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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Direct synthesis of the Janus-Head ligand $(^{\text{Me}}\text{Py})_3\text{Sn-Sn}(^{\text{Me}}\text{Py})_3$ using an unusual pyridyl-transfer reaction ($^{\text{Me}}\text{Py} = 6\text{-Methyl-2-pyridyl}$)

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The *in situ* reaction of the tripodal anion $[\text{EtAl}(^{\text{Me}}\text{Py})_3]^-$ ($^{\text{Me}}\text{Py} = 6\text{-Me-2-py}$) with SnCl_2 gives the Janus-Head ligand $(^{\text{Me}}\text{Py})_3\text{Sn-Sn}(^{\text{Me}}\text{Py})_3$, containing a Sn-Sn bond, through a novel, one-pot reaction involving a combination of pyridyl transfer and metal-oxidation.

Neutral tris(pyridyl) ligands of the general type $[\text{Y}(2\text{-py})_3]$ (2-py = 2-pyridyl, where Y can be a range of non-metallic bridgehead atom or group (e.g., CR, COR, CH, N, P, P=O, As. Fig. 1a), have been studied extensively in the last 30 years.¹ These ligands and related tris(pyrazolyl)borates and methanes^{2,3} have found a broad range of applications in organometallic, coordination and bioinorganic chemistry. Their applications include in catalysis, stoichiometric organic transformations and in models for the coordination in enzymatic metal sites.⁴ However, it has only been relatively recently that attention has turned to Group 13 and 14 congeners containing heavier, more metallic main group bridgeheads.⁵ These metal-based ligands introduce the possibility of redox activity and variable oxidation states at the bridgehead, as well as previously unknown anionic tris(pyridyl) ligands,⁶ such as tris(2-pyridyl)aluminates of the type shown in Fig. 1b.

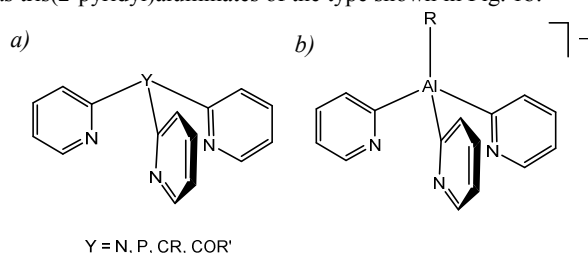
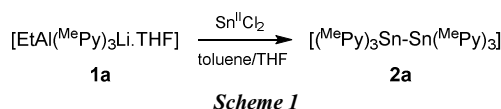


Fig. 1 a) Connectivity of tris(2-pyridyl) ligand systems containing bridgehead atoms or groups (Y) and b) the anionic tris(2-pyridyl)aluminate ligands.

Apart from the interesting coordination characteristics of this class of ligands revealed by a range of studies in the past 10 years,⁷ another potentially useful property of metal-based tris(pyridyl) arrangements is their ability to act as 'soft' pyridyl transfer reagent.^{5a,6} This is the result of the relatively low polarity of the C-Al bond, which is roughly comparable to the C-Zn bond. Unlike the Zn counterparts, however, 2-pyridyl-aluminium compounds are thermodynamically stable at room temperature and are therefore storable reagents. This soft nucleophilic behaviour was first suggested by the reaction of the lithium complex $[\text{MeAl}(2\text{-py})_3]\text{Li}\cdot\text{THF}$ with CuCl , which gives the

organo-Cu^I trimer $[\text{Cu}(2\text{-py})_3]_3$. In contrast, direct reaction of (2-Li-py) with CuCl only results in decomposition.⁶

Here we illustrate a further new facet of the reactivity of tris(2-pyridyl) reagents, with the discovery that the reaction of $[\text{EtAl}(^{\text{Me}}\text{Py})_3]\text{Li}\cdot\text{THF}$ (**1a**) ($^{\text{Me}}\text{Py} = 6\text{-Me-2-pyridyl}$) with $\text{Sn}^{\text{II}}\text{Cl}_2$ gives unique access to the Janus-Head ligand system $(^{\text{Me}}\text{Py})_3\text{Sn-Sn}(^{\text{Me}}\text{Py})_3$ (**2a**) in a single step, a reaction which involves a combination of 2-pyridyl ligand transfer and oxidation of the Sn^{II} centre (Scheme 1). The significance of this new reaction is that it provides the simplest access yet to a donor-functionalised Sn-Sn bonded framework of this type. For example, the most obvious alternative precursors to **2a** are the hexahalides Sn_2X_6 (X = halogen), however, these are difficult to prepare and either highly unstable (X = Cl)⁸ or are mixed valence compounds (X = F).⁹



The 1:1 reaction of $[\text{EtAl}(\text{MePy})_3]\text{Li}\cdot\text{THF}$ (**1a**) with SnCl_2 at room temperature in toluene/THF affords an orange reaction mixture containing several unidentified pyridyl compounds (see discussion below and figure S6 of the ESI†) from which colourless crystals of $[(\text{MePy})_3\text{Sn-Sn}(\text{MePy})_3]$ (**2a**) were isolated in a total yield up to 26%. A finely-divided black precipitate of Sn metal was also apparent upon prolonged storage of the reaction mixture. Compound **2a** was fully characterized by analytical and spectroscopic methods and its structure was determined by single-crystal X-ray diffraction. Particularly diagnostic are its ^{119}Sn NMR spectrum (singlet δ -218.9 ppm) and the presence of $^{117,119}\text{Sn}$ satellites for all of the C-atoms of the $^{\text{Me}}\text{Py}$ ligands in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (see Fig. S1-S5, ESI†). The single-crystal X-ray analysis of **2a** (Fig. 2) confirms the formation of a Sn-Sn single-bond in this reaction, the observed Sn-Sn bond length [2.7183(6) Å] being at the short end of the range of hexa-organo di-tin compounds $[\text{R}_3\text{Sn-SnR}_3]$.¹⁰

Two obvious mechanisms might be responsible for the formation of the Sn-Sn bonded compound **2a**, involving reductive elimination or disproportionation of $\text{Sn}^{\text{II/IV}}$ intermediates. An *in situ* multinuclear NMR study of the reaction of an equimolar mixture of **1a** with SnCl_2 in d_8 -THF was used to gain insights into the mechanism by which **2a** is formed. Within 15 min of mixing the reactants at ambient temperature an orange colouration

developed and **2a** was observed as the only Sn-containing species formed. The ^{27}Al NMR spectrum showed that a characteristic sharp resonance for AlCl_4^- was also present (δ 103 ppm),¹¹ together with other unidentified Al-containing species. No further changes in the ^{27}Al or ^{119}Sn spectra were observed after 24 h. At this stage, the ^1H NMR spectrum confirmed that none of the precursor **1a** remained. Importantly, no 6,6'-dimethyl-2,2'-dipyridyl is observed in the reaction at any point, despite the presence of several unidentified pyridyl signals (see Figs. S6 and S7, ESI[†]), ruling out a possible reductive elimination pathway to **2a** which involves the Sn^{IV} intermediate $\text{Sn}(\text{MePy})_4$ (e.g., Scheme 2a). Confirming this, $\text{Sn}(\text{MePy})_4$ is not observed in the ^{119}Sn NMR spectrum (lit. value δ -313 ppm in CDCl_3)¹² and we also find that heating an authentic sample of $\text{Sn}(\text{Py})_4$ at 80°C in toluene for 5 days results in only negligible decomposition (Fig. S8, ESI[†]).

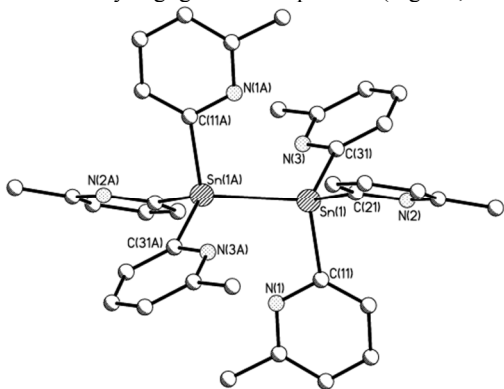
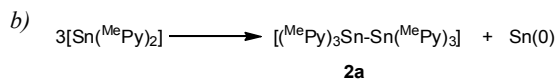
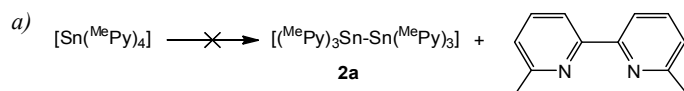


Fig. 2 Structure of $[(\text{Py}')_3\text{Sn-Sn}(\text{Py}')_3]$ (**2a**). The molecule is centrosymmetric, with only one-half contained in the asymmetric unit. Selected bond lengths (Å) and angles (°): Sn(1)-Sn(1A) 2.7183(6), Sn-C range 2.143(4)-2.148(4), C-Sn-Sn range 103.1(1)-117.5(1), C-Sn-C range 106.7(2)-110.7(2).

In a separate experiment, $\text{Sn}^{\text{II}}\text{Cl}_2$ was treated with 2 equivalents of 2-Li-MePy at -78°C and the mixture allowed to warm to room temperature. After 1h, a mixture of at least five Sn-species was formed, with the presence of **2a** being apparent in both the ^1H and ^{119}Sn NMR spectra (Fig. S9, ESI[†]). This observation provided initial evidence that a disproportionation pathway involving a 2-pyridyl Sn^{II} species (of the type $[\text{Sn}(\text{MePy})_n]^{x-}$) is likely in the formation of **2a** (e.g., Scheme 2b), which is also consistent with the formation of Sn metal in the reaction.



Scheme 2

The equimolar reaction of $[\text{EtAl}(\text{Py})_3\text{Li-THF}]$ (**1b**) (containing unsubstituted 2-pyridyl groups, Py) with SnCl_2 in d_8 -THF was also investigated in order to determine the substrate-dependent behavior of this reaction. An *in situ* ^{119}Sn NMR spectroscopic investigation shows that three major Sn-containing products are

generated after 24h (Fig. S10, ESI[†]), an unidentified species at δ -130 ppm (s.), $[(\text{Py})_3\text{Sn-Sn}(\text{Py})_3]$ (**2b**) [assigned on the basis of its chemical shift, δ -218.6 ppm (s)] and another species (**3**) observed as two singlets (δ -264.5 and -348.3 ppm). The *in situ* NMR spectroscopic studies therefore indicate that similar reactivity occurs for the unsubstituted 2-pyridyl groups, but the reaction becomes slower and less selective.

In both the *in situ* NMR spectroscopic investigations and on the preparative scale, **3** precipitates cleanly from the reaction mixture. The single-crystal X-ray structural analysis shows that **3** is the heterometallic $\text{Sn}^{\text{II}}/\text{Al}^{\text{III}}$ complex $[\{\text{Sn}(\text{Py})_3\}\text{Al}\{\mu\text{-Cl}\}(\text{Py})_2\text{Sn}(\text{Cl})\}]$ (Fig. 3), containing a six-coordinate Al^{III} centre that is complexed by a monoanionic $[\text{Sn}^{\text{II}}(\text{Py})_3]^-$ and a dianionic $[(\text{Py})_2\text{Sn}^{\text{II}}\text{Cl}_2]^{2-}$ ligand in a sandwich-type arrangement. The presence of pyramidal and trigonal bipyramidal geometries at the two Sn centres (with stereochemically-active metal lone pairs) strongly supports the oxidation state formulation of the complex as $\text{Sn}^{\text{II}}/\text{Al}^{\text{III}}/\text{Sn}^{\text{II}}$. The structure of **3** is consistent with the previously mentioned ^{119}Sn NMR spectrum, with the resonance at δ -266.3 being the Sn^{II} centre of the $[\text{Sn}^{\text{II}}(\text{Py})_3]^-$ ligand,¹³ while the resonance at δ -347.5 corresponds to the $[(\text{Py})_2\text{Sn}^{\text{II}}\text{Cl}_2]^{2-}$ ligand.^{14,15} Interestingly, there is also a very large change in chemical shift in the ^{27}Al NMR spectrum on reaction of the precursor $[\text{EtAl}(\text{Py})_3\text{Li-THF}]$ (**1b**) (δ 125) to the product **3** (δ 24), signifying the increase in the metal coordination number from four to six (Fig. S11-S13, ESI[†]).^{11b,16}

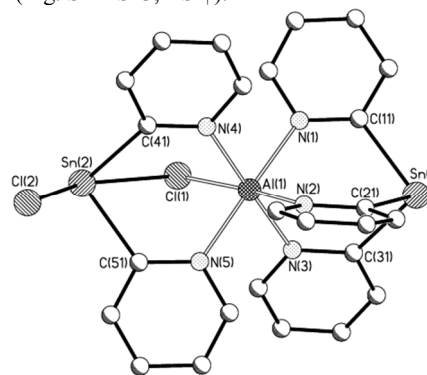


Fig. 3 Structure of the heterometallic complex **3**. Only one of the two crystallographically-independent (chemically-identical) molecules found in the lattice is shown. H-atoms and THF lattice solvation have been removed for clarity. Selected bond lengths (Å) and angles (°): Al-N range 2.049(9)-2.077(9), Al-Cl 2.300(4), $\text{Sn}(\text{Py})_3(\text{ligand})\text{-C}$ range 2.19(1)-2.24(1), $\text{Sn}(\text{Py})_2(\text{Cl})_2(\text{ligand})\text{-C}$ range 2.23(1)-2.25(1), C-Sn-C range 87.2(5) - 91.1(5), N-Al-Cl range 172.3(3)-175.1(3).

Viewed as a model intermediate, **3** provides a snap-shot of the likely stages of the reactions producing **2a** and **2b**. Although the precise detail of the mechanism remains elusive at this stage, the key structural components of **3** provide further support for the conclusion that the formation of **2a** and **2b** involves (i) initial transfer of the 2-py groups from Al^{III} to Sn^{II} and (ii) the disproportionation of the resulting 2-pyridyl Sn^{II} complex into **2a** and **2b** (as concluded earlier in regard to Scheme 2b).

In summary, we have demonstrated in this paper a new feature of the reactivity of tris(2-pyridyl) aluminate anions, their ability to act as 2-pyridyl transfer reagents in combination with

oxidation of metal centres. The formation of $(^{\text{Me}}\text{Py})_3\text{Sn-Sn}(^{\text{Me}}\text{Py})_3$ (**2a**) in a one-pot reaction avoids the use of highly unstable or poorly defined Sn^{IV} hexahalides and may have extensive applications elsewhere in the *p*-block.¹⁷ Furthermore, the Janus-head ligand properties of **2a** and related Group 14 arrangements should be of great interest in their own right. Future studies will be aimed at assessing the use of this new type of reaction in the synthesis of other main group $\text{Py}'_n\text{M-MPy}'_n$ arrangements (Py' = a substituted or unsubstituted pyridyl ligand) and the investigation of their coordination chemistry.

RG-R acknowledges the EU for a Marie Curie Intra European Fellowship) and D.S.W. acknowledges the EU for an ERC Advanced Investigator Grant.

Notes and references

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† Electronic Supplementary Information (ESI) available: Additional figures and tables and NMR spectra. See DOI: 10.1039/b000000x/

All manipulations were carried out under dry, O_2 -free argon on a vacuum line. Compounds **1a** and **1b** were synthesized as described previously.^{7c}

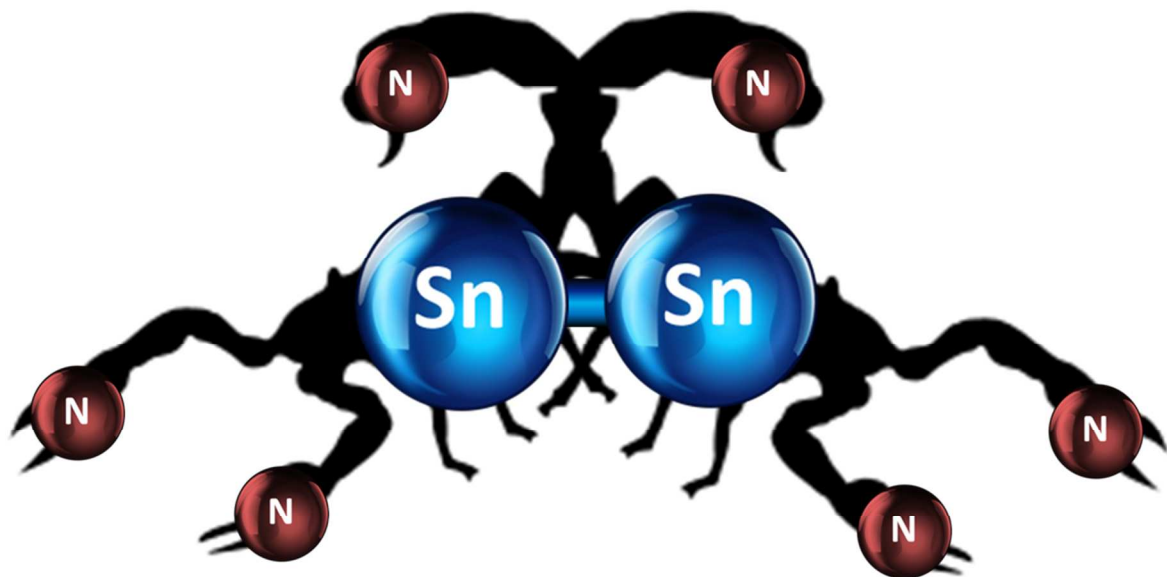
‡ *Synthesis of 2a*: To a Schlenk tube was added **1a** (200mg, 0.49mmol) and SnCl_2 (93mg, 0.49mmol) in a glove box. The Schlenk tube was transferred to a vacuum line and toluene (15mL) and THF (5mL) were added. After the addition of THF a solution was obtained which quickly changed from pale yellow to deep orange. The mixture was stirred for 36h at room temperature and then filtered through Celite to remove a small amount of precipitate and an oily residue. The majority of the solvent was removed *in vacuo* until the precipitation of a solid was observed, which was heated gently back into solution. Storage at -15°C (24 h) afforded a few colourless crystals of **2a** along with an orange residue. The supernatant was transferred using a canula to another Schlenk tube, concentrated and stored at -15°C (48 h) affording colourless crystals of **2a**. Total yield up to 26% (51mg, 0.0645 mmol). Elem. anal. calc. for **2a** C: 54.7 H: 4.6 N: 10.6, found C: 54.4 H: 4.7 N: 10.2. ^1H NMR (298 K, 500 MHz, thf-d_8), δ = 7.68 (m, 6H, C(3)-H py), 7.36 (m, 6H, C(4)-H py), 6.94 (m, 6H, C(5)-H py), 2.39 (s, 18H, C(6)-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, 125.7 MHz, thf-d_8), δ = 173.47 (C(2)), $^1\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 550/525 Hz, $^2\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 74/71 Hz, 158.77 (C(6)), $^3\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 76/73 Hz, $^4\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 5 Hz, 134.16 (C(4)), $^3\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 38/36 Hz, $^4\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 3 Hz, 131.82 (C(3)), $^2\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 97/93 Hz, $^3\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 9 Hz, 122.03 (C(5)), $^4\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 12 Hz, 24.43 (C(6)-Me), $^4\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ = 4 Hz. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186.5 MHz, 298K, rel solution of SnMe_4), δ = -218.7 [$s(\nu_{1/2} = 52 \text{ Hz})$]. No $^{119}\text{Sn}-^{117}\text{Sn}$ coupling could be detected.

§ *Synthesis of 3*: To a Schlenk tube was added **1b** (181mg, 0.49mmol) and SnCl_2 (93mg, 0.49mmol) in a glove box. The Schlenk tube was transferred to a vacuum line and toluene (15mL) and THF (5mL) were added. After the addition of THF a yellow mixture was obtained which was stirred at room temperature for 40h. A cloudy orange mixture was obtained. The supernatant was removed with a canula and the resultant orange solid dried *in vacuo*. Even though this orange solid was only partially soluble in THF, a few colourless crystals of **3** could be obtained from a concentrated sample in THF at room temperature. ^1H NMR (298 K, 500 MHz, thf-d_8), δ = 8.78 (d(6 Hz), 2H), 8.58 (d(7 Hz), 2H), 8.18 (d(7 Hz), 2H), 7.62-7.55 (m, 3H), 7.49 (t(7Hz), 2H), 7.15 (m, 1H, overlapped with toluene resonances), 7.04 (t(7 Hz), 2H), 6.88 (d(6 Hz), 2H), 6.81 (t(7 Hz), 1H), 6.55 (t(7Hz), 1H). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186.5 MHz, 298K, rel solution of SnMe_4), δ = -264.5(br, s), -348.3 (br, s). Changes up to 2 ppm were observed for the chemical shift. ^{27}Al NMR (298K, d_8 - thf-d_8 , 130.3 MHz, rel. solution of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$), δ = 23.8 ($\nu_{1/2} = 210 \text{ Hz}$)

§ Crystal data: The data were collected on Bruker SMART X2S diffractometer using a monochromatic Mo-K α microfocus source with a BREEZE CCD detector, and equipped with an Oxford Cryosystem Desk Top cooler at 200 K. Data were collected by Bruker GIS, processed using Bruker SAINT and were refined using the SHELXTL-97 suite of

programs. CCDC 1008866 and 1008867 contain the supplementary crystallographic data for **2a** and **3**, respectively.

- 70 1 L. F. Szczepura, L. M. Witham and K. J. Takeuchi, *Coord. Chem. Rev.*, 1998, **174**, 5.
- 2 (a) S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; (b) D. L. Reger, *Comments Inorg. Chem.*, 1999, **21**, 1.
- 3 (c) S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999;
- 75 4 (a) G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291; (b) E. L. Hegg, R. Y. N. Ho and L. Que, Jr., *J. Am. Chem. Soc.*, 1999, **121**, 1972; (c) N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419.
- 5 (a) H. R. Simmonds and D. S. Wright, *Chem. Commun.*, 2012, **48**,
- 80 8617; (b) D. Morales, J. Perez, L. Riera, V. Riera and D. Miguel, *Organometallics*, 2001, **20**, 4517; (c) K. Zeckert, S. Zahn and B. Kirchner, *Chem. Commun.*, 2010, **46**, 2638; (d) K. Zeckert, J. Griebel, R. Kirmse, M. Weiss and R. Denecke, *Chem. - Eur. J.*, 2013, **19**, 7718.
- 85 6 F. Garcia, A. D. Hopkins, R. A. Kowenicki, M. McPartlin, M. C. Rogers and D. S. Wright, *Organometallics*, 2004, **23**, 3884.
- 7 (a) C. S. Alvarez, F. Garcia, S. M. Humphrey, A. D. Hopkins, R. A. Kowenicki, M. McPartlin, R. A. Layfield, R. Raja, M. C. Rogers, A. D. Woods and D. S. Wright, *Chem. Commun.*, 2005, 198; (b) F. Garcia, A. D. Hopkins, R. A. Kowenicki, M. McPartlin, M. C. Rogers, J. S. Silvia and D. S. Wright, *Organometallics*, 2006, **25**, 2561; (c) T. H. Bullock, W. T. K. Chan, D. J. Eisler, M. Streib and D. S. Wright, *Dalton Trans.*, 2009, 1046; (d) T. H. Bullock, W. T. K. Chan and D. S. Wright, *Dalton Trans.*, 2009, 6709.
- 95 8 E. Wiberg and H. Behringer, *Z. Anorg. Allg. Chem.*, 1964, **329**, 290.
- 9 (a) T. Birchall, J. P. Johnson and V. Manivannan, *Hyperfine Interact.*, 1986, **28**, 685; (b) P. E. Lippens, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **60**, 4576.
- 10 (a) M. Saito, R. Haga and M. Yoshioka, *Chem. Commun.*, 2002, 1002; (b) H. Puff, B. Breuer, G. Gehrke-Brinkmann, P. Kind, H. Reuter, W. Schuh, W. Wald and G. Weidenbrueck, *J. Organomet. Chem.*, 1989, **363**, 265.
- 11 (a) K. Knabel and H. Noeth, *Z. Naturforsch., B: Chem. Sci.*, 2005, **60**, 1027; (b) G. E. Tranter, J. L. Holmes and J. C. Lindon, *Encyclopedia of spectroscopy and spectrometry*, San Diego, Calif. ;London, 2000, 2000. Vol 1 pp 696-700
- 12 M. Bette and D. Steinborn, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2012, **187**, 1271.
- 13 K. Zeckert, *Dalton Trans.*, 2012, **41**, 14101.
- 110 14 V. Chandrasekhar, S. Nagendran and V. Baskar, *Coord. Chem. Rev.*, 2002, **235**, 1.
- 15 A. G. Davies and I. Wiley, *Tin chemistry : fundamentals, frontiers, and applications*. John Wiley & Sons, Ltd: 2008, p 17-283.
- 16 (a) R. Benn, A. Rufinska, H. Lehmkuhl, E. Janssen and C. Krueger, *Angew. Chem.*, 1983, **95**, 808; (b) J. M. Bakker, L. J. Barbour, G. B. Deacon, P. C. Junk, G. O. Lloyd and J. W. Steed, *J. Organomet. Chem.*, 2010, **695**, 2720; (c) R. Benn, E. Janssen, H. Lehmkuhl and A. Rufinska, *J. Organomet. Chem.*, 1987, **333**, 155.
- 17 It can be noted that a similar Pb-compound [(6- t -BuO-Py) $_3$ PbPb[(6- t -BuO-Py) $_3$] has been obtained using oxidative coupling of the plumbate ion [(2- t -BuO-Py) $_3$ Pb] $^-$ in the presence of Eu(II) (see ref. 5d). This reaction differs fundamentally from the current study in that no additional oxidising metal is required in the formation of **2a**.
- 120



The *in situ* reaction of the tripodal anion $[\text{EtAl}(\text{}^{\text{Me}}\text{Py})_3]^-$ ($\text{}^{\text{Me}}\text{Py}' = 6\text{-Me-2-py}$) with SnCl_2 gives the Janus-Head ligand $(\text{}^{\text{Me}}\text{Py}')_3\text{Sn-Sn}(\text{}^{\text{Me}}\text{Py}')_3$, containing a Sn-Sn bond, through a novel, one-pot reaction involving a combination of pyridyl transfer and metal-oxidation.