

A Tripodal Triaminostannate as a Metal Nucleophile: Synthesis of Transition Metal–Tin Heterodimetallic Complexes

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In memoriam Sallaraisa Pulkkinen

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The coordination capability of the previously reported triamidostannate [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)}] (**1**) as a precursor for transition metal–tin heterodimetallic complexes is presented. Whereas reaction with CH₃I, Me₃SiCl, or Me₃SnCl yielded the derivatives [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–R}] (R = Me, **2**; Me₃Si, **3**; Me₃Sn, **4**), demonstrating the nucleophilic properties of the stannate(II), its complexation to transition metal centres was achieved by halide

substitution with [CuCl(PPh₃)₄], [CpM(CO)₂X] (M = Fe, X = Cl; M = Ru, X = Br), [CpM(CO)₃Cl] (M = Mo, W) and *trans*(Cl)-[RuCl₂(bpy)(CO)₂] to give [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Cu(PPh₃)}] (**5**), [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–M(CO)₂Cp] (M = Fe: **6**; Ru: **7**), [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–M(CO)₂Cp] (M = Mo: **8**; W: **9**) and [(MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn)₂Ru(bpy)(CO)₂] (**10**), of which **6**, **9** and **10** were characterized by X-ray diffraction.

Introduction

Transition metal–tin heterodimetallic complexes were among the first metal–metal bonded compounds to be studied in detail,^[1] and since the pioneering work of the 1960's a great number of such complexes have been synthesized and characterized.^[2] Apart from the fundamental aspect of bonding between transition metals and main group metals, the fact that the formation and transformation of transition metal–main group metal bonds are crucial steps in a variety of catalytic processes as well as semiconductor growth has created a great deal of interest.^[4,5] In spite of the multitude of known transition metal–tin compounds, some transition metal complex fragments, notably the more highly oxidizing species, do not form stable dimetallic complexes with tin fragments. In order to suppress degenerative intramolecular redox reactions, an appropriate ligand shell for the group 14 element has to be chosen.

The tripodal amido ligands developed by us^[6] were found to be ideally suited for the synthesis of group 14 triamidometallates, in particular triamidostannates.^[7–9] These triamidostannates were found to bind to potentially highly oxidizing metal centres such as the tetravalent group 4 metals^[10] as well as Ag^I, Au^{II} and Au^{III} to give thermally stable heterometallic compounds.^[11–13] The electronegative nitrogen substituents at divalent group 14 metal centres

thus appear to stabilize the metals with respect to oxidation by a heterometal centre to which they are bonded.

In view of the relative chemical inertness to oxidation by transition metals of the triamidostannates and the facile variability of their peripheral tripodal amido unit, we have recently begun to explore their properties as monoanionic “ligands” in transition metal chemistry, along with their isoelectronic neutral group 15 analogues.^[14] In this work we present a detailed study of the coordination capability of the previously reported triamidostannate [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)}] (**1**).^[11]

Results and Discussion

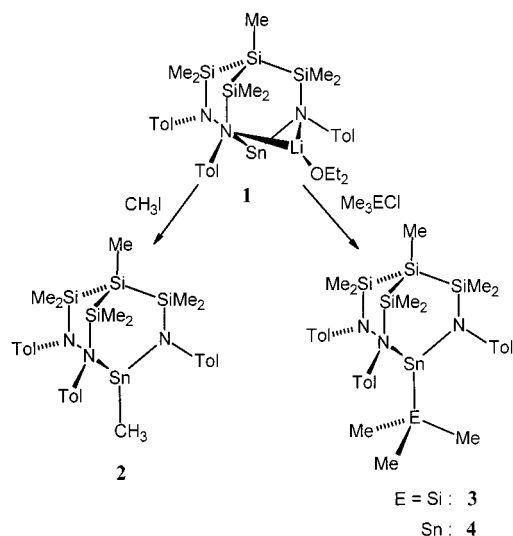
The properties of the amidostannate complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)}] (**1**)^[11] as a metal nucleophile were initially tested by reaction with CH₃I, Me₃SiCl, and Me₃SnCl. Stirring the reagents in toluene whilst warming the reaction mixture from –20 °C to ambient temperature gave the corresponding coupling products as thermally stable solids in moderate to high yields (Scheme 1).

Elemental analyses and the ¹H, ¹³C and ²⁹Si NMR spectroscopic data are in agreement with their formulation as [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–R}] (R = Me, **2**; Me₃Si, **3**; Me₃Sn, **4**); the molecular structures are depicted in Scheme 1. All three compounds display the expected three-fold symmetry in solution as indicated by the signal patterns in the NMR spectra.

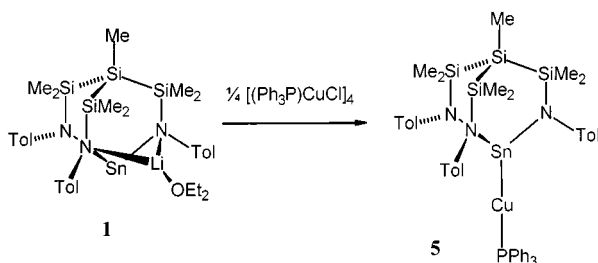
Reaction of **1** with 0.25 molar equivalents of [CuCl(PPh₃)₄] in toluene at room temperature immediately gave the Sn–Cu complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–

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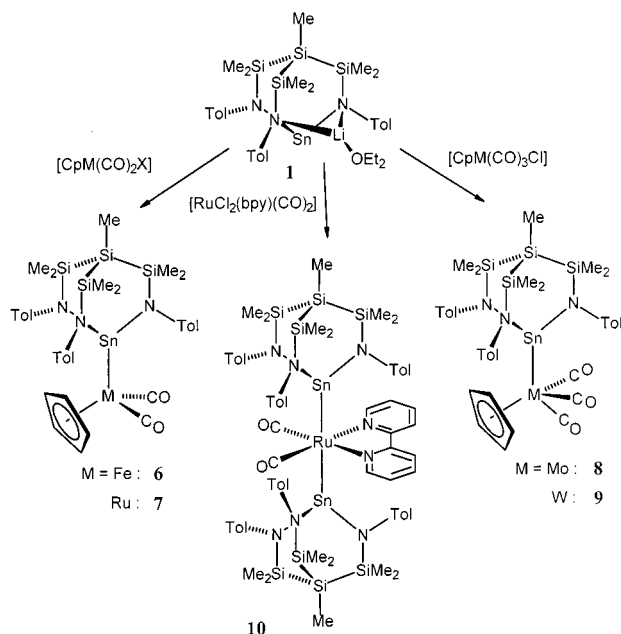
Scheme 1. Reaction of the triaminostannate with metal and non-metal electrophiles to give Sn–element bonds



Scheme 2. Synthesis of the Cu–Sn compound 5

Cu(PPh₃)] (**5**) (Scheme 2).^[15] The formation of a Sn–Cu bond in this complex is supported by the observation of ^{117/119}Sn satellites in the ³¹P NMR spectra, which appear at room temperature as an averaged ²*J*(^{117/119}Sn–³¹P) coupling satellite pattern associated with the ³¹P NMR resonance at $\delta = 0.7$. The characteristic ^{117/119}Sn–³¹P splitting pattern [²*J*(^{117/119}Sn–³¹P) = 634.2 Hz/662.8 Hz] could be observed upon lowering the temperature to 205 K. The Cu–Sn compound apparently does not undergo detectable redistribution reactions in solution and thus resembles more closely the previously characterized analogous Au–Sn complex^[12] than the Ag–Sn compound bearing the same triamidostannate unit.^[11]

As we have previously performed studies of group 4/8 heterodimetallic complexes^[16] in which the early transition metal is coordinated by the amido tripod employed in the synthesis of **1**, it was of interest to find out whether the corresponding group 14 derivatives are accessible and how their structures and properties are related to the early transition metal derivatives. [MeSi{SiMe₂N(4-CH₃C₆H₄)₃}₃SnLi(OEt₂)] (**1**) reacts with [CpM(CO)₂X] (M = Fe, X = Cl; M = Ru, X = Br) to afford the corresponding heterodimetallic complexes [MeSi{SiMe₂N(4-CH₃C₆H₄)₃}₃Sn–



Scheme 3. Synthesis of transition metal–tin heterodimetallic complexes 6–10

M(CO)₂Cp] (M = Fe: **6**; Ru: **7**; Scheme 3). They were characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy, infrared spectroscopy, and elemental analysis. The NMR spectra recorded at 295 K established the effective threefold symmetry of the heterodinuclear complexes in solution and thus indicated a rapid internal rotation of the molecules around the metal–metal axis. Cooling of these solutions led to the broadening of the resonances at 200 K but it was not possible to reach the low temperature limit corresponding to a frozen internal rotation on the NMR time scale. In the CO stretching region of the IR spectrum, [MeSi{SiMe₂N(4-CH₃C₆H₄)₃}₃Sn–M(CO)₂Cp] exhibits two bands of approximately equal intensity (**6**: 2016 and 1971 cm^{−1}; **7**: 2031 and 1981 cm^{−1}). These values are lower than those of CpM(CO)₂X (M = Fe, X = Cl: 2050, 2004 cm^{−1} in toluene; M = Ru, X = Br: 2049, 1999 cm^{−1} in toluene) (see Table 1), due to coordination of the two strongly σ -donating and weakly π -accepting amidostannyl ligands causing an increased π back-donation to the CO ligands.

In order to establish the details of the molecular structure of the type of group 8-tin complex discussed above, a single crystal X-ray structure analysis of compound **6** was carried out. The molecular structure of **6** is shown in Figure 1, along with the principal bond lengths and angles. The tripod amido-tin unit is characterized by its rigid cage structure as found in related tin complexes previously characterized by us. The peripheral tolyl groups adopt a “lampshade” arrangement to make space for the CpFe(CO)₂ fragment bonded through a metal–metal bond. The Sn–Fe bond length found in **6** [2.5146(3) Å] is similar to those found in structurally related Fe–Sn heterodimetallics, such as [Cp(CO)₂Fe–SnPh₃] (2.533 Å),^[17] [Cp(CO)₂Fe–SnCl₃] [2.467(1) Å],^[18] [Cp(CO)₂Fe–SnBr₃] [2.462(2) Å],^[19]

Table 1. Comparison of CO stretching frequencies

Compound	ν_{CO} [cm^{-1}]	Compound	ν_{CO} [cm^{-1}]
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}]$	2050, 2004 ^[a]	(6)	2016, 1971 ^[a]
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}]$	2049, 1999 ^[a]	(7)	2030, 1981 ^[a]
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}]$	2054, 1977, 1959 ^[a]	(8)	2021, 1954, 1937 ^[a]
$[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}]$	2046, 1960, 1943 ^[a]	(9)	2018, 1944, 1930 ^[a]
<i>trans</i> - $[\text{Cl}_2\text{Ru}(\text{CO})_2(\text{bpy})]$	2065, 2004 ^[b]	(10)	2039, 1990 ^[a]

^[a] Measured in toluene. – ^[b] Measured in CH_2Cl_2 .

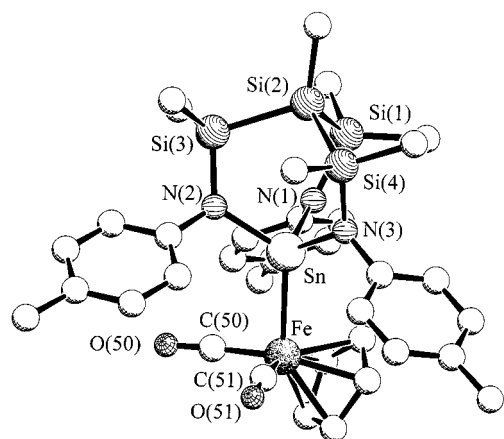


Figure 1. View of the molecular structure of **6**; principal bond lengths (Å) and angles (°): N(1)–Sn(1) 2.0652(17), N(2)–Sn(1) 2.0885(17), N(3)–Sn(1) 2.0785(18), Fe(1)–C(28) 2.099(2), Fe(1)–C(29) 2.101(2), Fe(1)–C(30) 2.088(2), Fe(1)–C(31) 2.098(2), Fe(1)–C(32) 2.102(2), Fe(1)–Sn(1) 2.5146(3), Fe(1)–C(50) 1.763(3), Fe(1)–C(51) 1.760(2), C(50)–O(50) 1.148(3), C(51)–O(51) 1.151(3); N(1)–Sn(1)–N(2) 100.81(7), N(1)–Sn(1)–N(3) 103.73(7), N(2)–Sn(1)–N(3) 99.41(7), N(1)–Sn(1)–Fe(1) 114.18(5), N(2)–Sn(1)–Fe(1) 113.13(5), N(3)–Sn(1)–Fe(1) 122.54(5), C(50)–Fe(1)–Sn(1) 89.46(8), C(51)–Fe(1)–Sn(1) 94.37(7), O(50)–C(50)–Fe(1) 177.6(2), O(51)–C(51)–Fe(1) 173.3(2)

$[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SnCl}_2$ [2.492(8) Å],^[20] $[\text{Cp}(\text{CO})_2\text{Fe}-\text{Sn}\{\text{N}(\text{tBu})_2\text{SiMe}_2\}_2\text{Me}]$ [2.532(2) Å],^[21] $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{Sn}(\text{N}(\text{tBu})_2\text{SiMe}_2)_2\}]$ [2.605(2) Å],^[21] $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{Sn}(\text{N}_3)_2$ [2.504(1) Å],^[22] and $[\text{Cp}(\text{CO})_2\text{Fe}-\text{Sn}(\text{SiMe}_3\text{NCH}_2)_3\text{CCH}_3]$ [2.539(1) Å].^[24] The Sn–Fe–C(carbonyl) bond angles are nearly perpendicular [89.46(8)° and 94.37(7)°] and resemble those in $[\text{Cp}(\text{CO})_2\text{Fe}-\text{Sn}(\text{SiMe}_3\text{NCH}_2)_3\text{CCH}_3]$.^[24]

In analogy to the formation of the Fe–Sn and Ru–Sn complexes, compound **1** reacts with the group 6 metal complexes $[\text{CpM}(\text{CO})_3\text{Cl}]$ (M = Mo, W) to afford the corresponding heterodimetallic complexes $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}-\text{M}(\text{CO})_2\text{Cp}]$ (M = Mo: **8**; W: **9**) (Scheme 3). However, their NMR spectral patterns recorded at room temperature differ considerably from those found for the Fe and Ru analogues. The ^1H NMR spectrum exhibits two singlets for the SiMe_2 groups (**8**: δ = 0.58, 0.62; **9**: δ = 0.54, 0.62), two singlets for the $\text{CH}_3(\text{C}_6\text{H}_4)$ groups (**8**: δ = 2.17, 2.19; **9**: δ = 2.12, 2.15), and four doublets for the aromatic protons (**8**: δ = 6.94, 7.05, 7.18, 7.21; **9**: δ = 6.88, 7.03, 7.14, 7.20). In addition, two ^{13}C NMR carbonyl resonances (**8**: δ = 224.7, 230.0; **9**: δ = 213.5, 217.4) and three ^{29}Si NMR signals [**8**: δ = –89.0 (SiMe), 1.9, 2.4

(SiMe_2); **9**: δ = –89.1 (SiMe), 1.7, 2.2 (SiMe_2)] have been detected at room temperature. It is thus clear that the internal rotation around the metal–metal bond axis is frozen out on the NMR time scale at 295 K. This is a consequence of the sterically more encumbered coordination sphere around the group 6 metal bearing an additional carbonyl ligand with respect to **6** and **7**.

In a series of high temperature ^1H NMR spectra of **8** and **9** coalescence of the proton resonances was observed and the high temperature limit attained at 340 K for **8** and at 350 K for **9**. At these temperatures the ^1H NMR spectra of both compounds show one singlet for the SiMe_2 groups (**8**: δ = 0.52; **9**: δ = 0.51), one singlet for the $\text{CH}_3(\text{C}_6\text{H}_4)$ groups (**8**: δ = 2.16; **9**: δ = 2.17), and two doublets for the aromatic protons (**8**: δ = 6.94, 7.13; **9**: δ = 6.94, 7.14), whereas only one ^{13}C NMR carbonyl resonance (**8**: δ = 224.9; **9**: δ = 213.7) has been observed. Coalescence of the SiMe_2 and $\text{CH}_3(\text{C}_6\text{H}_4)$ resonances is observed at T_c = 313 K (**8**), and T_c = 316 K (**9**), and an activation enthalpy for the rotation around the Sn–M bond of ΔG^\ddagger = 67.8 ± 1.0 kJ·mol^{–1} (**8**) and 68.3 ± 1.0 kJ·mol^{–1} (**9**) may be estimated based on these data.

The different dynamic behaviour in solution of the group 6 tricarbonyl derivatives in comparison with the group 8 dicarbonyl complexes made a detailed structural characterization desirable. To this end a single crystal X-ray diffraction study of compound **9** was carried out. The molecular structure of **9** is depicted in Figure 2 along with the principal bond lengths and interbond angles.

The overall molecular structure resembles that of **6**, the triamidotin unit being structurally very similar. The Sn–W bond length in **9** [2.7826(2) Å] is comparable to those found in structurally related W–Sn heterodimetallics, such as $[\text{Cp}(\text{CO})_3\text{W}-\text{SnCl}_2(\text{tBu})]$ (2.752 Å),^[25] $[(\text{Ph}_2\text{Si}-\text{O}-\text{SiPh}_2)_2\text{O}_2\text{Sn}(\text{tBu})-\text{W}(\text{CO})_3\text{Cp}]$ (2.779 Å and 2.761 Å),^[26] $[\text{Cp}(\text{CO})_3\text{W}-\text{SnCl}_2-\{\text{Os}(\text{CO})_4\}_2\text{Os}(\text{CO})_4\text{Cl}]$ (2.756 Å),^[27] $[\text{Ph}_3\text{Sn}-\text{W}(\text{Cp})_2-\text{SnCl}(\text{tBu})_2]$ (2.811 Å and 2.794 Å)^[28] and $[\text{IHg}-\text{W}(\text{Cp})_2-\text{SnPh}_3]$ (2.768 Å).^[17] The Sn–W–C(carbonyl) bond angles are 75.79(9)°, 74.83(9)°, and 126.44(10)° and reflect the steric hindrance around the W centre. The W–C distances of the two carbonyl ligands pointing towards the tin fragment are virtually identical [C(50)–W(1): 1.996(4) Å; C(51)–W(1): 1.987(3) Å] to that of the carbonyl pointing away from the W–Sn bond [C(52)–W(1): 2.002(3) Å].

In the synthesis of complexes **6–9** the triamidostannate was reacted with transition metal monohalide complexes to

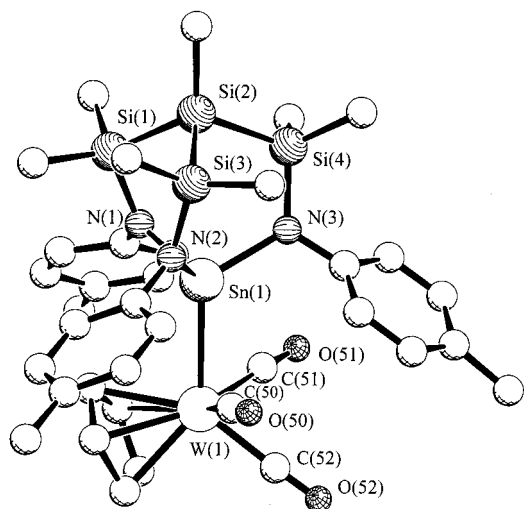


Figure 2. View of the molecular structure of **9**; principal bond lengths (Å) and angles (°): N(1)–Sn(1) 2.084(2), N(2)–Sn(1) 2.068(3), N(3)–Sn(1) 2.078(3), W(1)–C(28) 2.316(3), W(1)–C(29) 2.345(3), W(1)–C(30) 2.355(3), W(1)–C(31) 2.340(3), W(1)–C(32) 2.319(3), W(1)–Sn(1) 2.7826(2), W(1)–C(50) 1.996(4), W(1)–C(51) 1.987(3), W(1)–C(52) 2.002(3), C(50)–O(50) 1.140(4), C(51)–O(51) 1.146(4), C(52)–O(52) 1.135(4); N(1)–Sn(1)–N(2) 100.30(10), N(1)–Sn(1)–N(3) 101.64(10), N(2)–Sn(1)–N(3) 102.51(10), N(1)–Sn(1)–W(1) 114.47(7), N(2)–Sn(1)–W(1) 116.95(7), N(3)–Sn(1)–W(1) 118.30(7), C(50)–W(1)–Sn(1) 75.79(9), C(51)–W(1)–Sn(1) 74.83(9), C(52)–W(1)–Sn(1) 126.44(10), O(50)–C(50)–W(1) 174.8(3), O(51)–C(51)–W(1) 174.2(3), O(52)–C(52)–W(1) 177.4(3).

form a single metal–metal bond. To extend this synthetic approach, a coupling with a “difunctional” transition metal complex (bearing two displaceable halide ligands) was attempted. Reaction of *trans*(Cl)–[RuCl₂(bpy)(CO)₂]^[30] with two molar equivalents of **1** in THF afforded the trinuclear complex **10** in moderate yield (Scheme 3). Its NMR spectroscopic data (¹H, ¹³C, ²⁹Si) indicate a local threefold symmetry of the stannate fragment in solution. The IR spectrum of **10** shows two equally intense bands in the CO stretching region at 2039 and 1990 cm^{−1}, which can be assigned to ν_s(CO) and ν_{as}(CO), respectively. The strongly σ-donating and weakly π-accepting amidostannyl ligands shift the wavenumbers to smaller values than those of *trans*(Cl)–[RuCl₂(bpy)(CO)₂] (2065, 2004 cm^{−1} in CH₂Cl₂) (see Table 1). It is noteworthy that the reaction of *trans*(Cl)–[RuCl₂(bpy)(CO)₂] with one molar equivalent of **1** instantaneously yields **10** and 0.5 molar equivalent of unchanged *trans*(Cl)–[RuCl₂(bpy)(CO)₂]. The substitution of the second chloro ligand therefore appears to be accelerated by the strong trans effect of the triamidostannate bonded to the ruthenium centre upon the first substitution step. This trinuclear complex is the first of its type using the triamidostannate cages and was therefore structurally characterized by X-ray diffraction.

The molecular structure of **10** is depicted in Figure 3, along with the principal bond lengths and angles. The two [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn}][−] ligands are bonded to the Ru centre in a nearly linear fashion [Sn(1)–Ru–Sn(2):

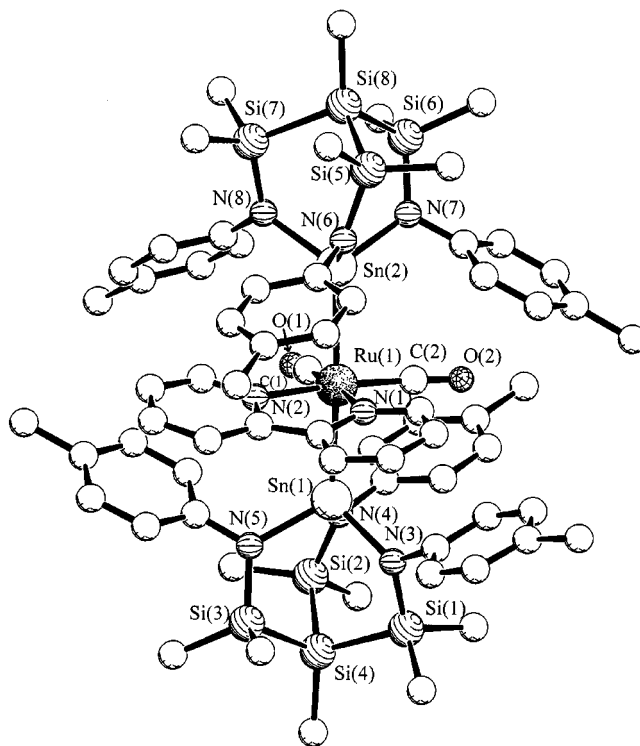


Figure 3. View of the molecular structure of **10**; principal bond lengths (Å) and angles (°): N(3)–Sn(1) 2.098(4), N(4)–Sn(1) 2.107(4), N(5)–Sn(1) 2.113(3), N(6)–Sn(2) 2.098(4), N(7)–Sn(2) 2.109(3), N(8)–Sn(2) 2.113(4), Ru(1)–N(1) 2.117(4), Ru(1)–N(2) 2.113(3), Ru(1)–Sn(1) 2.7085(5), Ru(1)–Sn(2) 2.7324(5), Ru(1)–C(1) 1.863(5), Ru(1)–C(2) 1.877(5), C(1)–O(1) 1.148(6), C(2)–O(2) 1.148(5); N(3)–Sn(1)–N(4) 101.61(14), N(4)–Sn(1)–N(5) 97.10(14), N(6)–Sn(2)–N(7) 96.40(14), N(6)–Sn(2)–N(8) 99.45(14), N(7)–Sn(2)–N(8) 100.26(14), Sn(1)–Ru(1)–Sn(2) 174.26(2), N(1)–Ru(1)–Sn(1) 91.67(10), N(2)–Ru(1)–Sn(1) 90.25(10), N(1)–Ru(1)–Sn(2) 93.98(10), N(2)–Ru(1)–Sn(2) 90.12(10), N(1)–Ru(1)–N(2) 76.15(15), C(1)–Ru(1)–C(2) 87.6(2), C(1)–Ru(1)–N(1) 173.35(18), C(2)–Ru(1)–N(2) 171.80(19), O(1)–C(1)–Ru(1) 174.3(4), O(2)–C(2)–Ru(1) 176.9(5).

174.26(2) °] and are staggered with respect to their tolyl groups. The Ru–Sn bond lengths of 2.7085(5) and 2.7324(5) Å are slightly longer than the typical values for Ru–Sn bonds (2.55–2.69 Å).^[31] Similar structural parameters have been recently described in the closely related compound [Ru(SnPh₃)₂(CO)₂](iPr-DAB) (iPr-DAB = *N,N'*-diisopropyl-1,4-diaza-1,3-butadiene),^[32] where Ru–Sn bond lengths of 2.686(2) and 2.691(2) Å, and an Sn–Ru–Sn bond angle of 173.45(7)° were found. The shorter carbonyl C–O bond lengths [1.133(22) and 1.123(20) Å] in the precursor complex *trans*(Cl)–[RuCl₂(bpy)(CO)₂]^[30] compared to those of **10** [1.148(6) and 1.148(5) Å] may be due to the strong σ-donation of the stannyl ligands in the latter and confirm the results obtained by IR spectroscopy. The pyridine rings in the bpy subunit are slightly twisted with respect to each other, probably due to the steric demand of the tolyl groups [torsional angles: N(1)–C(14)–C(15)–N(2): 1.1(6)° and C(13)–C(14)–C(15)–C(16): 2.8(8)°].

Conclusion

This study has not only established new types of transition metal–tin complexes but introduced the monoanionic triamidostannate $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}]^-$ as a “ligand” in transition metal chemistry. This system is iso-electronic to the neutral group 15 analogues but, due to its charge, gives access to structures which are complementary to those of phosphane, arsane or stibane complexes. A particularly interesting aspect of its chemistry is the *trans* effect of the stannate established for the substitution of the two *trans* disposed chloro ligands in the synthesis of **10**. Along with further aspects of the structural chemistry it is this point which we are currently studying in the context of the potential of the stannates in homogeneous catalysis.

Experimental Section

General: All manipulations were performed under argon (desiccant P_4O_{10} , Granusic®, J.T. Baker) on a high vacuum line using standard Schlenk techniques, or in a glovebox. All reaction flasks were heated prior to use using three evacuation-refill cycles. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with argon. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive “freeze–pump–thaw” cycles and stored over 4 Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite. The ^1H , ^{13}C , ^{29}Si and ^{31}P NMR spectra were recorded on a Bruker AC 200, a Bruker Avance 250 and a Bruker AMX 400 FT NMR spectrometer, respectively. ^1H and ^{13}C data are listed in parts per million [ppm] relative to tetramethylsilane and were referenced using the residual protonated solvent peak (^1H) or the carbon resonance (^{13}C). ^{29}Si data are listed in ppm relative to tetramethylsilane as an external standard. ^{31}P data are listed in ppm relative to 85% H_3PO_4 as an external standard. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out with a Leco CHNS-932 microanalyzer and a CE-instruments EA 1110 CHNS-O microanalyzer, respectively. The compounds $[\text{CpFe}(\text{CO})_2\text{Cl}]$,^[33] $[\text{CpRu}(\text{CO})_2\text{Br}]$,^[34] *trans*- $[\text{RuCl}_2(\text{bpy})-(\text{CO})_2]$,^[35] $[\text{CpMo}(\text{CO})_3\text{Cl}]$,^[36] $[\text{CpW}(\text{CO})_3\text{Cl}]$,^[36] $[\text{CuCl}(\text{PPh}_3)]_4$ ^[37] and $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{SnLi}(\text{OEt}_2)]^{[11]}$ were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{SnCH}_3]$ (2**):** Methyl iodide (30 μL , 67.4 mg, 0.475 mmol) was added to a solution of $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{SnLi}(\text{OEt}_2)]$ (**1**) (348 mg, 0.474 mmol) in 15 mL of toluene at -20°C . The reaction mixture was subsequently warmed to ambient temperature, centrifuged, and the filtrate evaporated to dryness. The colourless, microcrystalline residue was washed twice with cold pentane and then dried in vacuo. Yield: 307 mg (97%). – ^1H NMR (200.13 MHz, C_6D_6 , 295 K): δ = 0.03 (s, 3 H, SnCH_3), 0.20 (s, 3 H, SiCH_3), 0.57 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.10 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.88 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, $\text{ToI-H}^{2,6}$), 6.98 (d, 6 H, $\text{ToI-H}^{3,5}$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, C_6D_6 , 295 K): δ = –15.0 (SiCH_3), –9.3 (SnCH_3), 3.4 [$\text{Si}(\text{CH}_3)_2$], 20.7 ($\text{CH}_3\text{C}_6\text{H}_4$), 125.9 ($\text{ToI-C}^{2,6}$), 130.1 ($\text{ToI-C}^{3,5}$), 130.9 (ToI-C^4), 147.6 (ToI-C^1). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (39.76 MHz, C_6D_6 , 295 K): δ = –91.3 (SiCH_3), 4.3 [$\text{Si}(\text{CH}_3)_2$]. – $^{29}\text{H}_4\text{N}_3\text{Si}_4\text{Sn}$ (666.73): calcd. C 52.24, H 6.80, N 6.30; found C 52.57, H 6.97, N 6.41.

Preparation of $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{Sn–SiMe}_3]$ (3**) and $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{Sn–SnMe}_3]$ (**4**):** Me_3SiCl or Me_3SnCl (0.475 mmol) was added to a solution of $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{SnLi}(\text{OEt}_2)]$ (**1**) (365 mg, 0.490 mmol) in 15 mL of toluene at -20°C . The reaction mixture was subsequently warmed to ambient temperature, centrifuged, and the filtrate evaporated to dryness. The colourless, microcrystalline residue was washed twice with cold pentane and then dried in vacuo. Yields: **3**: 341 mg, 96%; **4**: 388 mg, 97%.

3: ^1H NMR (200.13 MHz, C_6D_6 , 295 K): δ = –0.34 [s, 9 H, $\text{SnSi}(\text{CH}_3)_3$], 0.21 (s, 3 H, SiCH_3), 0.59 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.10 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.91 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, $\text{ToI-H}^{2,6}$), 7.05 (d, 6 H, $\text{ToI-H}^{3,5}$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, C_6D_6 , 295 K): δ = –14.4 (SiCH_3), 0.3 [$\text{Si}(\text{CH}_3)_3$], 3.4 [$\text{Si}(\text{CH}_3)_2$], 20.7 ($\text{CH}_3\text{C}_6\text{H}_4$), 125.2 ($\text{ToI-C}^{2,6}$), 130.0 ($\text{ToI-C}^{3,5}$), 130.2 (ToI-C^4), 150.3 (ToI-C^1). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (39.76 MHz, C_6D_6 , 295 K): δ = –87.0 (SiCH_3), 2.1 [$\text{Si}(\text{CH}_3)_2$], 9.6 [$\text{Si}(\text{CH}_3)_3$]. – $\text{C}_{31}\text{H}_{51}\text{N}_3\text{Si}_5\text{Sn}$ (724.88): calcd. C 51.37, H 7.09, N 5.80; found C 51.86, H 7.24, N 5.91.

4: ^1H NMR (200.13 MHz, C_6D_6 , 295 K): δ = –0.26 [s, 9 H, $\text{SnSn}(\text{CH}_3)_3$], 0.22 (s, 3 H, SiCH_3), 0.60 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.10 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.91 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 6 H, $\text{ToI-H}^{2,6}$), 6.98 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 6 H, $\text{ToI-H}^{3,5}$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, C_6D_6 , 295 K): δ = –8.4 (SiCH_3), 3.5 [$\text{Si}(\text{CH}_3)_2$], 15.6 [$\text{Sn}(\text{CH}_3)_3$], 20.7 ($\text{CH}_3\text{C}_6\text{H}_4$), 124.9 ($\text{ToI-C}^{2,6}$), 130.1 ($\text{ToI-C}^{3,5}$), 130.2 (ToI-C^4), 150.0 (ToI-C^1). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (39.76 MHz, C_6D_6 , 295 K): δ = –87.3 (SiCH_3), 2.0 [$\text{Si}(\text{CH}_3)_2$]. – $\text{C}_{31}\text{H}_{51}\text{N}_3\text{Si}_4\text{Sn}_2$ (815.49): calcd. C 45.66, H 6.30, N 5.15; found C 45.80, H 6.54, N 5.33.

$[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn–Cu}(\text{PPh}_3)]$ (5**):** Precooled (-40°C) toluene (10 mL) was added to a mixture of solid $[\text{MeSi}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3\text{SnLi}(\text{OEt}_2)]$ (**1**) (376 mg, 0.51 mmol) and solid $[\text{CuCl}(\text{PPh}_3)]$ (186 mg, 0.51 mmol). The stirred solution was subsequently warmed to ambient temperature, the LiCl which precipitated removed by filtration and the concentrated filtrate (1 mL) stored for several days at -30°C . The colourless crystals of compound **5** were collected after decanting of the mother liquor and dried in vacuo. Yield: 349 mg (43%). – ^1H NMR (250.13 MHz, C_6D_6 , 295 K): δ = 0.38 (s, 3 H, SiCH_3), 0.73 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.05 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.52 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 6 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 6.85–6.96 (m, 15 H, PPh_3), 7.02 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 6 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (62.89 MHz, C_6D_6 , 295 K): δ = –13.9 (SiCH_3), 4.2 [$\text{Si}(\text{CH}_3)_2$], 20.9 ($\text{CH}_3\text{C}_6\text{H}_4$), 125.7, 126.7, 128.6, 129.3, 129.8, 132.9, 134.0, 152.6 (all tol and PPh_3). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (49.69 MHz, C_6D_6 , 295 K): δ = –88.7 (SiCH_3), –3.4 [$\text{Si}(\text{CH}_3)_2$]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.03 MHz, C_6D_6 , 295 K): δ = 0.70 (br, PPh_3). – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.03 MHz, $[\text{D}_8]\text{toluene}$, 205 K): δ = 6.6 [$^2J(^{117/119}\text{Sn–}^{31}\text{P}) = 634.2/662.8$ Hz, PPh_3]. $\text{C}_{46}\text{H}_{57}\text{CuN}_3\text{PSi}_4\text{Sn}$ (984.68): calcd. C 56.52, H 5.88, N 4.30; found C 56.19, H 5.73, N 4.29.

$[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn–Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (6**):** A mixture of solid $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}]$ (116 mg, 0.55 mmol) and $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{SnLi}(\text{OEt}_2)]$ (**1**) (400 mg, 0.55 mmol) was dissolved at room temperature in toluene (15 mL) and stirred for 3 h. The solution was filtered through Celite and the residue was extracted with toluene (10 mL). After complete removal of the solvent, a bright yellow, crystalline solid was obtained, which was subsequently washed with pentane (10 mL) and dried in vacuum (yield: 308 mg, 68%). Suitable crystals for the structure determination could be obtained from a saturated solution of **6** (100 mg) in benzene (0.5 mL) at room temperature. – ^1H NMR (200.13 MHz, C_6D_6 , 295 K): δ = 0.28 (s, 3 H, SiCH_3), 0.62 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.16 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.43 (s, 5 H, C_5H_5), 7.01 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 6 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.19 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 6 H, $\text{H}^{3,5}$

of $\text{CH}_3\text{C}_6\text{H}_4$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, C_6D_6 , 295 K): δ = –14.6 (SiCH_3), 3.8 [$\text{Si}(\text{CH}_3)_2$], 20.8 ($\text{CH}_3\text{C}_6\text{H}_4$), 81.8 (C_5H_5), 128.9 ($\text{C}^{2,6}$), 129.7 ($\text{C}^{3,5}$), 131.4 (C^4), 149.7 (C^1), 212.8 (CO). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (39.76 MHz, C_6D_6 , 295 K): δ = –90.0 (SiCH_3), 0.8 [$\text{Si}(\text{CH}_3)_2$]. – IR (toluene): $\nu(\text{CO})$ = 2016, 1971 cm^{-1} . – $\text{C}_{35}\text{H}_{47}\text{FeN}_3\text{O}_2\text{Si}_4\text{Sn}$ (828.65): calcd. C 50.73, H 5.72, N 5.07; found C 50.83, H 5.91, N 5.23.

[MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Ru(η^5 -C₅H₅)(CO)₂] (7): An analogous procedure described to prepare **6**, with 61.8 mg (0.21 mmol) of [$(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$] and 150 mg (0.21 mmol) of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (**1**) dissolved in 10 mL of toluene, afforded compound **7** (100 mg, 56%) as a yellow, crystalline solid. – ^1H NMR (250.13 MHz, C_6D_6 , 295 K): δ = 0.29 (s, 3 H, SiCH_3), 0.63 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.16 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.88 (s, 5 H, C_5H_5), 7.01 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.16 (d, $J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (62.89 MHz, C_6D_6 , 295 K): δ = –14.6 (SiCH_3), 3.8 [$\text{Si}(\text{CH}_3)_2$], 20.8 ($\text{CH}_3\text{C}_6\text{H}_4$), 84.6 (C_5H_5), 128.8 ($\text{C}^{2,6}$), 129.7 ($\text{C}^{3,5}$), 130.5 (C^4), 149.9 (C^1), 199.4 (CO). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (49.69 MHz, C_6D_6 , 295 K): δ = –89.7 (SiCH_3), 0.7 [$\text{Si}(\text{CH}_3)_2$]. – IR (toluene): $\nu(\text{CO})$ = 2030, 1981 cm^{-1} . – $\text{C}_{35}\text{H}_{47}\text{N}_3\text{O}_2\text{RuSi}_4\text{Sn}$ (873.88): calcd. C 48.11, H 5.42, N 4.81; found C 48.39, H 5.80, N 4.46.

[MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Mo(η^5 -C₅H₅)(CO)₃] (8): A solution of [$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$] (38.3 mg, 0.14 mmol) in toluene (2 mL) was added at –78 °C to a vigorously stirred solution of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (**1**) (100 mg, 0.14 mmol) in toluene (2 mL). The solution was slowly warmed up to room temperature over a period of 12 h and subsequently filtered through Celite. The solvent was removed under reduced pressure and the resulting residue was washed with pentane (1 mL). Compound **8** (74.6 mg, 61%) was obtained as a pale orange, microcrystalline solid. – ^1H NMR (400.13 MHz, [D_8]toluene, 290 K): δ = 0.26 (s, 3 H, SiCH_3), 0.58 [s, 12 H, $\text{Si}(\text{CH}_3)_2$], 0.62 [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 2.17 (s, 6 H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.19 (s, 3 H, $\text{CH}_3\text{C}_6\text{H}_4$), 4.07 (s, 5 H, C_5H_5), 6.94 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 4 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.05 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.18 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 4 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.21 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – ^1H NMR (400.13 MHz, [D_8]toluene, 340 K): δ = 0.24 (s, 3 H, SiCH_3), 0.52 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.16 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 4.19 (s, 5 H, C_5H_5), 6.94 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.13 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, [D_8]toluene, 290 K): δ = –14.2 (SiCH_3), 4.1, 4.2 [$\text{Si}(\text{CH}_3)_2$], 20.9 ($\text{CH}_3\text{C}_6\text{H}_4$), 89.7 (C_5H_5), 117.1, 117.2 (C^4), 129.0, 129.1 ($\text{C}^{2,6}$), 130.8, 131.0 ($\text{C}^{3,5}$), 148.3, 149.8 (C^1), 224.7, 230.0 (CO). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, [D_8]toluene, 340 K): δ = –14.6 (SiCH_3), 4.1 [$\text{Si}(\text{CH}_3)_2$], 20.6 ($\text{CH}_3\text{C}_6\text{H}_4$), 89.6 (C_5H_5), 117.8 (C^4), 129.8 ($\text{C}^{2,6}$), 131.4 ($\text{C}^{3,5}$), 149.8 (C^1), 224.9 (CO). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (49.69 MHz, [D_8]toluene, 295 K): δ = –89.1 (SiCH_3), 1.9, 2.4 [$\text{Si}(\text{CH}_3)_2$]. – IR (toluene): $\nu(\text{CO})$ = 2021 (s), 1954 (m), 1937 (s) cm^{-1} . – $\text{C}_{36}\text{H}_{47}\text{MoN}_3\text{O}_3\text{Si}_4\text{Sn}$ (896.76): calcd. C 48.22, H 5.28, N 4.69; found C 48.60, H 5.42, N 4.87.

[MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–W(η^5 -C₅H₅)(CO)₃] (9): An analogous procedure described to prepare **8**, with 251 mg (0.68 mmol) of [$(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$] and 500 mg (0.68 mmol) of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (**1**) dissolved in 20 mL of toluene, afforded compound **9** (504 mg, 75%) as a yellow, crystalline solid. Suitable crystals for the structure determination could be obtained from a saturated solution of **9** (100 mg) in benzene (0.5 mL) at room temperature. – ^1H NMR (400.13 MHz, [D_8]toluene, 290 K): δ = 0.21 (s, 3 H, SiCH_3), 0.54 [s, 12 H, $\text{Si}(\text{CH}_3)_2$], 0.58 [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 2.12 (s, 6 H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.15 (s, 3 H, $\text{CH}_3\text{C}_6\text{H}_4$), 4.02 (s, 5 H, C_5H_5), 6.88 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 4 H, $\text{H}^{2,6}$

of $\text{CH}_3\text{C}_6\text{H}_4$), 7.03 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.14 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 4 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.20 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – ^1H NMR (400.13 MHz, [D_8]toluene, 350 K): δ = 0.24 (s, 3 H, SiCH_3), 0.51 [s, 18 H, $\text{Si}(\text{CH}_3)_2$], 2.17 (s, 9 H, $\text{CH}_3\text{C}_6\text{H}_4$), 4.22 (s, 5 H, C_5H_5), 6.94 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.14 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 6 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, [D_8]toluene, 295 K): δ = –14.4 (SiCH_3), 4.0, 4.1 [$\text{Si}(\text{CH}_3)_2$], 20.8 ($\text{CH}_3\text{C}_6\text{H}_4$), 88.2 (C_5H_5), 128.6, 128.8 ($\text{C}^{2,6}$), 129.0, 130.1 ($\text{C}^{3,5}$), 130.5, 130.9 (C^4), 145.8, 149.9 (C^1), 213.5, 217.4 (CO). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, [D_8]toluene, 350 K): δ = –14.6 (SiCH_3), 4.1 [$\text{Si}(\text{CH}_3)_2$], 20.8 ($\text{CH}_3\text{C}_6\text{H}_4$), 88.2 (C_5H_5), 126.3 ($\text{C}^{2,6}$), 129.6 ($\text{C}^{3,5}$), 129.9 (C^4), 131.4 (C^1), 213.7 (CO). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (49.69 MHz, [D_8]toluene, 295 K): δ = –89.1 (SiCH_3), 1.7, 2.2 [$\text{Si}(\text{CH}_3)_2$]. – IR (toluene): $\nu(\text{CO})$ = 2018 (s), 1944 (m), 1930 (s) cm^{-1} . – $\text{C}_{36}\text{H}_{47}\text{N}_3\text{O}_3\text{Si}_4\text{SnW}$ (984.67): calcd. C 43.91, H 4.81, N 4.27; found C 43.98, H 4.83, N 4.21.

[(MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn)₂–Ru(bpy)(CO)₂] (10): A solution of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (200 mg, 0.27 mmol) in THF (30 mL) was added at –40 °C to solid [*trans*-RuCl₂(bpy)(CO)₂] (52.4 mg, 0.14 mmol), resulting in an immediate change of colour from pale yellow to deep orange. The reaction mixture was warmed up to ambient temperature over a period of 4 h and subsequently filtered through Celite. Removal of the solvent in vacuum, extraction of the residue with toluene (30 mL), and concentration of the solution to about 3 mL yielded a microcrystalline powder after storage at –50 °C. The supernatant solution was removed by decantation and the solid was washed with pentane (5 mL) and dried in vacuum to yield **10** (147 mg, 66%) as a deep orange solid. Suitable crystals for the structure determination could be obtained from a saturated solution of **10** (80 mg) in benzene (0.5 mL) at room temperature. – ^1H NMR (250.13 MHz, [D_8]THF, 295 K): δ = –0.08 (s, 6 H, SiCH_3), –0.04 [s, 36 H, $\text{Si}(\text{CH}_3)_2$], 2.39 (s, 18 H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.29 (dt, $^3J_{\text{H,H}} = 5.7$, $^4J_{\text{H,H}} = 1.1$ Hz, 2 H, $\text{H}^{5,5'}$ of bpy), 6.47 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 12 H, $\text{H}^{2,6}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 6.71 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 12 H, $\text{H}^{3,5}$ of $\text{CH}_3\text{C}_6\text{H}_4$), 7.04 (dd, $^3J_{\text{H,H}} = 5.7$, $^4J_{\text{H,H}} = 1.1$ Hz, 2 H, $\text{H}^{6,6'}$ of bpy), 7.32 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $\text{H}^{3,3'}$ of bpy), 7.45 (dt, $^3J_{\text{H,H}} = 7.8$, $^4J_{\text{H,H}} = 1.6$ Hz, 2 H, $\text{H}^{4,4'}$ of bpy). – $^{13}\text{C}\{^1\text{H}\}$ NMR (62.89 MHz, [D_8]THF, 295 K): δ = –13.7 (SiCH_3), 4.2 [$\text{Si}(\text{CH}_3)_2$], 21.3 ($\text{CH}_3\text{C}_6\text{H}_4$), 117.5 (bpy), 123.0 (bpy), 124.6 (bpy), 128.2 (tol), 130.1 (tol), 137.7 (bpy), 151.1 (tol), 153.8 (tol), 154.4 (bpy), 199.1 (CO). – $^{29}\text{Si}\{^1\text{H}\}$ NMR (49.69 MHz, [D_8]THF, 295 K): δ = –81.4 (SiCH_3), 3.0 [$\text{Si}(\text{CH}_3)_2$]. – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, [D_8]THF, 295 K): δ = –123.9 (N_3SnRu). – IR (toluene): $\nu(\text{CO})$ = 2039, 1990 cm^{-1} . – $\text{C}_{68}\text{H}_{92}\text{N}_8\text{O}_2\text{RuSi}_8\text{Sn}_2$ (1616.66): calcd. C 50.52, H 5.74, N 6.93; found C 50.15, H 5.64, N 6.49.

X-ray Crystallographic Study of 6, 9 and 10: The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo- K_α radiation ($\lambda = 0.71073$ Å) and the Collect^[38] data collection program. The Denzo and Scalepack^[39] programs were used for cell refinements and data reduction. The structures were solved by Patterson methods using the DIRDIF-99^[40] and the WinGX graphical user interface.^[41] A multi-scan absorption correction based on equivalent reflections (XPRED in SHELXTL v. 5.1)^[42] was applied to **6** and **9** ($T_{\text{max}}/T_{\text{min}}$ were 0.2529/0.2166 and 0.2766/0.2206, respectively). Structural refinements were carried out with the SHELXL-97 program.^[40] All hydrogens were placed in an idealised position and constrained to ride on their parent atom. The crystallographic data are summarised in Table 2. The molecular structures of the complexes along with principal bond lengths and angles are presented in Figure 1–3.

Table 2. Crystal data and structure refinement for **6**, **9** and **10**

	6	9	10
Molecular formula	C ₃₅ H ₄₇ FeN ₃ O ₂ Si ₄ Sn·1/2C ₆ D ₆	C ₃₆ H ₄₇ N ₃ O ₃ Si ₄ SnW	C ₆₈ H ₁₂ N ₈ O ₂ RuSi ₈ Sn ₂ ·2C ₆ D ₆
<i>M</i> _r	870.73	984.67	1784.95
Temperature	120(2) K	120(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	2	4	2
Unit cell dimensions	<i>a</i> = 10.97620(10) Å <i>b</i> = 11.36830(10) Å <i>c</i> = 17.6453(3) Å α = 88.1369(6)° β = 79.2840(6)° γ = 72.5050(7)°	<i>a</i> = 11.33020(10) Å <i>b</i> = 21.5079(2) Å <i>c</i> = 16.5450(2) Å α = 90° β = 92.6662(4)° γ = 90°	<i>a</i> = 14.2978(2) Å <i>b</i> = 15.4300(2) Å <i>c</i> = 20.9716(3) Å α = 89.9010(7)° β = 83.4869(7)° γ = 69.0371(8)°
Volume	2062.68(4) Å ³	4027.47(7) Å ³	4288.77(10) Å ³
<i>D</i> _{calcd.}	1.402 g cm ^{−3}	1.624 g cm ^{−3}	1.382 g cm ^{−3}
Absorption coefficient	1.108 mm ^{−1}	3.630 mm ^{−1}	0.912 mm ^{−1}
<i>F</i> (000)	894	1952	1824
Crystal size	0.30 × 0.20 × 0.20 mm	0.30 × 0.20 × 0.20 mm	0.20 × 0.10 × 0.10 mm
θ range for data collection	2.11 to 27.53°	2.03 to 27.49°	2.69 to 25.32°
Limiting indices	−14 ≤ <i>h</i> ≤ 14 −14 ≤ <i>k</i> ≤ 14 −22 ≤ <i>l</i> ≤ 22	−14 ≤ <i>h</i> ≤ 13 −27 ≤ <i>k</i> ≤ 27 −21 ≤ <i>l</i> ≤ 21	−17 ≤ <i>h</i> ≤ 17 −18 ≤ <i>k</i> ≤ 18 −25 ≤ <i>l</i> ≤ 25
Reflections collected	31634	49083	30106
Independent reflections (<i>R</i> _{int})	9382 (0.0360)	9238 (0.0528)	15558 (0.0466)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9382/0/452	9238/0/443	15558/0/930
<i>T</i> _{min} /max	0.8087/0.7321	0.27659/0.22064	0.9144/0.8387
Goodness-of-fit on <i>F</i> ²	1.062	1.063	1.056
Final <i>R</i> indices	<i>R</i> ₁ = 0.0299	<i>R</i> ₁ = 0.0288	<i>R</i> ₁ = 0.0436
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.0649	<i>wR</i> ₂ = 0.0661	<i>wR</i> ₂ = 0.0810
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0398	<i>R</i> ₁ = 0.0377	<i>R</i> ₁ = 0.0820
	<i>wR</i> ₂ = 0.0688	<i>wR</i> ₂ = 0.0703	<i>wR</i> ₂ = 0.0932
Largest diff. Peak and hole	0.554 and −0.622 e·Å ^{−3}	1.195 and −2.031 e·Å ^{−3}	0.682 and −0.612 e·Å ^{−3}

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-165210 (**6**), -165211 (**9**) and -165212 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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