Tripodal Triamidostannates as Building Blocks in the Generation of Sn–M-Bonded Heterobimetallics (M = Fe, Ru)

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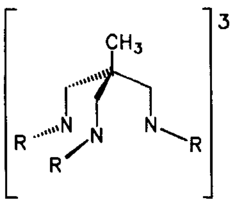
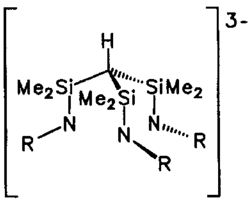
By in situ lithiation of the trifunctional amines $H_3CC(CH_2NHSiMe_3)_3$, $PhC(CH_2NHSiMe_3)_3$, and $HC\{SiMe_2NH(p\text{-Tolyl})\}_3$ and subsequent reaction with $SnCl_2$ the corresponding triamidostannates were obtained. These were coupled with $CpM(CO)_2Cl$ (M = Fe, Ru) to yield the M–Sn-bonded heterobimetallics **9**–**14** of which $H_3CC(CH_2NSiMe_3)_3SnFe(CO)_2Cp$ (**9**) was characterized by a single-crystal X-ray structure analysis. Of the in situ-generated amidostannates only $[HC\{SiMe_2N(p\text{-Tolyl})\}_3Sn][Li(THF)_3]$ (**8**) could be isolated as a uniform product and characterized analytically and spectroscopically.

We have recently studied the coordination chemistry of several novel types of early transition metal amido complexes containing tripodal ligand systems **A**–**C** which not only effectively shield a large sector in the coordination sphere of these compounds but also control their "electronic" properties (i.e. their Lewis acidity and redox behaviour)[1,2]. With the aid of these ligands it was possible, for instance, to devise a generalized approach to the stabilization of early-late heterobimetallics containing highly polar unsupported metal-metal bonds between the elements of the Ti triad and those of the Fe and Co groups[3]. This has for the first time opened up the possibility of a systematic investigation into their chemical reactivity.



A



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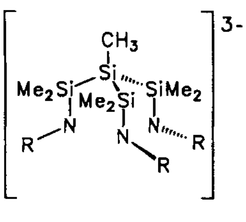

We now have extended this approach to include the main group metals of the p-block in the periodic table[4]. In view of the previously noted analogies in the amide chemistry of group IVa and group IVb elements[5] it was of particular interest to investigate the chemistry of the heavier congeners of carbon. The isolation and structural characterization by X-ray crystallography of highly stable Sn(II) and Pb(II) triamidometallates[6] is yet another manifestation of the capability of the multifunctional amide ligands to stabilize otherwise labile coordination environments. In the context of the structural and chemical investigation of the heterobimetallics mentioned above, we set out to extend the approach taken to the heavier group IVb metals, in particular, tin[7]. The generation of metal-metal bonds would in this case be achieved most conveniently by an "inverse" coupling strategy, employing the main group complex fragment as a nucleophile in subsequent condensation reactions.

In this paper we report the synthesis of a new tripodal ligand which is related to **A**, the in situ generation of the triamidostannates derived from this new system as well as from **A** and **B** and their use as nucleophiles in the coupling reactions with $CpM(CO)_2Cl$ (M = Fe, Ru) to yield the corresponding M–Sn bonded heterobimetallics.

Results and Discussion

A. Synthesis of the Tripodamide Precursor $C_6H_5C(CH_2NHSiMe_3)_3$ (5)

The starting material for the synthesis of the triamine $C_6H_5C(CH_2NHSiMe_3)_3$ was the corresponding alcohol $C_6H_5C(CH_2OH)_3$ (**1**) which may be readily obtained by a "Tollens" condensation of phenylacetaldehyde with formaldehyde (Eq. 1)[8,9]. Compound **1** was first obtained by Dermer and Solomon (yield 5%)[8c]. An improved preparative procedure has recently been published by Cho et al. which formed the basis of the synthesis reported in this

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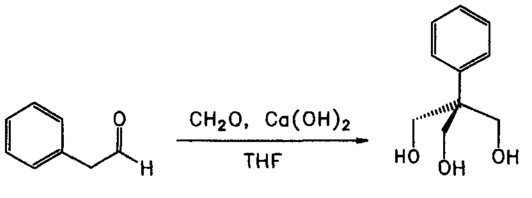
paper[9]. This strategy for the generation of tripod-ligand precursors has been used extensively by Huttner and coworkers in their design of new tridentate phosphane ligands[10].

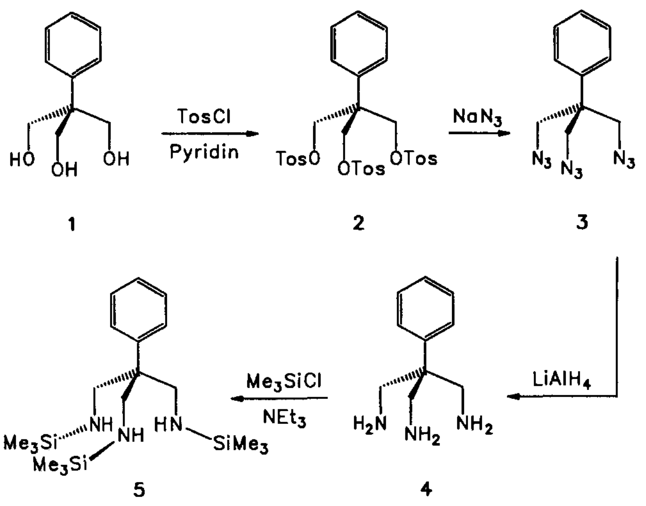


[Eq. 1]

1

The conversion of **1** to the amine **4** proceeds along the same synthetic route taken in the synthesis of the type **A** ligands[11], i.e. generation of the tosylate **2**, reaction with NaN_3 to give the triazide **3** and subsequent reduction with $LiAlH_4$ generating the primary amine (Scheme 1). Trimethylsilylation of **4** yields the desired secondary triamine $C_6H_5C(CH_2NHSiMe_3)_3$ (**5**).

Scheme 1. Conversion of the triol **1** to the corresponding tris(silylamine) **5**



The introduction of an aryl group into the bridgehead position is to be seen in connection with a potential fixation of the tripod to a solid support material, an effort to be discussed elsewhere.

B. In Situ Generation of the Tripodal Triamidostannates and their Coupling with $CpM(CO)_2Cl$ (M = Fe, Ru) to Give the M–Sn-Bonded Heterobimetallics

By reaction of $RC\{CH_2N(Li)SiMe_3\}_3(THF)_3$ (R = Me: **6**[12]; C_6H_5: **7**) with an equimolar amount of $SnCl_2$ at −50°C in THF, warming of the mixture to ambient temperature and subsequent removal of the solvent highly viscous oils were obtained which, according to ^1H- and ^{13}C-NMR spectroscopy, contained a mixture of several Sn-containing species. These could, however, be neither separated nor isolated, but the materials thus produced proved to be the reagents of choice in the subsequent metal-metal bond formation reactions (vide infra). On the other hand, the equivalent reaction of $HC\{SiMe_2N(Li)(p\text{-Tolyl})\}_3(THF)_2$[1b,2c] yielded a single product which could be recrystallized from diethyl ether to give a colourless highly crystalline solid **8** (Eq. 2).

$RC\{CH_2N(Li)SiMe_3\}_3(THF)_3$
6: $R = CH_3$
7: $R = C_6H_5$

$$HC\{SiMe_2N(Li)(p\text{-Tolyl})\}_3(THF)_2 \xrightarrow[\;-2\ LiCl\;]{SnCl_2} HC\{SiMe_2N(p\text{-Tolyl})\}_3SnLi(THF)_3 \qquad [Eq.\ 2]$$

8

The formulation of **8** as $HC\{SiMe_2N(p\text{-Tolyl})\}_3SnLi(THF)_3$ was established by its analytical data, and the ^1H-, ^{13}C-, and ^{29}Si-NMR data at 295 and 190 K ($[D_8]$toluene) indicate an effective threefold symmetry of the stannate unit in solution. It was therefore of interest whether **8** was a solvent-separated ion pair, as we had previously established by X-ray crystallography and NMR spectroscopy for its crystalline derivative containing the coligand $MeN(CH_2CH_2NMe_2)_2$ (PMDETA)[6]. Alternatively, a molecular species containing a direct Sn–Li bond was conceivable, as observed recently by Wright and coworkers in $Ph_3Sn{-}Li(PMDETA)$[13]. Since even at 190 K ^{119}Sn-^7Li coupling was not observed in the ^7Li spectra a more detailed structural assignment will remain to be achieved by X-ray crystallography.

Table 1. Selected IR and ^1H-NMR spectroscopic data of the $CpM(CO)_2$ derivatives

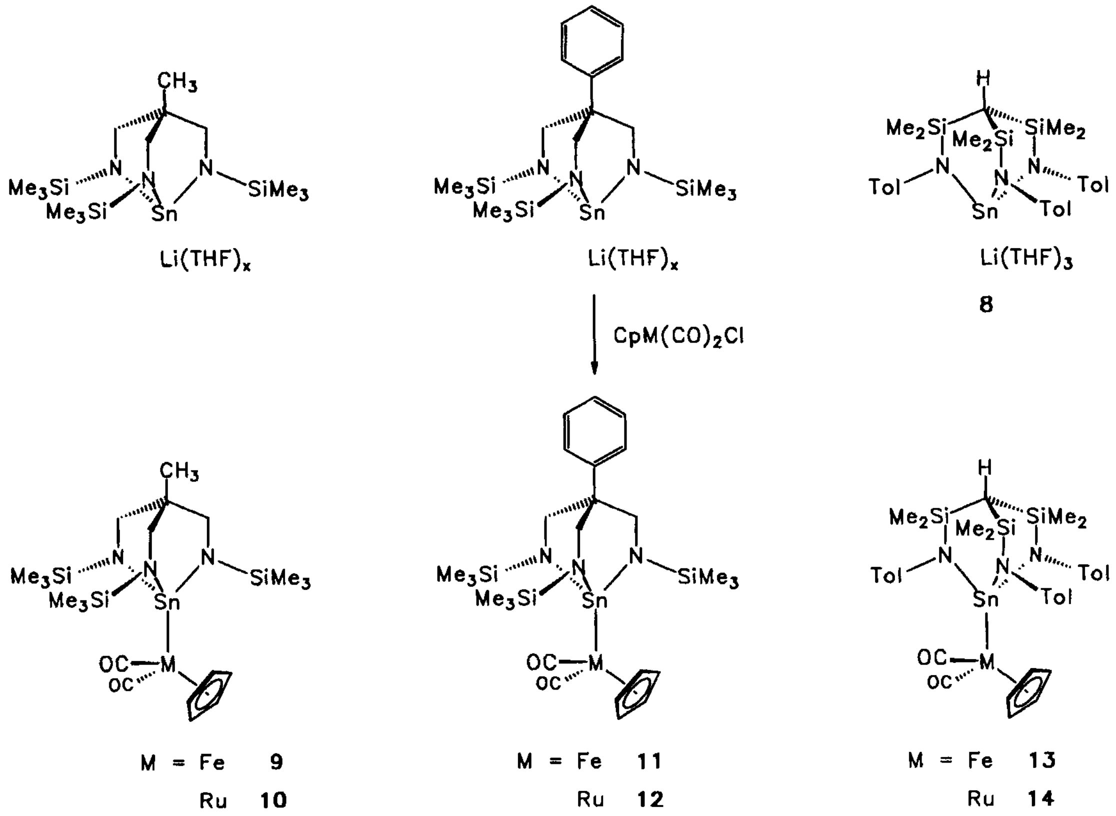
Compound	IR [a]	^1H-NMR [b]	
	ν(CO)	C_5H_5	CH_2N
$CpFe(CO)_2Cl$ [c]	2045, 2001	4.15	-
$CpRu(CO)_2Cl$ [d]	2053, 1995	4.37	-
9	1999, 1959	4.26	3.50
10	2017, 1968	4.59	3.50
11	2003, 1966	4.26	4.06
12	2009, 1969	4.59	4.07
13	2001, 1963	3.53	-
14	2021, 1975	4.00	-

[a] Recorded in toluene. – [b] Recorded in C_6D_6. – [c] From ref.[15a]. – [d] From ref.[15b].

Reaction of the in situ-generated stannates derived from **6** and **7** as well as the isolated stannate **8** with $CpM(CO)_2Cl$ (M = Fe, Ru) gave the M–Sn heterobimetallic compounds **9**–**14** in good yields (Scheme 2, Table 1)[14].

The formation of the metal-metal-bonded compounds was initially established by IR spectroscopy which indicated the expected shift of the two-band ν(CO) spectra to lower wavenumbers in comparison with those of the halides by ca. 40 and ca. 30 cm^{-1} for the iron and ruthenium compounds, respectively[15]. The resonance patterns in the ^1H-, ^{13}C- and ^{29}Si-NMR spectra of compounds **9**–**14** are consistent with an effective threefold symmetry of the amido-tin unit in these bimetallic complexes in solution, thus indicating free

Scheme 2. Coupling of the in situ-generated tripodal triamidostannates with $CpM(CO)_2Cl$ (M = Fe, Ru) to give the Sn–M-bonded heterobimetallics



rotation about the metal-metal bond. This behaviour resembles that found in the corresponding Ti–M heterobimetallics which we recently investigated[3]. As in the case of the Ti–M-bonded analogues of **13**, **14**, a remarkable ^1H-NMR spectroscopic feature in the coupled product is the considerable shift of the Cp-ring signal to higher field (**13**: $\delta = 3.53$; **14**: $\delta = 4.00$ vs. 4.15 and 4.37 in the respective starting materials). Thus, the chemical shifts of the Cp protons in **13** and **14** are almost identical with those found for the Ti–M analogues. This again is thought to be due to the "lamp shade" arangement of the tolyl groups in the bimetallic complexes. As a consequence of this preferred conformation, the Cp protons lie in the high-field shift region of the anisotropy cones of the tolyl groups in the ligand. The geometrical and magnetic influence of the "lamp shade" therefore appears to be the determining factor for the ^1H-NMR spectroscopic properties of the protons at the Cp rings rather than the polar metal-metal bond itself. This notion is supported by the comparison of the NMR spectra of **9** and **10** with those of their Ti analogues. Whereas the corresponding signals in the Ti–Fe and Ti–Ru compounds with this ligand appear at $\delta = 4.59$ and 4.99, respectively, those in **9** and **10** are observed at $\delta = 4.26$ and 4.59, thus at significantly higher field!

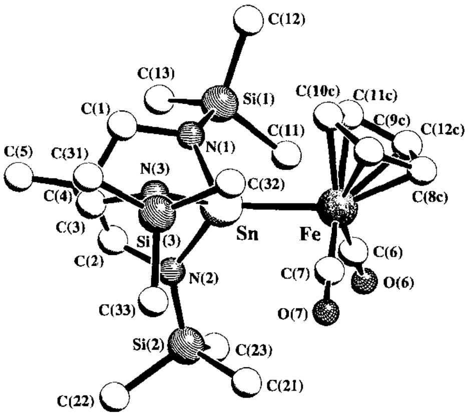
Another "ring current" effect is the down-field shift of the CH_2N protons in the tripodal amido ligand systems on going from the methyl-substituted apices in **9** and **10** [$\delta(CH_2N) = 3.50$ for **9** and **10**] to the phenyl substituents in the corresponding complexes **11** and **12** [$\delta(CH_2N) = 4.06$ (**11**) and 4.07 (**12**)].

C. Crystal Structure of $H_3CC(CH_2NSiMe_3)_3Sn{-}Fe(CO)_2Cp$ (9)

In order to establish the molecular structures of the heterobimetallics as deduced from the spectroscopic data but, most of all, to relate the bimetallic complexes reported here to those containing titanium (and thus a highly Lewis-acidic metal centre) instead of tin, a single-crystal X-ray structure analysis of **9** was carried out. Its molecular structure in the crystal is depicted in Figure 1 along with the principal bond lengths and interbond angles.

The most prominent structural feature is the bicyclo[2.2.2]octane-derived triamidostannate cage comprising the hydrocarbon ligand backbone and the SnN_3 unit. In contrast to the structure of the trisilylmethane-derived triamidostannate $[HC\{SiMe_2N(p\text{-Tolyl})\}_3Sn]^-$ which we determined recently[6] as well as the tripodal transition metal amido complexes[2,3], the coordination geometry at two of the amido-N atoms in **9** deviates significantly from a planar arrangement [sum of angles at N(1): 356.9(4)° and N(3): 351.1(4)°]. Since the tin atom apparently does not enforce a significantly distorted ligand backbone (the bond parameters of the ligand in **9** are far closer to the idealized values than for instance those found for the corresponding lithium amide $[H_3CC\{CH_2N(Li)SiMe_3\}_3]_2$)[1a], the nonplanar nitrogen environment is reflecting a lack of N–Sn

Figure 1. The molecular structure of **9** in the crystal. Principal bond lengths [Å] and interbond angles [°]: Sn−Fe 2.539(1), Sn−N(1) 2.066(6), Sn−N(2) 2.064(6), Sn−N(3) 2.071(6), Fe−C(6) 1.751(10), Fe−C(7) 1.762(8), N(1)−Si(1) 1.715(6), N(2)−Si(2) 1.713(6), N(3)−Si(3) 1.728(6); N(1)−Sn−Fe 116.8(2), N(2)−Sn−Fe 128.2(2), N(3)−Sn−Fe 122.0(2), N(1)−Sn−N(2) 93.3(2), N(1)−Sn−N(3) 95.7(2), N(2)−Sn−N(3) 93.0(2), C(6)−Fe−Sn 90.8(3), C(7)−Fe−Sn 92.0(3), C(6)−Fe−C(7) 94.5(4), Si(1)−N(1)−Sn 131.4(3), C(1)−N(1)−Sn 107.6(4), C(1)−N(1)−Si(1) 117.9(5), Si(2)−N(2)−Sn 133.2(4), C(2)−N(2)−Sn 108.1(4), C(2)−N(2)−Si(2) 117.7(5), Si(3)−N(3)−Sn 129.5(3), C(3)−N(3)−Sn 108.2(4), C(3)−N(3)−Si(3) 113.4(5)



π-donor interaction in this system. The situation is additionally highlighted by the fact that both in **9** and in the Ti analogue two of the *N*-bonded $SiMe_3$ groups are forced appart by the Cp ring at the Fe atom. However, only in the case of **9** is a significant deviation of the N atoms observed from a planar arrangement. A significant parameter reflecting the steric interaction between the two metal complex fragments in **9** as well as the Ti compounds is the M−Fe−$Cp_{(centre)}$ angle [M = Sn: 119.6(4); Ti: 121.0(8)°]. The average Sn−N and Si−N distances of, respectively, 2.067 and 1.719 Å lie within the expected range[16]. As a consequence of the larger atomic radius of tin in comparison with tetravalent titanium, the amide-bonded metal atom slightly protrudes from the cage [average ∡(N−Sn−Fe) = 122.3(2)° in comparison with $∡_{av}$(N−Ti−Fe) = 115.8(5)° in the titanium analogue]. This particular situation leads to a markedly reduced steric interaction between the amide ligand and the $CpM(CO)_2$ unit compared to that observed in either the Ti−Ru or Ti−Fe heterobimetallics. The average ∡(N−Sn−N) of 94° (and thus close to 90°!) indicates that N−Sn σ-bonding is dominated by the tin-centred valence p orbitals as has been observed previously in the crystal structures of stannates[4,6]. The carbonyl ligands at the iron stay well clear of the Sn centre [d_{av}(Sn−CO) = 3.12 Å; $∡_{av}$(Sn−Fe−CO) = 92°] and there is thus no indication of any kind of carbonyl interaction with the group IVb metal. The Fe−Sn distance [2.539(1) Å] is comparable to those previously found in Fe−Sn heterobimetallics, such as $Cp(CO)_2Fe-SnPh_3$ (2.533 Å)[17], $Cp(CO)_2Fe-SnCl_3$ [2.467(1) Å][18], $Cp(CO)_2$-$Fe-SnBr_3$ [2.462(2) Å][19], as well as $[Cp(CO)_2Fe]_2SnCl_2$ [2.492(8) Å][20], $[CpFe(CO)_2-Sn\{(NtBu)_2SiMe_2\}Me]$ [2.532(2) Å][21], $[CpFe(CO)_2\{Sn(NtBu)_2SiMe_2\}]_2$ [2.605(2) Å][21] and $[Cp(CO)_2Fe]_2Sn(N_3)_2$ [2.504(1) Å][22].

Conclusion

This study has established the use of tripodal triamidostannates as nucleophilic building blocks in the generation of Sn−M (M = Fe, Ru) heterobimetallic complexes. This represents the "inverse" coupling strategy to that employed in the generation of early-late transition metal heterobimetallic compounds reported previously by us. Current work carried out in this area focuses upon the application of the highly nucleophilic Sn compounds in selective transformations of functionalized hydrocarbons.

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Experimental

All manipulations were performed under dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves.

^1H, ^{13}C, ^{29}Si, and ^7Li NMR: Bruker AC 200, equipped with a B-VT-2000 variable-temperature unit (at 200.13, 50.32, 39.76, and 77.88 MHz, respectively), tetramethylsilane and LiI/H_2O (1 M, external) as references. − IR: Bruker IRS 25 FT. − Elemental analyses: Microanalytical laboratory of the Chemistry Department at Würzburg. − $H_3CC(CH_2NHSiMe_3)_3$[1a] and $HC\{SiMe_2NH(p\text{-}Tolyl)\}_3$[2c] were prepared as reported previously. All other chemicals used as starting materials were obtained commercially and used without further purification.

1) *Preparation of a,a,a-Tris{[(trimethylsilyl)amino]methyl}toluene* (**5**)

a) *a,a,a-Tris(hydroxymethyl)toluene* (**1**): A suspension of 107.5 g (0.90 mol) of phenylacetaldehyde, 168 g (5.60 mol) of paraformaldehyde, and 52 g (0.70 mol) of $Ca(OH)_2$ in 600 ml of THF was stirred at 60−65°C for 4 d. After cooling to room temp. the reaction mixture was filtered through Celite and the solvent removed in vacuo. Vacuum distillation of the residue yielded **1** as a yellow highly viscous oil (b.p. 135°C/0.05 Torr) which crystallized upon standing at room temp. Yield 95.5 g (58%). − ^1H NMR ($CDCl_3$, 295 K): δ = 3.94 (s, 6H, CH_2OH), 7.20−7.36 (m, 5H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 48.6 (PhC), 66.0 (CH_2OH), 126.7 (C^3), 127.0 (C^4), 128.7 (C^2), 139.5 (C^1). − IR ($CHCl_3$): $\tilde{\nu}$ = 3470 cm^{-1} s br, 3080 w, 3055 w, 2997 s, 2930 s, 2880 s, 1725 w, 1715 w, 1640 m, 1595 m, 1498 m, 1492 m, 1483 m, 1465 m, 1445 m, 1415 m, 1383 m, 1170 m, 1102 s, 1065 vs, 1047 vs, 1010 vs, 992 s, 702 vs, 645 m. − $C_{10}H_{14}O_3$ (182.2): calcd. C 65.92, H 7.74; found C 66.27, H 7.30.

b) *a,a,a-Tris[(4-tolylsulfonyl)methyl]toluene* (**2**): To a solution of 87.17 g (0.48 mol) of **1** in 900 ml of pyridine, which was cooled at 0°C, toluenesulfonyl chloride (365 g, 1.91 mol) was added in small portions so as to keep the reaction temp. between 5 and 10°C. After stirring at ambient temp. for 16 h the reddish-coloured reaction mixture was poured into 1.5 l of ice/water. The precipitate thus obtained was filtered off, washed with three 200-ml portions of diethyl ether and dried in vacuo to yield **2** as a white solid (277.65

g, 90%), m.p. 136°C. – ^{1}H NMR ($CDCl_3$, 295 K): $\delta = 2.43$ (s, 9H, CH_3), 4.17 (s, 6H, CH_2), 6.92–7.22 (m, 5H, C_6H_5), 7.28 (d, 6H, H^3, $^3J_{HH} = 8.4$ Hz), 7.60 (d, 6H, H^2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = 21.6$ (CH_3), 45.9 (Ph*C*), 68.8 (CH_2), 126.2 (Ph: C^4), 127.9 (Tos: C^2), 128.0 (Ph: C^3), 128.8 (Ph: C^2), 130.0 (Tos: C^3), 131.7 (Tos: C^4), 134.8 (Ph: C^1), 145.3 (Tos: C^1). – IR (KBr): $\tilde{\nu} = 3090\ cm^{-1}$ w, 3060 w, 2960 w, 2920 w, 1920 vw, 1795 vw, 1730 vw, 1645 vw, 1595 s, 1490 m, 1465 m, 1455 m, 1442 m, 1398 s, 1360 vs, 1305 m, 1290 m, 1220 m, 1190 vs, 1170 vs, 1140 m, 1120 m, 1093 s, 1070 m, 1035 w, 1018 m, 980 vs, 952 vs, 910 w, 870 m, 845 vs, 810 vs, 780 vs, 760 vs, 740 m, 690 m, 665 vs, 625 m. – $C_{31}H_{32}O_9S_3$ (644.8): calcd. C 57.75, H 5.00; found C 57.67, H 5.01.

c) *a,a,a-Tris(azidomethyl)toluene* (**3**): A solution of 56.8 g (88.1 mmol) of **2** und 31.5 g (485 mmol) of NaN_3 in 350 ml of diethylene glycol was stirred at 135°C for 16 h. After cooling to room temp., the deeply coloured reaction mixture was poured into 750 ml of H_2O and the suspension extracted with 800 ml of diethyl ether. The organic phase was dried with Na_2SO_4 and stirred in the presence of activated carbon, filtered and the solvent evaporated in vacuo to yield crude **3** as an orange-brown oil which was used in the subsequent conversions (**CAUTION:** *Alkyl azides are potentially hazardous chemicals!*). Yield of crude product: 18.87 g (83%). – ^{1}H NMR ($CDCl_3$, 295 K): $\delta = 3.71$ (s, 6H, CH_2), 7.21–7.46 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = 46.9$ (Ph*C*), 54.3 (CH_2), 126.2 (C^3), 127.8 (C^4), 128.8 (C^2), 138.3 (C^1). – IR (neat): $\tilde{\nu} = 3340\ cm^{-1}$ m br, 3050 m, 3020 m, 2925 s, 2865 s, 2095 vs, 1720 w, 1635 w, 1595 m, 1493 s, 1445 s, 1345 s, 1285 vs, 1155 s, 1115 s br, 1065 s, 1025 m, 905 m, 880 m, 812 m, 762 s, 698 vs, 662 m.

d) *a,a,a-Tris(aminomethyl)toluene* (**4**): A solution of 18.87 g (73.3 mmol) of **3** in 80 ml of THF was added dropwise to a suspension of 10 g (264 mmol) of $LiAlH_4$ in 170 ml of THF, and the reaction mixture was subsequently refluxed for 16 h. It was then carefully hydrolyzed by successively adding 10 g of ice, 15 ml of 15% NaOH, and again 30 g of ice. The lithium and aluminium salts which precipitated were separated by filtration and the product extracted with THF in a Soxhlet apparatus overnight. The extract was combined with the filtrate, the THF removed in vacuo and the water in the residue removed by azeotropic distillation with 300 ml of benzene using a Dean-Stark trap. After removal of the solvent the reaction product **4** was obtained by vacuum distillation as a light yellow oil (b.p. 113°C/0.08 Torr). Yield 8.48 g (65%). – ^{1}H NMR ($CDCl_3$, 295 K): $\delta = 2.98$ (s, 6H, CH_2), 7.18–7.33 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = 44.8$ (CH_2), 48.2 (Ph*C*), 125.8 (C^4), 126.5 (C^3), 128.2 (C^2), 141.7 (C^1). – IR (neat): $\tilde{\nu} = 3360$ s cm^{-1}, 3280 s, 3160 s, 3080 s, 3041 m, 3010 m, 2910 s, 2870 s, 1590 m, 1485 m, 1435 m, 1345 w, 1255 w, 1130 m, 1055 m, 1026 m, 852 s, 802 s, 755 s, 695 vs. – $C_{10}H_{17}N_3$ (179.3): calcd. C 67.00, H 9.56, N 23.44; found C 66.68, H 9.81, N 23.23.

e) *Product* **5**: The trimethylsilylation of **4** was carried out as described previously for similar triamines[1a]. B.p. 106°C/0.05 Torr, yield 75%. – ^{1}H NMR ($CDCl_3$, 295 K): $\delta = 0.02$ [s, 27H, $Si(CH_3)_3$], 2.99 (d, 6H, CH_2NH, $^3J_{HH} = 8.0$ Hz), 7.20–7.35 (m, 5H, C_6H_5). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = -0.1$ [$Si(CH_3)_3$], 46.7 (CH_2N), 48.9 (Ph*C*), 125.8 (C^4), 127.6 (C^3), 128.2 (C^2), 143.6 (C^1). – $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = 3.6$. – IR (neat): $\tilde{\nu} = 3390\ cm^{-1}$ m, 3078 w, 3040 m, 3025 m, 2950 vs, 2890 s, 2860 s, 1940 vw, 1860 vw, 1795 vw, 1600 w, 1575 vw, 1495 m, 1445 m, 1395 s, 1285 m, 1245 vs, 1115 vs, 1025 w, 855 vs br, 745 vs, 700 vs, 680 s. – $C_{19}H_{41}N_3Si_3$ (395.8): calcd. C 57.66, H 10.44, N 10.62; found C 57.68, H 9.97, N 10.68.

2) *[HC{SiMe₂N(p-Tolyl)}₃Sn][Li(THF)₃]* (**8**): To a stirred solution of 317 mg (0.63 mmol) of $HC[SiMe_2NH(p\text{-Tolyl})]_3$ in 40 ml of THF which was cooled at −40°C was added 0.75 ml (1.88 mmol) of an *n*-butyllithium/hexane solution (2.5 M), and the reaction mixture was slowly warmed to room temp. and stirred for 2 h. Then 119 mg (0.63 mmol) of $SnCl_2$ was added to the reaction mixture which was held at −60°C. After warming up to room temp. and stirring for another 1 h the solvent was removed in vacuo and the residue extracted with 30 ml of toluene. Lithium chloride generated in the reaction was separated from the reaction product by filtration through Celite. The solution of the crude product was concentrated to ca. 10 ml and stored at −35°C. Compound **8** precipitated as a colourless, highly crystalline solid which was isolated by filtration. Yield 0.42 g (79%). – ^{1}H NMR (C_6D_6, 295 K): $\delta = -0.14$ (s, $HC[Si...]_3$), 0.61 [s, $Si(CH_3)_2$], 1.23 (m, CH_2CH$_2$O), 2.24 (s, 4-$CH_3C_6H_4$), 3.14 (m, CH_2CH_2O), 6.94 (d, H^2, $^3J_{HH} = 8.2$ Hz), 7.08 (d, H^3). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 6.0$ [$Si(CH_3)_2$], 11.9 ($HC[Si...]_3$), 20.8 (4-$CH_3C_6H_4$), 25.3 (CH_2CH_2O), 68.2 (CH_2CH_2O), 124.6 (C^3), 126.0 (C^2), 129.3 (C^4), 153.5 (C^1). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = -1.0$. – $^7Li\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.59$. – $C_{40}H_{64}LiN_3O_3Si_3Sn$ (844.8): calcd. C 56.87, H 7.64, N 4.97; found C 56.92, H 7.82, N 5.01.

3) *General Procedure for the Synthesis of the Heterobimetallics* **9–14**: A solution of the tripodal triamine (2.0 mmol) in 25 ml of THF was allowed to react with 2.4 ml of an *n*-butyllithium/hexane solution (2.5 M) at −40°C, then slowly warmed to room temp. and subsequently briefly refluxed to complete lithiation. To this reactant solution was added 375 mg (2.0 mmol) of $SnCl_2$ at −60°C, the mixture warmed to room temp. and stirred for 1 h. After removal of the solvent the oily residue was dissolved in toluene and the solution again cooled to −60°C. Solid $CpM(CO)_2Cl$ (2.0 mmol) was added and the reaction mixture warmed to room temp. over a period of 16 h. After filtration the solvent was removed, the solid residue washed with cold pentane and dried in high vacuo.

9: Yield 83%, m.p. 58°C (dec.). – ^{1}H NMR (C_6D_6, 295 K): $\delta = 0.30$ [s, $Si(CH_3)_3$], 0.67 (s, CH_3C), 3.50 (s, CH_2N), 4.26 (s, C_5H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.0$ [$Si(CH_3)_3$], 26.8 (CH_3C), 40.2 (CH_3C), 59.7 (CH_2N), 83.7 (C_5H_5), 213.5 (CO). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.5$. – IR (toluene): ν(CO) 1999 cm^{-1}, 1959. – $C_{21}H_{41}FeN_3O_2Si_3Sn$ (626.4): calcd. C 40.27, H 6.60, N 6.71; found C 39.89, H 6.32, N 6.51.

10: Yield 85%, m.p. 104°C (dec.). – ^{1}H NMR (C_6D_6, 295 K): $\delta = 0.27$ [s, $Si(CH_3)_3$], 0.67 (s, CH_3C), 3.50 (s, CH_2N), 4.59 (s, C_5H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.2$ [$Si(CH_3)_3$], 25.9 (CH_3C), 40.2 (CH_3C), 59.4 (CH_2N), 86.7 (C_5H_5), 200.1 (CO). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.2$. – IR (toluene): ν(CO) 2017 cm^{-1}, 1968. – $C_{21}H_{41}N_3O_2RuSi_3Sn$ (671.6): calcd. C 35.22, H 6.15, N 6.26; found C 34.98, H 6.02, N 6.09.

11: Yield 76%. – ^{1}H NMR (C_6D_6, 295 K): $\delta = 0.29$ [s, $Si(CH_3)_3$], 4.06 (s, CH_2N), 4.26 (s, C_5H_5), 7.53 (m, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.2$ [$Si(CH_3)_3$], 48.0 (Ph*C*), 58.8 (CH_2N), 83.6 (C_5H_5), 125.6, 128.3, 128.8 ($C^{2,3,4}$), 149.2 (C^1), 213.4 (CO). – IR (toluene): ν(CO) 2003 cm^{-1}, 1966. – $C_{26}H_{43}FeN_3O_2Si_3Sn$ (656.5): calcd. C 47.58, H 6.60, N 6.40; found C 48.02, H 6.95, N 6.51.

12: Yield 85%, m.p. 63°C (dec.). – ^{1}H NMR (C_6D_6, 295 K): $\delta = 0.29$ [s, $Si(CH_3)_3$], 4.07 (s, CH_2N), 4.59 (s, C_5H_5), 7.25 (m, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 2.3$ [$Si(CH_3)_3$], 48.0 (Ph*C*), 58.4 (CH_2N), 86.5 (C_5H_5), 125.8, 126.2, 128.4 ($C^{2,3,4}$), 149.1 (C^1), 200.0 (CO). – IR (toluene): ν(CO) 2009 cm^{-1}, 1969. – $C_{26}H_{43}N_3O_2RuSi_3Sn$ (701.7): calcd. C 44.51, H 6.18, N 5.99; found C 45.02, H 6.35, N 6.21.

13: Yield 74%, m.p. 75°C (dec.). – ^{1}H NMR (C_6D_6, 295 K): $\delta = -0.30$ (s, $HC[Si...]_3$), 0.32 [s, $Si(CH_3)_2$], 2.16 (s, 4-$CH_3C_6H_4$), 3.53 (s, C_5H_5), 6.89 (d, H^2, $^3J_{HH} = 7.7$ Hz), 7.02 (d, H^3). –

$^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 5.5 [$Si(CH_3)_2$], 9.4 (HC[Si...]$_3$), 20.8 (4-$CH_3C_6H_4$), 81.8 (C_5H_5), 127.7 (C^2), 129.8 (C^3), 130.6 (C^4), 149.5 (C^1), 212.3 (CO). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = 3.8. – IR (toluene): ν(CO) 2001 cm^{-1}, 1963. – $C_{35}H_{45}FeN_3O_2Si_3Sn$ (798.6): calcd. C 52.64, H 5.68, N 5.26; found C 53.01, H 6.10, N 5.63.

14: Yield 77%, m.p. 60°C (dec.). – ^1H NMR (C_6D_6, 295 K): δ = –0.29 (s, HC[Si...]$_3$), 0.59 [s, $Si(CH_3)_2$], 2.21 (s, 4-$CH_3C_6H_4$), 4.00 (s, C_5H_5), 7.05 (d, H^2, $^3J_{HH}$ = 8.0 Hz), 7.17 (d, H^3). – $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): δ = 5.5 [$Si(CH_3)_2$], 9.2 (HC[Si...]$_3$), 20.8 (4-$CH_3C_6H_4$), 84.5 (C_5H_5), 127.8 (C^2), 129.8 (C^3), 130.2 (C^4), 149.6 (C^1), 198.8 (CO). – $^{29}Si\{^1H\}$ NMR (C_6D_6, 295 K): δ = 3.7. – IR (toluene): ν(CO) 2021 cm^{-1}, 1975. – $C_{35}H_{45}N_3O_2RuSi_3Sn$ (843.8): calcd. C 49.82, H 5.38, N 4.98; found C 50.01, H 5.49, N 5.04.

4) *X-Ray Crystallographic Study of* **9**: Clear yellow crystals of **9** were obtained from toluene and had a prismatic habit. A regular, block-shaped single crystal was mounted under argon in a Lindemann capillary. The X-ray diffraction data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range of 10° $< \Theta <$ 15°. Data were collected at 295 K in the range of Θ = 3–25° with a scan width of 0.80° by using a technique described previously[23]. An empirical absorption correction using the program DIFABS[24] was applied, and the data were corrected for Lorentz and polarization effects. The intensities of three representative reflections were measured every 5 h of X-ray exposure time; they remained constant throughout the data collection, thus indicating crystal and electronic stability (no decay correction was applied). Neutral atom scattering factors were taken from D. T. Cromer, J. T. Waber, *International Tables of X-ray Crystallography*, The Kynoch Press, Birmingham, **1974**. Crystal data: $C_{21}H_{41}FeN_3O_2Si_3Sn$, M = 626.39, orthorhombic, space group *Pbcn* (no. 60), a = 16.224(3), b = 19.511(4), c = 18.739(4) Å, V = 5931.77 Å^3, $F(000)$ = 2576, $\rho_{calcd.}$ = 1.403 g cm^{-3}, μ(Mo-K_α) = 1.40 mm^{-1}, R = 0.040, R_w = 0.046, N = 3115 [$I > 3\sigma(I)$]. – The data analysis and refinement were carried out with the programs of the SHELX 76 software package[25]. The coordinates of the metal atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined with anisotropic thermal parameters. The positions of the hydrogen atoms were located in electron density difference maps and were included in the structure factor calculations with thermal factors of 0.08 Å^2, but their parameters not refined[26].

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