers built on this work, describing the closely related (IPr)CuSnMe<sub>3</sub> as well as [IME<sub>4</sub>CuSnMe<sub>3</sub>]<sub>3</sub> (IME<sub>4</sub> = 1,3,4,5-tetramethyl-imidazol-2-ylidene), synthesised through a Cu–O/Sn–B σ-bond metathesis between (NHC)CuO<sup>t</sup>Bu and Me<sub>3</sub>SnB((N<sup>i</sup>Pr)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)).<sup>20</sup> (IPr)CuSnR<sub>3</sub> (R = Me, Ph) each contained a two-coordinate near linear copper(i) atom, whilst [IME<sub>4</sub>CuSnMe<sub>3</sub>]<sub>3</sub> formed a stannyl-bridged trimer with extremely short Cu...Cu distances (Scheme 1).

Scheme 1 Synthesis and reactivity of (NHC)CuSnR<sub>3</sub> complexes.

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These sparse examples are matched by a correspondingly limited, although intriguing, set of reactivity studies. Sadighi and co-workers showed that  $(\text{IPr})\text{CuSnPh}_3$  acts not as a stannyl transfer agent, but as a source of the phenyl anion alongside diphenylstannylene, generating benzoates on reaction with  $\text{CO}_2$  and benzene when reacted with proton sources.<sup>19</sup> These authors proposed two possible mechanisms for this reactivity, postulating that either concerted phenyl transfer from the intact  $(\text{IPr})\text{CuSnPh}_3$  was operant, or that  $(\text{IPr})\text{CuSnPh}_3$  exists in equilibrium with  $(\text{IPr})\text{CuPh}$  and  $\text{SnPh}_2$ .

We and others have recently reported on the effects of ring-expanded NHCs on their copper(I) complexes.<sup>22–27</sup> Notably, RE-NHC copper(I) complexes often show reduced molecularity and/or enhanced stability with respect to their 5-membered cousins. For example, we recently reported the synthesis and structures of a number of NHC-copper(I) phosphides including  $[(\text{NHC})\text{CuPPh}_2]_2$  (NHC = SIMes, 6-Mes) which were dimeric in the solid state but where the 6-Mes supported system was proposed to monomerise in solution.<sup>27</sup> We also recently described the formation of  $(6\text{-Dipp})\text{CuBpin}$  which showed profoundly greater stability than  $(\text{IPr})\text{CuBpin}$ .<sup>28</sup>

In order to explore the effect of RE-NHC ligands on copper(I) systems more thoroughly, and with the hope of gaining additional insight into the reactivity of copper(I)-triphenylstannyl systems, we set out to synthesise a range of systems of the form  $(\text{RE-NHC})\text{CuSnPh}_3$ .

Herein we report the results of these explorations; the synthesis and characterisation of  $(\text{RE-NHC})\text{CuSnPh}_3$  (RE-NHC = 6-Mes, **1**; 6-Dipp, **2**; 7-Dipp, **3**), and examples of their reactivity.  $(6\text{-Mes})\text{CuSnPh}_3$  was found to transfer a phenyl group to both phenyl isocyanate and di-*p*-tolyl carbodiimide to generate an benzamidate and benzamidinate respectively.

Compounds **1–3** were initially synthesised by the reaction of an equimolar mixture of triphenyltin hydride and  $(\text{RE-NHC})\text{CuO}^t\text{Bu}$  in  $\text{C}_6\text{D}_6$ , and the reaction mixture interrogated by NMR spectroscopy (see Fig. S1–S6†). In each case,  $^1\text{H}$  NMR spectroscopy reflected the formation of  $^t\text{BuOH}$  and  $^{119}\text{Sn}$  NMR spectroscopy suggested the formation of a copper(I)-triphenylstannyl by resonances at  $-79.1$  (**1**),  $-83.1$  (**2**) and  $-85.4$  ppm (**3**) respectively. Repetition of these reactions on a preparative scale in toluene, followed by removal of all solvent *in vacuo* gave yellow powders in good yields (**1**, 84%; **2**, 79%; **3**, 77%) which provided NMR spectroscopy data consistent with the formation of the desired  $(\text{RE-NHC})\text{CuSnPh}_3$  systems (see Fig. S24–S32†). Recrystallisation of **1** by diffusion of hexane into its saturated toluene solution, and of **2** and **3** by cooling their saturated toluene solutions to *ca.*  $-18$  °C provided material suitable for single crystal X-ray crystallography which confirmed the structures of **1–3** as RE-NHC supported copper(I) triphenylstannyl complexes (Fig. 1, Table 1).

Compounds **1–3** all crystallise as monomers with 2-coordinate near linear copper(I) atoms. The Cu–Sn parameters for **1–3** (**1**, 2.4567(4) Å; **2**, 2.4742(4) Å; **3**, 2.4686(3) Å) are similar to previously reported terminal copper(I) triorganostannyl complexes, which show Cu–Sn distances in the range of 2.47–2.50 Å.<sup>19,20</sup>

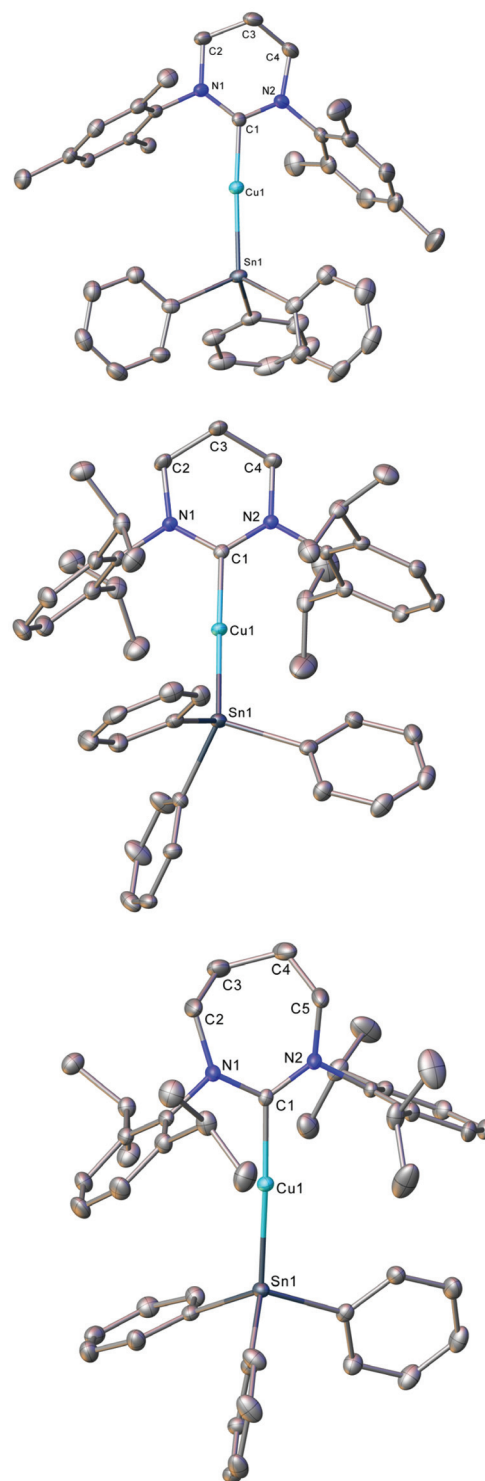


Fig. 1 Molecular structure (30% probability ellipsoids) of compounds **1–3**. Hydrogen atoms are omitted for clarity.

Furthermore, the variation in ligand identity seems to have negligible effects on the C–Cu–Sn core, with other metric parameters being essentially unchanged between IPr (C–Cu, 1.914 (2) Å; C–Cu–Sn, 169.6(8)°),<sup>19</sup> 6-Mes (C–Cu, 1.927(3) Å; C–Cu–



**Table 1** Selected bond lengths and angles for (IPr)CuSnPh<sub>3</sub> and compounds 1–3

	(IPr)CuSnPh <sub>3</sub> <sup>19</sup>	1	2	3
N–C <sub>carbene</sub> (Å)	1.353(2)	1.331(4)	1.333(4)	1.331(3)
	1.358(2)	1.334(4)	1.343(4)	1.347(3)
C <sub>carbene</sub> –Cu (Å)	1.914(2)	1.927(3)	1.934(3)	1.938(2)
Cu–Sn (Å)	2.469(5)	2.4567(4)	2.4742(4)	2.4686(3)
Sn–C <sub>phenyl</sub> (Å)	2.168(2)	2.171(3)	2.176(3)	2.175(3)
	2.176(2)	2.173(3)	2.188(4)	2.176(2)
	2.1852(19)	2.184(3)	2.190(3)	2.182(2)
N–C <sub>carbene</sub> –N (°)	103.84(15)	118.5(3)	117.9(3)	120.0(2)
C <sub>carbene</sub> –Cu–Sn (°)	169.6(8)	172.87(10)	171.27(9)	172.02(7)

Sn, 172.87(10)°, 6-Dipp (C–Cu, 1.934(3) Å; C–Cu–Sn, 171.27(9)°) and 7-Dipp (C–Cu, 1.938(2) Å; C–Cu–Sn, 172.02(7)°).

These consistent parameters are in contrast to a significant variation in N–C–N angle for each of these species (IPr, 103.84(15)°;<sup>19</sup> 6-Mes, 118.5(3)°; 6-Dipp, 117.9(3)°; 7-Dipp 120.0(2)°), which is itself unsurprising in light of the varying ring size of these species.

With these complexes characterised, we were anxious to explore their reactivities. We have recently reported on the reaction of a number of (RE-NHC)CuPPh<sub>2</sub> systems with heterocumulenes, often noting distinct structural features and reactivity during reactions with CO<sub>2</sub>, CS<sub>2</sub>, isocyanates, and isothiocyanates.<sup>27</sup> In light of the thorough exploration of the reaction of (IPr)CuSnPh<sub>3</sub> with CO<sub>2</sub> reported by Sadighi and co-workers,<sup>19</sup> we turned our attention to the reactivity of **1** towards carbodiimides, isocyanates and isothiocyanates. Compound **1** was reacted with one equivalent of di-*p*-tolyl carbodiimide in C<sub>6</sub>D<sub>6</sub> (see Fig. S7 and S8†). Within minutes, the <sup>119</sup>Sn NMR spectrum of this reaction showed consumption of **1** and formation of a peak at –43.6 ppm. Sadighi and co-workers noted a corresponding resonance in the <sup>119</sup>Sn NMR spectrum of the reaction between (IPr)CuSnPh<sub>3</sub> and CO<sub>2</sub> attributing it to an unknown (Ph<sub>2</sub>Sn) derived product. In the <sup>1</sup>H NMR spectrum of **1**, resonances ascribed to a new 6-Mes supported copper species were observed, as well as complete consumption of the carbodiimide. From these data, we inferred the formation of an amidinate in an analogous fashion, yielding (6-Mes)Cu(*p*-Tol-N)C(=N-*p*-Tol)Ph. This interpretation was corroborated by the presence of the [M + H]<sup>+</sup> ion peak with an *m/z* of 301.1703, attributed to HN(*p*-Tol)C(=N-*p*-Tol)Ph, in the mass spectrum.

The purported formation of a copper amidate, and the synthetic route used to access 1–3 raised an intriguing possibility; that under catalytic conditions the amidinate, (6-Mes)CuN(*p*-Tol)C(=N-*p*-Tol)Ph, could deprotonate Ph<sub>3</sub>SnH to regenerate **1**. In the presence of excess *p*-TolNCN-*p*-Tol and stannane, the net hydroarylation of a carbodiimide might thus be accessible with concomitant formation of (Ph<sub>2</sub>Sn)<sub>6</sub>. Attempts to extend this transformation to a catalytic regime (triphenylstannane, di-*p*-tolyl carbodiimide and **1** in a 10:10:1 ratio in C<sub>6</sub>D<sub>6</sub>) proved unsuccessful, with significant competition from stannane dimerisation (see Fig. S9 and S10†).<sup>9,29</sup> This result is

unsurprising in light of the competence of (6-Mes)CuO<sup>t</sup>Bu in mediating this same reaction (see Fig. S11 and S12†).

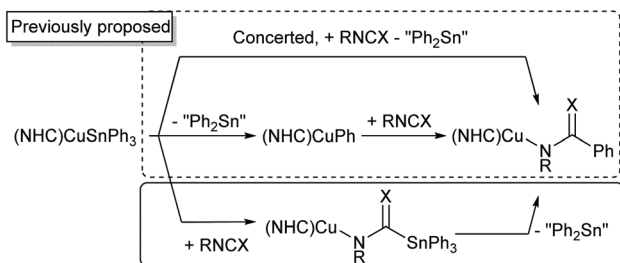
Addition of one equivalent of phenyl isocyanate to **1** in C<sub>6</sub>D<sub>6</sub> resulted in a rapid attenuation of the peaks associated with **1** in the <sup>119</sup>Sn NMR spectrum, and the growth of a resonance at –209.4 ppm, which was assigned to (Ph<sub>2</sub>Sn)<sub>6</sub> based on literature precedent (see Fig. S13 and S14†).<sup>29</sup> These data were interpreted as an implication that phenyl transfer occurs to the isocyanate to generate (6-Mes)CuN(Ph)C(O)Ph in a manner analogous to the formation of (IPr)CuOC(O)Ph from (IPr)CuSnPh<sub>3</sub> and CO<sub>2</sub>. Mass spectrometry of the reaction mixture between **1** and PhNCO provided further evidence for this thesis, by the presence of the [M + H]<sup>+</sup> ion peak with an *m/z* of 198.0914. This corresponds to *N*-phenylbenzamide, PhN(H)C(O)Ph, which was, most likely, protonated away from the copper centre due to the sample preparation in wet acetonitrile. Reactions attempted with (IPr)CuSnPh<sub>3</sub> showed analogous reactivity (see Fig. S15 and S16†).

Interrogation of a preliminary reaction between Ph<sub>3</sub>SnH and PhNCO in the presence of 10 mol% of **1** in C<sub>6</sub>D<sub>6</sub>, by <sup>1</sup>H NMR spectroscopy, revealed the complete consumption of both starting materials by the loss of their resonances in the spectrum (see Fig. S17 and S18†). Examination of the corresponding <sup>119</sup>Sn NMR spectrum was somewhat less promising, however, indicating the presence of Ph<sub>3</sub>SnSnPh<sub>3</sub> and a number of other phenylstannane derivatives, once again thought to originate from stannane dimerisation.<sup>9,29</sup> These data compelled a reexamination of the <sup>1</sup>H NMR spectrum where a resonance at *ca.* 4.5 ppm was attributed to the presence of H<sub>2</sub>.<sup>30</sup> Thus, the ultimate fate of the PhNCO was found to be trimerisation to the corresponding isocyanurate, based on the presence of this species in the mass and <sup>1</sup>H NMR spectra of the reaction mixtures.<sup>31</sup>

Addition of 1 equivalent of PhNCS to **1** gave somewhat divergent results (see Fig. S19–S21†). After 30 minutes, the <sup>119</sup>Sn NMR spectrum contained resonances at –43.6 and –202.5 ppm. The latter resonance reduced in intensity overnight, and the resultant <sup>1</sup>H NMR spectrum contained features consistent with (6-Mes)CuN(Ph)C(=S)Ph. The presence of the corresponding thioimidate anion was once again verified by appropriate mass spectral data. More notably, however, was the mass spectrum after 30 minutes which contained an [M + H]<sup>+</sup> peak with an *m/z* of 488.0491. This aligns to the expected mass of HN(Ph)C(=S)SnPh<sub>3</sub>, and allows the tentative attribution of the peak at –202.5 ppm in the <sup>119</sup>Sn NMR spectrum to (6-Mes)CuN(Ph)C(=S)SnPh<sub>3</sub> which converts to (6-Mes)CuN(Ph)C(=S)Ph and “Ph<sub>2</sub>Sn” overnight. Overall, these observations indicate a third mechanistic possibility which may operate in the phenylation of heterocumulenes as shown in Scheme 2.

These results raised the possibility that this mechanism may also contribute to the reactivity of **1** towards di-*p*-tolyl carbodiimide and phenyl isocyanate. Whilst these reactions appeared to be quantitative within the timeframe of the initial NMR experiment, instantaneous quenching of the reaction mixture after the addition of the heterocumulene to **1** in wet





**Scheme 2** Possible mechanistic pathways in the phenylation of heterocumulenes by copper(I) triphenylstannyls. The binding mode of the amidinate, amidate and thioamidate ligands was not ascertained from current data.

acetonitrile followed by mass spectrometry was informative. In the case of di-*p*-tolyl carbodiimide, the mass spectrum contained a  $[M + H]^+$  peak with an  $m/z$  of 575.1494, whilst in the case of phenyl isocyanate a  $[M + Na]^+$  value of 494.0531 was obtained. These correspond to the masses of  $\text{HN}(p\text{-Tol})\text{C}(=\text{N}-p\text{-Tol})\text{SnPh}_3$  and  $\text{HN}(\text{Ph})\text{C}(=\text{O})\text{SnPh}_3$ , respectively.

The rapid consumption of **1** observed in these reactions prompted us to attempt to observe relevant intermediates using VT-NMR spectroscopy. An equimolar reaction of **1** and di-*p*-tolyl carbodiimide was made up in  $d_8$ -toluene and quickly frozen in liquid nitrogen. Thawing in the NMR spectrometer at  $-50^\circ\text{C}$  followed by interrogation by  $^{119}\text{Sn}$  NMR spectroscopy indicated the previously observed resonance of “(Ph<sub>2</sub>Sn)” at  $-43.6$  ppm and a hitherto unobserved peak at  $-245.3$  ppm, attributed to  $(6\text{-Mes})\text{CuN}(p\text{-Tol})\text{C}(=\text{N}-p\text{-Tol})\text{SnPh}_3$ , which disappeared entirely within 45 minutes (see Fig. S22†). Reaction of **1** with phenyl isocyanate under equivalent conditions provided a new resonance at  $-216.7$  ppm, attributed to  $(6\text{-Mes})\text{CuN}(\text{Ph})\text{C}(=\text{O})\text{SnPh}_3$ , but which persisted at  $-50^\circ\text{C}$ . Slow warming of the reaction mixture to room temperature resulted in attenuation and eventually disappearance of this peak, favouring its assignment as an intermediate.

At this stage it is impossible to definitively conclude which pathway (or pathways) are operant during this class of reactions. Nevertheless, these preliminary results raise an intriguing mechanistic possibility and demand further exploration to elucidate the molecular origin of this unusual reactivity. We note the extensive computational work performed on the reaction of copper tetryls with  $\text{CO}_2$ <sup>32</sup> and hope this experimental study will, in time, allow a more conclusive theoretical understanding of these intriguing C–C bond forming reactions.

## Conclusions

In conclusion, we have described three new  $(\text{NHC})\text{CuSnPh}_3$  species, supported by the ring-expanded NHCs; 6-Mes (**1**), 6-Dipp (**2**) and 7-Dipp (**3**). In addition to characterisation of these compounds by NMR spectroscopy and X-ray crystallography we have also investigated the reactivity of **1** towards carbodiimides, isocyanates and isothiocyanates broadening the

scope of the unusual phenyl transfer ability of copper(I) triphenylstannyls to generate benzamidates, benzamides, and benzothiamides respectively. Furthermore, *in situ* reaction monitoring has provided evidence for the possibility of an additional mechanistic pathway in the phenylation of heterocumulenes by copper(I) triphenylstannyls.

## Conflicts of interest

There are no conflicts to declare.

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