warm to room temperature and then stirred for 30 min. The volatiles were removed in vacuo and the resultant solid dissolved in dichloromethane (15 mL). Ethanol (7 mL) was then added and the dichloromethane removed in vacuo to precipitate a white solid, which was collected and washed with ethanol and *n*-hexane. The solid was recrystallized from dichloromethane/ethanol to give pure **7a**. Yield 0.324 g (74 %); ^{1}H NMR (24 °C): $\delta = 1.74$ (s, 3H, $C_6H_4CH_3$), 6.33 (t, $J = 6.8$ Hz, 1H, $C_6H_4CH_3$), 6.72 (m, 2H, Bcat), 6.80 (m, 3H, Bcat and $C_6H_4CH_3$), 6.85 (d, $J = 6.8$ Hz, 1H, $C_6H_4CH_3$), 7.08–7.25 (m, 30H, PPh_3); $^{13}C\{^1H\}$ NMR (24 °C): $\delta = 31.17$ (s, $C_6H_4CH_3$), 110.27 (s, Bcat), 119.85 (s, Bcat), 122.55 (s, $C_6H_4CH_3$), 124.13 (s, $C_6H_4CH_3$), 127.47 (t′, $^{2,4}J$(C,P) = 9 Hz, *o*-PPh_3), 127.98 (s, $C_6H_4CH_3$), 129.48 (s, *p*-PPh_3), 133.60 (t′, $^{3,5}J$(C,P) = 9 Hz, *m*-PPh_3), 134.70 (t′, $^{1,3}J$(C,P) = 51 Hz, *i*-PPh_3), 146.47 (t, ^2J(C,P) = 9 Hz, *i*-C_6H_4Me), 149.41 (s, $C_6H_4CH_3$), 149.84 (s, $C_6H_4CH_3$), 150.35 (s, Bcat), 189.75 (t, ^2J(C,P) = 7 Hz, CO), 192.71 (t, ^2J(C,P) = 7 Hz, CO); IR (Nujol): $\tilde{\nu} = 1941$ (vs), 2038 cm^{-1} (w, CO); elemetal analysis calcd for $C_{51}H_{41}BO_4OsP_2 \cdot 1.2\,CHCl_3$ (%): C 55.77, H 3.78; found: C 55.74, H 3.82.

5: A mixture of **3** (89 mg, 0.091 mmol) and B_2cat_2 (60 mg, 0.25 mmol) was dissolved in benzene (10 mL) and stirred at room temperature for 16 h. The benzene was removed from the resulting orange solution, and then dichloromethane (10 mL) was added. The resultant suspension was filtered through Celite, and ethanol (5 mL) was added to the filtrate. The dichloromethane was removed in vacuo to give **5** as a white precipitate which was collected and washed with ethanol. Yield 46 mg (50 %); ^{1}H NMR: $\delta = 6.69$ (m, 4H, Bcat), 6.82 (m, 4H, Bcat), 7.08–7.18 (m, 18H, PPh_3), 7.30 (m, 12H, PPh_3); $^{13}C\{^1H\}$ NMR: $\delta = 110.71$ (s, Bcat), 120.04 (s, Bcat), 127.86 (t′, $^{2,4}J$(C,P) = 10 Hz, *o*-PPh_3), 129.49 (s, *p*-PPh_3), 133.20 (t′, $^{3,5}J$(C,P) = 12 Hz, *m*-PPh_3), 136.40 (m, *i*-PPh_3), 150.17 (s, Bcat), 189.76 (t, ^2J(C,P) = 8.5 Hz, CO); IR (Nujol): $\tilde{\nu} = 1963$ cm^{-1} (vs, CO); elemental analysis calcd for $C_{50}H_{38}B_2O_6OsP_2$ (%): C 59.54, H 3.80; found: C 59.30, H 3.51.

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[9] Data for the X-ray structure analyses: **3**: Crystals from chloroform/toluene (−20 °C), $C_{51}H_{41}BO_4OsP_2 \cdot C_7H_8$ ($M_r = 1072.92$); crystal dimensions $0.15 \times 0.08 \times 0.05$ mm; triclinic; space group $P\bar{1}$; $a = 12.06320(10)$, $b = 13.7859(2)$, $c = 15.2392(2)$ Å, $\alpha = 73.9760(10)$, $\beta = 86.6520(10)$, $\gamma = 85.8510(10)^\circ$, $Z = 2$, $V = 2427.51(5)$ Å^3, $\rho_{calcd} = 1.468$ g cm^{-3}; $T = 203$ K; $2\theta_{max} = 50^\circ$; total reflections 22672 of which 8466 were unique ($R_{int} = 0.0703$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 2.740$ mm^{-1}, $T_{min}/T_{max} = 0.6840/0.8752$). The structure was solved by Patterson methods and refined by full matrix least squares on F^2 on all data. The asymmetric unit cell contains one molecule of **3** and one molecule of toluene. $R_1 = 0.0473$ for the 6469 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.0845$ for all data. Goodness of fit (F^2) = 1.035. **7a**: Crystals from chloroform/*n*-hexane, $C_{51}H_{41}BO_4OsP_2 \cdot CHCl_3$ ($M_r = 1100.16$); crystal dimensions $0.42 \times 0.27 \times 0.09$ mm; triclinic; space group $P\bar{1}$; $a = 10.6356(5)$, $b = 14.5521(7)$, $c = 19.4083(9)$ Å, $\alpha = 68.9500(10)$, $\beta = 76.4950(10)$, $\gamma = 73.2160(10)^\circ$, $Z = 2$, $V = 2655.5(2)$ Å^3, $\rho_{calcd} = 1.376$ g cm^{-3}; $T = 203$ K; $2\theta_{max} = 55.02^\circ$; total reflections 22438 of which 11362 were unique ($R_{int} = 0.0366$); Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); empirical absorption correction ($\mu = 2.652$ mm^{-1}, $T_{min}/T_{max} = 0.4021/0.7963$). The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 on all data. The asymmetric unit cell contains one molecule of **7a** and one molecule of chloroform split between two sites; $R_1 = 0.0557$ for the 10128 observed data ($I > 2\sigma(I)$) and w$R_2 = 0.1640$ for all data. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-104125 (**3**) and CCDC-104126 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Thermally Stable Heterobinuclear Bivalent Group 14 Metal Complexes $Ar_2M{-}Sn[1,8\text{-}(NR)_2C_{10}H_6]$ (M = Ge, Sn; Ar = 2,6-$(Me_2N)_2C_6H_3$; R = CH_2tBu)[**]

Christian Drost, Peter B. Hitchcock, and
Michael F. Lappert*

Homobinuclear tin(II) compounds $Sn_2R'_4$, free of bridging ligands, and their germanium(II) analogues have attracted much attention.[1] The first such crystallographically characterized compound **I** was reported 25 years ago,[2] followed more recently by **II**,[3] **III**,[4] and **IV**.[5] Only one example of a crystalline, bivalent bis[tin(II)] compound with different ligands attached to each tin atom, namely, the thermally labile **V**, had previously been described.[6] In **I**–**III** and **V**, the Sn–Sn distance *l* was in the range 2.77–2.91 Å (cf. 2.81 Å in tetrahedral tin), while in **IV** (which has close Sn ⋯ F contacts) the tin–tin distance of 3.64 Å is too large for significant Sn ⋯ Sn bonding. Each of **I**–**IV**, unlike **V**, was either partially (**III** > **I**[1]) or completely dissociated in toluene or methylcyclohexane. There was some evidence for formation of the transient

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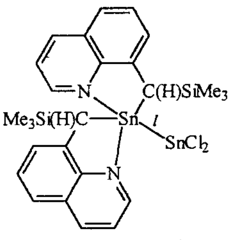
low-temperature dimer **VI** from the crystalline cyclotrimer (SnR'_2)$_3$ (R' = 2,4,6-iPr$_3$C$_6$H$_2$) by dissolution in MeC$_6$H$_{11}$ and photolysis at 205 K.[7] Two transient heterobinuclear complexes **VII**[8] and **VIII**[9] were identified by spectroscopy or by trapping experiments.

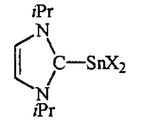
$R'_2Sn\overset{l}{-}SnR'_2$

I R' = CH(SiMe$_3$)$_2$, l = 2.768(1) Å
II R' = Si(SiMe$_3$)$_3$, l = 2.825(1) Å
III R' = 2,4,6-Me$_3$-2-tBuC$_6$H, l = 2.910(1) Å
IV R' = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, l = 3.64 Å
VI R' = 2,4,6-iPr$_3$C$_6$H$_2$

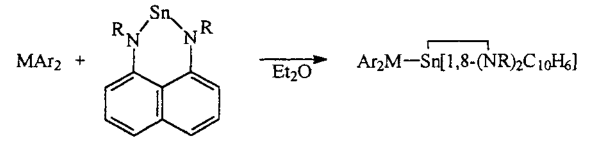

V, l = 2.961(1) Å

$R'_2M{-}Ge(2,4,6\text{-}Me_3C_6H_2)_2$

VII R'$_2$M = Si(2,4,6-Me$_3$C$_6$H$_2$)$_2$
VIII R'$_2$M = Sn(2,4,6-iPr$_3$C$_6$H$_2$)$_2$


IXa X = Cl
IXb X = 2,4,6-iPr$_3$C$_6$H$_2$

We now report the synthesis and characterization of two novel, thermally stable, crystalline compounds: the first thermally robust heterobimetallic Ge^{II}–Sn^{II} compound **4** and a second (cf. **V**) Sn^{II}–Sn'^{II} compound **5**, which maintain the integrity of their metal–metal bonds in solution. Treatment of the crystalline, monomeric, base-stabilized yellow diarylgermylene GeAr$_2$ (**1**) or -stannylene SnAr$_2$ (**2**)[10] with a suspension of the new [(1,8-dineopentylamino)naphthalene]-based stannylene **3**[11] in diethyl ether afforded after workup orange-red crystals of **4** or **5** in good yields (Scheme 1).


1 M = Ge **2** M = Sn **3** **4** M = Ge **5** M = Sn

Scheme 1. Synthesis of the diarylmetallene–stannylene adducts **4** and **5** (Ar = 2,6-(Me$_2$N)$_2$C$_6$H$_3$, R = CH$_2$$t$Bu).

Compounds **3**–**5** gave satisfactory microanalytical as well as EI-MS and multinuclear NMR spectroscopic data (Table 1). In addition, single-crystal X-ray diffraction studies revealed the molecular structure of crystalline **5** (Figure 1). Complex **3** is sparingly soluble in diethyl ether and aliphatic hydrocarbons, whereas not only **1** and **2**[10] but also **4** and **5** are readily soluble in these solvents.

The asymmetric unit cell of crystalline **5** contains two independent molecules of essentially identical geometry (structural parameters of only one are discussed) and a molecule of diethyl ether. The molecular structure of **5** is best described as a heteroleptic distannene comprising two independent stannylene moieties **2** and **3** linked solely by their tin–tin "bond" (Sn1–Sn2 3.087(2) Å), which is only slightly longer than those of **I**–**III**, **V**,[2–4, 6] and tetrahedral tin. The tin atoms of **5** differ in their coordination number, Sn1 being five- and Sn2 three-coordinate. The Sn1–C and Sn1–N distances in the Sn1Ar$_2$ fragment of **5** are significantly shorter than those of free **2**,[10] a feature previously observed, but in a much more pronounced fashion, in Ar$_2$Sn · BH$_3$[13] (Table 2). The sum of the three angles subtended at Sn1 by the *ipso*-C atoms C1 and C11 and Sn2 is 356.1°, and this indicates that C1, C11, and Sn2 are equatorially disposed about a distorted trigonal Sn1 centroid; N1 and N3 occupy quasi-axial positions; the N1-Sn1-N3 bond angle is 132.2(2)°. To ensure optimal electron saturation at Sn1, the Sn1–C1 and Sn1–C11 bonds are strongly tilted towards the coordinating nitrogen atoms N1 and N3, leaving the nonbonding nitrogen atoms N2 and N4 remote from Sn1.

The sum (Σ) of the bond angles subtended at Sn2 in **5** is 279.4°, with Sn2 in a pyramidal (PX$_3$-like) environment (bite angle N5-Sn2-N6 86.9(2), N5-Sn2-Sn1 95.8(2), N6-Sn2-Sn1

Table 1. Selected data for **3**–**5**. NMR spectra at 298 K in C$_6$D$_6$ (^{1}H, ^{13}C) or PhMe/C$_6$D$_6$. ^{1}H NMR: 250.0 MHz; ^{13}C{^{1}H} NMR: 62.86 MHz; ^{119}Sn{^{1}H} NMR: 186.36 MHz.

3: Orange-red; 81 % yield; m.p. ca. 154 °C; ^{119}Sn{^{1}H} NMR: $\delta = 183$; EI-MS (70 eV): m/z (%): 416 (40) [M^+].

4: Orange; 72 % yield; m.p. ca. 115 °C; ^{1}H NMR: $\delta = 1.12$ (s, 18 H, CMe$_3$), 2.45 (s, 24 H, NMe$_2$), 3.49 (br, 4 H, CH_2CMe$_3$), 6.39 (d, 4 H, H-3/5, $^3J(^1H,^1H) = 7.9$ Hz), 7.04 (t, 2 H, H-4, $^3J(^1H,^1H) = 7.9$ Hz), 6.74–7.15 (m, 6 H, H$_{Napht}$); ^{13}C{^{1}H} NMR: $\delta = 29.6$ (CC_3), 35.5 (CC$_3$), 45.6 (NC$_2$), 62.0 (CH$_2$), 104.3, 111.8, 115.3, 125.7, 130.3, 140.8, 157.7 (C$_{Ar}$); ^{119}Sn{^{1}H} NMR: $\delta = -58$; EI-MS (70 eV): m/z (%): 812 (1) [M^+].

5: Orange; 87 % yield; m.p. (decomp) > 120 °C; ^{1}H NMR $\delta = 1.13$ (s, 18 H, CMe$_3$), 2.49 (s, 24 H, NMe$_2$), 3.54 (br, 4 H, CH_2CMe$_3$), 6.39 (d, 4 H, H-3/5, $^3J(^1H,^1H) = 7.9$ Hz), 7.04 (t, 2 H, H-4, $^3J(^1H,^1H) = 7.8$ Hz), 6.75–7.15 (m, 6 H, H$_{Napht}$); ^{13}C{^{1}H} NMR: $\delta = 29.5$ (CC_3), 35.5 (CC$_3$), 45.5 (NC$_2$), 61.8 (CH$_2$), 103.7, 111.1, 115.5, 125.6, 129.8, 140.9, 158.6 (C$_{Ar}$); ^{119}Sn{^{1}H} NMR: $\delta = -30$ (Sn$_{Napht}$), 275 (Sn$_{Ar}$); EI-MS (70 eV): m/z (%): 861 (3) [M^+].

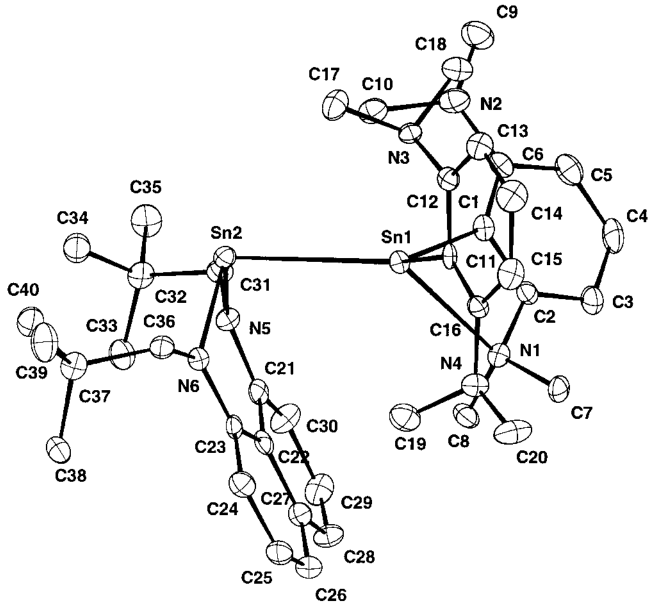


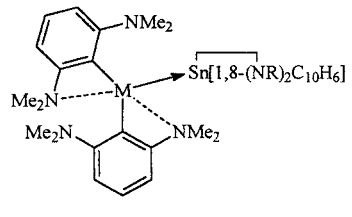
Figure 1. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Sn1–Sn2 3.087(2), Sn1–C1 2.196(7), Sn1–C11 2.186(6), Sn1–N1 2.517(5), Sn1–N3 2.580(5), Sn2–N5 2.083(6) Sn2–N6 2.086(6); C11-Sn1-C1 110.7(2), C1-Sn1-N1 59.9(2), C11-Sn1-N1 92.7(2), C11-Sn1-N3 59.2(2), C1-Sn1-N3 92.6(2), N1-Sn1-N3 132.2(2), C11-Sn1-Sn2 122.8(2), C1-Sn1-Sn2 122.6(2), N1-Sn1-Sn2 130.20(13), N3-Sn1-Sn2 97.32(13), N5-Sn2-N6 86.9(2), N5-Sn2-Sn1 95.8(2), N6-Sn2-Sn1 96.7(2).

Table 2. Selected structural parameters for the $SnAr_2$ moiety of **5**, $SnAr_2$ (**2**),[10] and $Ar_2Sn \cdot BH_3$.[13]

	5	**2**	$Ar_2Sn \cdot BH_3$
Sn-C [Å]	2.196(7), 2.186(6)	2.216(5), 2.212(5)	1.962(8), 1.959(8)
Sn-N [Å]	2.580(5), 2.517(5)	2.669(5), 2.607(5)	2.110(6), 2.110(6)
C-Sn-C′ [°]	110.7(2)	105.6(2)	112.7(3)
Coord. no.	5	4	5

96.7(2)°); hence, the three σ bonds to Sn2 have predominantly p character. This is similar to the situation in **V**[6] and [**IXa**],[14a] in which $SnCl_2$ acts as an acceptor: $\Sigma = 282.6$ [282.0]; Cl-Sn-Cl′ 94.5(1) [95.9(1)], Cl-Sn-Sn′(C) 91.8(1) [92.5(1)], and Cl′-Sn-Sn′(C′) 96.3(1)° [95.6(1)°]; and in **IXb** with $Sn(C_6H_2iPr_3)_2$ as acceptor ($\Sigma = 308.7°$).[14b] We infer that the Sn2–Sn1 bonding in **5** is best described as having the $Sn1Ar_2$ moiety primarily as donor and the $Sn2[1,8\text{-}(NR)_2C_{10}H_6]$ moiety primarily as acceptor, a view consistent not only with the structural data of the $SnAr_2$ moiety of **5** but also with the $^{119}Sn\{^1H\}$ NMR spectroscopic data (vide infra). Each of the nitrogen atoms N5 and N6 is in an approximately trigonal-planar environment ($\Sigma \approx 357°$). The attached neopentyl groups R are arranged in a cisoid manner. The Sn2 atom lies slightly out of the plane defined by N5, N6, and the C_{10} skeleton. The Sn2–N5 (2.083(6) Å) and Sn2–N6 (2.086(6) Å) bond lengths are unexceptional and can be compared to the average $Sn{-}N(SiMe_3)$ and Sn–N(R) bond lengths of 2.096(5) Å in $[Sn\{1,2\text{-}(NSiMe_3)_2C_6H_4\}]_2(\mu\text{-tmeda})$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) and 2.059(5) Å in $Sn[1,2\text{-}(NR)_2C_6H_4]$,[15] which have $N(sp^2)\text{-}Sn\text{-}N'(sp^2)$ bond angles of 91.9(2)° and 78.5(2)°, respectively.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** and **5** in C_6D_6 showed, like those of **1** and **2**,[10] only a single NMe_2 signal at ambient temperature. This indicates rapid exchange between the $2\text{-}Me_2N{-}M$ and $6\text{-}Me_2N{-}M$ groups (as in **1** and **2**), or that the weak dative bonding present in the solid is absent in solution (low-temperature measurements, as for **1** and **2**,[10] have not yet been carried out). The $^{119}Sn\{^1H\}$ NMR spectra showed a single signal for the Ge–Sn compound **4** at $\delta = -58$, but two signals for the Sn–Sn′ compound **5** at $\delta = -30$ and 275. The lower frequency signal of the latter, because of its similarity to that of **4**, is assigned to $Sn[1,8\text{-}(NR)_2C_{10}H_6]$. These values are compared with those of some related compounds in Table 3. The tin atom resonates at rather similar frequency in **4** ($\delta = -58$), **5** ($\delta = -30$ for the moiety **3**), and **IX** ($\delta = -59.4$), in each of which the tin atom is three-coordinate and, by analogy to **IX**, is the acceptor center. Moreover, the $^{119}Sn\{^1H\}$ chemical shift of the $SnAr_2$ moiety in **5** ($\delta = 275$) is of similar magnitude to that of $Ar_2Sn \cdot BH_3$ ($\delta = 328$). A comparison with free $SnAr_2$ **2** ($\delta = 442$) is more problematical, as there are differences in both the coordination number of tin and the Sn–N bond strength (see above). From these data we conclude that the bonding between the two tin atoms in **5** is best described as dative, wherein the $SnAr_2$ moiety is the donor and $Sn[1,8\text{-}(NR)_2C_{10}H_6]$ the acceptor. By analogy, $GeAr_2$ is assigned as the donor moiety in **4**. The recently reported crystalline compound Sn_2tBu_4 **X** is dimeric in concentrated solution but becomes monomeric on dilution.[16] In summary, both the structural data of crystalline **5** and the NMR spectroscopic data for a solution of **5** in C_6D_6 indicate that the bonding is best represented by **5a** and, by analogy, for **4** by **4a**; two of the Me_2N groups are also coordinatively linked to M, at least in the crystalline state.



4a M = Ge
5a M = Sn

The thermal stability of **4** and **5** contrasts with that of $\overline{\mathrm{(LL)Sn}}\mathrm{SnCl_2}$ (**V**), which in THF at 25 °C yields $\overline{\mathrm{(LL)Sn}}\mathrm{Cl}$.[6] Likewise, whereas transient intermediates were postulated for reactions analogous to those of Scheme 1 between $Si[1,2\text{-}(NR)_2C_6H_4]$ [$\equiv \overline{\mathrm{Si(NN}}\mathrm{)}$] with i) $SnAr_2$ to give $\mathrm{Sn[}\overline{\mathrm{Si(NN}}\mathrm{)Ar]Ar}$,[18] or ii) $M[N(SiMe_3)_2]_2$ to give $\mathrm{M[Si(N}\overline{\mathrm{N)\{N}}\mathrm{(SiMe_3)_2\}]_2}$ (M = Sn or Pb) or $\overline{\mathrm{GeH[}\overline{\mathrm{Si(NN}}\mathrm{)\{N(SiMe_3)_2\}][}\overline{\mathrm{Si(NN}}\mathrm{)N(SiMe_3)SiMe_2C}}\mathrm{H_2}$ (M = Ge),[19] it is evident that these, if formed, rapidly underwent 1,2-shifts of a ligand from Sn or M to Si. We conclude that **3** may be a weaker donor than $\overline{\mathrm{Si(NN}}\mathrm{)}$ and that because it is a chelate, a 1,2-shift of a ligand from **3** to Ge or Sn in **4** or **5** is unfavorable. The isolation of the stable compounds **4** and **5** supports the above postulates;[18, 19] **4** and **5** may well be forerunners of a larger class of heterobinuclear, bivalent compounds of the Group 14 elements.

Experimental Section

3: An orange solution of $Sn[N(SiMe_3)_2]_2$[20] (2.56 g, 5.83 mmol) in hexane (ca. 50 mL) was added by cannula without stirring to a solution of $1,8\text{-}[H(R)N]_2C_{10}H_6$[11] (1.74 g) in *n*-hexane (100 mL). The clear solution was set aside (72 h), protected from light; dark red crystals of **3** deposited. After removal of the supernatant solution the crystals were washed with hexane and dried in vacuo to yield **3** (1.96 g, 81 %). Compound **3** was only sparingly soluble in benzene or toluene at room temperature (pale orange solutions) but dissolved rapidly in THF. For further purification, **3** was recrystallized from a hot (> 100 °C) solution in toluene to yield very fine orange-yellow needles or sublimed in vacuo (195–205 °C at 10^{-5} Torr).

4 and **5**: A yellow solution of **1** (for **4**; 0.79 g, 1.979 mmol)[10] or **2** (for **5**; 0.82 g, 1.842 mmol)[10] in Et_2O (ca. 50 mL) was added by cannula to a stirred suspension of **3** (for **4**, 0.82 g; for **5**, 0.76 g) in Et_2O (ca. 100 mL) at 25 °C. Compound **3** slowly dissolved, and the orange solution was stirred overnight. Filtration to remove unconverted **3**, concentration of the filtrate in vacuo and cooling to −30 °C afforded orange, cubic crystals of **4** (1.16 g,

Table 3. $^{119}Sn\{^1H\}$ NMR spectral chemical shifts (δ) for **5** and some reference compounds.

5	**4**	**2**[10]	**3**	$SnCl_2$[6]	**IXa**[14a]	**IXb**[14b]	**X**[16]	**V**[6]	**I**[a][17]	$Ar_2Sn \cdot BH_3$[13]
−30[b]	−58	442	183	−388	−59.4		−690	−637.2[f]	692	328
275[c]				−240[d]		710	+413[e]	1264		

[a] By CP-MAS. [b] Sn2. [c] Sn1. [d] In THF, J. M. Keates, personal communication. [e] $J(^{119}Sn,^{117}Sn) = 2135$ Hz. [f] $SnCl_2$.

72%) or **5** (1.30 g, 87%). Recrystallization from hexane yielded very fine needles of both compounds.

Crystal data for **5**: $C_{84}H_{126}N_{12}OSn_4$, $M_r = 1794.73$, monoclinic, space group $P2_1/c$ (no. 14), $a = 22.911(4)$, $b = 18.441(6)$, $c = 22.250(13)$ Å, $\beta = 115.30(3)°$, $V = 8499(6)$ Å^3, $F(000) = 3688$; $Z = 4$, $\rho_{calcd} = 1.40\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 14.2\ \mathrm{cm^{-1}}$, crystal dimensions 0.3 × 0.2 × 0.1 mm, 12145 reflections collected for $2 < \theta < 23°$, 11805 independent reflections, $R1 = 0.047$ for 8396 reflections with $I > 2\sigma(I)$, $wR2 = 0.09$ (for all data), $S = 0.989$. Data collected at $T = 173(2)$ K, Enraf Nonius CAD-4 diffractometer, absorption correction, structural solution by direct methods, full-matrix least-squares refinement on F^2 with SHELXL-93 with non-hydrogen atoms anisotropic. The asymmetric unit contains two independent molecules of the Sn_2 complex and one molecule of diethyl ether solvent. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-107662. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Kinetic Resolution of Diiron Acyl Complexes—An Approach to Asymmetric Bicyclic β-Lactams**

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In the last few years we have been interested in the dipolar cycloaddition of nitrones with diiron acyl complexes.[1, 2] This chemistry has been shown to be effective in the diastereo- and enantioselective addition of a variety of nitrones to mono- and disubstituted α,β-unsaturated acyl complexes. It was found that, after cycloaddition, oxidation of the resultant complex gives a thioester isoxazolidine product.[1–3] It has been shown that isoxazolidines can be converted to amino alcohols through reduction of the N–O bond.[4–6] In the case of the cycloadducts discussed below, this results in the formation of thioester derivatives of β-amino acids. Here in we show that reaction of a cyclic nitrone derived from proline proceeds with one enantiomer of the diiron complex significantly faster than with the other enantiomer. Additionally the utility of this approach is demonstrated through the synthesis of a simple carbapenem.

Reaction of complex **1** with the *Z*-nitrone **2** gave the expected isoxazolidine product, which could be oxidized to the corresponding thioester **4**. Reaction with zinc and acetic acid then yielded the β-amino β-hydroxy thioester **5**. The hope was that treatment of the thioester with mercury trifluoroacetate would result in removal of the sulfur with commensurate trapping by the amine group to give the β-lactam.[7–9] Since optically active diiron acyl complexes are accessible, this approach would potentially provide a mild route to optically active β-lactams.[2] Unfortunately the initial attempt to form the β-lactam from amino alcohol **5** resulted in less than a 15% yield of the desired product **6**. It has been reported that the cyclization to give β-lactams with groups *cis* on the adjacent carbon atoms of the four-membered ring is difficult (Scheme 1).[10]

Because of this observation, and the fact that a large number of the known β-lactam antibiotics possess the opposite stereochemistry, the dipolar cycloaddition was run on an *E*-nitrone. The stereochemistry of acyclic nitrones is typically *Z*. Consequently, it was necessary to attempt the cyclization with a cyclic nitrone. *Endo* addition of such a nitrone would give a β-amino acid with the correct stereochemistry to readily form a β-lactam. Cyclization of nitrone **7** with diiron complex **1** followed by oxidative removal of the

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