DOI: 10.1002/ejic.200701240

Synthesis and Structural Characterization of New Rhodium-Tin Heterodimetallic Complexes

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Keywords: Rhodium / Tin / Triamidostannates / Heterodimetallic complexes

Reaction of the triamidostannates(II) MeSi{$SiMe_2N$(*p*-tol)}$_3$SnLi(OEt_2) (**1a**) and MeSi{$SiMe_2N$(3,5-xyl)}$_3$SnLi(OEt_2) (**1b**) with 1/2 molar equiv. of [RhCl(diolefin)]$_2$ (diolefin = COD, NBD) and phosphanes, phosphites or isonitriles ("L") gave the square-planar complexes [MeSi{$SiMe_2$NAryl}$_3$-SnRh(L)(diolefin)] (Aryl = 3,5-xyl, *p*-tol) in which the stannates are directly bonded to rhodium through Rh–Sn bonds. In contrast, the analogous transformation of **1b** with 1/2 equiv. of [RhCl(C_2H_4)$_2$]$_2$ and P*i*Pr$_3$ in toluene did not lead to a square-planar bisethylene complex [MeSi{$SiMe_2$N(3,5-xyl)}$_3$SnRh(C_2H_4)$_2$(P*i*Pr$_3$)] but the brown 18e π-arene complex [MeSi{$SiMe_2$N(3,5-xyl)}$_3$SnRh(P*i*Pr$_3$)(η^6-toluene)] (**6**). Equilibria of the square planar diolefin complexes with π-arene systems such as **6** were observed upon their dissolution in toluene.

Introduction

More than a decade ago, Veith and co-workers demonstrated that mixed-metal alkoxide cages may be employed as (neutral) ligands in transition metal complexes.[1,2] Anionic main group donors with interesting ligand properties are obtained if low-coordinate ate complexes of the heavy *p*-block elements are incorporated into such arrays without "intra-cage" charge compensation. A conceptually simple approach that employs this strategy is based on a polydentate ligand with podand topology coordinating to a low-valent *p*-block metal which forms the keystone of a ligand cage.

The tripodal amides which we developed in the early 1990s[3] proved to provide ideal platforms for the preparation of triamidometallates(II) of the group 14 metals,[4] in particular triamidostannates(II), which are both kinetically robust and relatively inert towards oxidation by way of intramolecular electron transfer.[5] First studies have revealed their applicability in the synthesis of M–Sn complexes for metal across the whole d-block.[4,6] That such a role as ligating molecular fragments may not be limited to the rigid [2,2,2]bicyclooctane-derived metallate cages has been demonstrated by Veith et al. who reported the synthesis of the more flexible triamidogermanate(II) [*t*BuSi(OSiMe_2NPh)-Ge]$^-$ although the potential of these systems remains to be investigated.[7]

The most characteristic structural consequence of the rigid amido cages is the well-defined orientation of the peripheral N-substituents, which give rise to very large cone angles for mondentate ligands in their transition metal complex derivatives. These angles considerably exceed those of "ordinary" metallate groups [MR_3]$^-$[8] or their isolobal neutral group 15 ligands[9] and thus render them interesting ancillary ligating units.

We have recently begun to investigate the coordination chemistry of such triamidostannates bonded to rhodium and iridium, which has revealed the way that the ligand periphery and the donor elements intervene in their interaction with the transition metals.[10] In this work, we extend this study in a systematic investigation of the structural chemistry of Rh-Sn complexes.

Results and Discussion

Preparation of Square Planar Rh-Sn Heterodimetallic Complexes

As previously described, triamidostannates react with [RhCl(diolefin)]$_2$ complexes initially forming zwitterions which may be isolated in favourable cases.[10] However, these are readily converted into the corresponding square planar 16e rhodium complexes by addition of donor molecules which may ligate to the transition metal. In this work, the synthesis of new phosphane, phosphite and isocyanide complexes with such a coordination pattern is described. Scheme 1 represents the strategy for the direct preparation of such systems without isolating the intermediate zwitterions. The tris(arylamido)stannates(II) **1a**[6c] and **1b**[10] have been reacted with half a molar equivalent of the dimeric [RhCl(COD)]$_2$ complex, and the subsequent addition of PR_3 (R = Et, *i*Pr, OPh[10]), or CNR (R = *t*Bu, Cy[10]) gave the target complexes.

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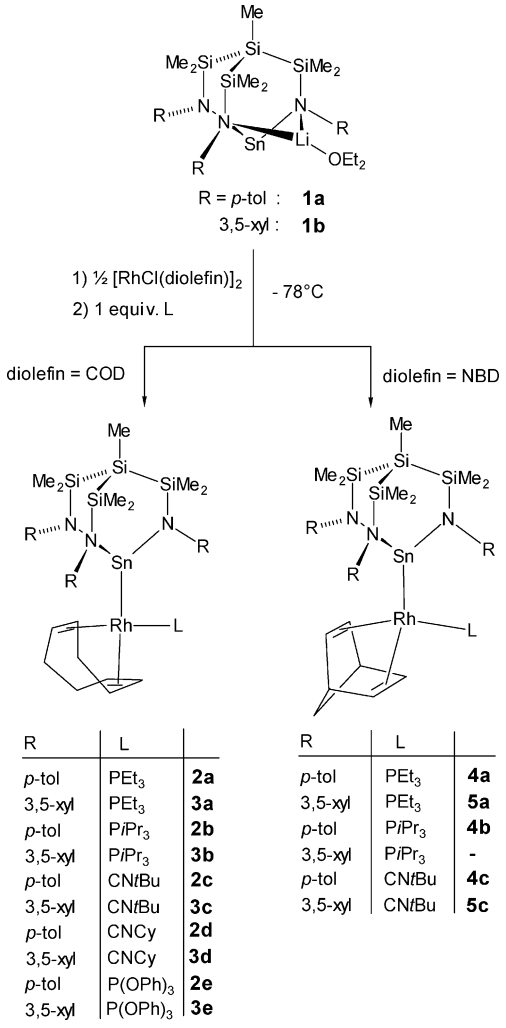


R	L	
p-tol	PEt_3	**2a**
3,5-xyl	PEt_3	**3a**
p-tol	P*i*Pr$_3$	**2b**
3,5-xyl	P*i*Pr$_3$	**3b**
p-tol	CN*t*Bu	**2c**
3,5-xyl	CN*t*Bu	**3c**
p-tol	CNCy	**2d**
3,5-xyl	CNCy	**3d**
p-tol	$P(OPh)_3$	**2e**
3,5-xyl	$P(OPh)_3$	**3e**

R	L	
p-tol	PEt_3	**4a**
3,5-xyl	PEt_3	**5a**
p-tol	P*i*Pr$_3$	**4b**
3,5-xyl	P*i*Pr$_3$	-
p-tol	CN*t*Bu	**4c**
3,5-xyl	CN*t*Bu	**5c**

Scheme 1. Synthesis of the Rh-Sn heterodimetallic complexes **2a**–**e**, **3a**–**e**, **4a**–**c**, **5a** and **5c**.

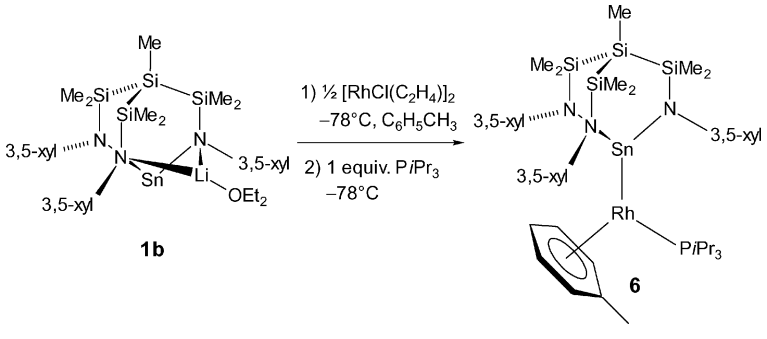
The reaction products, yellow to red microcrystalline solids, have been isolated in good yields except for the P*i*Pr$_3$ derivatives **2b** and **3b**. For the latter, their high solubility in organic solvents along with the presence of an equilibrium with another species in solution limited the isolated yields to a mere 37–38%. In the ^{31}P-NMR spectra, which are characterized by doublet resonances at 43.0 ($^1J_{RhP}$ = 142 Hz: **2b**) and 43.3 ppm ($^1J_{RhP}$ = 144 Hz: **3b**), a second doublet is observed at 67.6 (**2b**-crude) and 68.0 ppm (**3b**-crude) with large coupling constants to rhodium (205 Hz). These large coupling constants are similar to those observed for π-arene complexes as previously reported for [MeSi{SiMe$_2$N(aryl)}$_3$SnRh(PPh$_3$)(η^6-arene)] (aryl = 4-tol, 3,5-xyl; arene = C_6H_6, $C_6H_5CH_3$)[10b] (214–215 Hz), an observation which will be further elaborated below. Crystallizing of the crude mixtures at –30 °C separated the COD complexes **2b** and **3b** from these byproducts.

The ^{119}Sn-NMR resonances for all Rh-Sn compounds were found to be strongly dependant on the nature of the additional ligand L and the diolefin. All isocyanide complexes resonate in the same ^{119}Sn-NMR chemical shift range as the lithium stannates [**2c**: –112.2; **2d**: –113.0; **3c**: –113.9; **3d**: –115.1 ppm]. However, for phosphane and phosphite complexes a high field coordination shift is detected, increasing from PEt_3 [**2a**: –140.5; **3a**: –146.6 ppm], via $P(OPh)_3$ [**2e**: –146.3; **3e**: –152.7 ppm] to P*i*Pr$_3$ [**2b**: –187.4; **3b**: –192.8 ppm].

It has also been possible to isolate the NBD derivatives of the Rh-Sn complexes by reacting the stannates **1a** and **1b** with 1/2 equiv. of [RhCl(NBD)]$_2$ and the respective donor molecule (PEt_3, P*i*Pr$_3$, CN*t*Bu). In analogy to the method described for the COD derivatives, the square-planar complexes **4**–**5** are isolated. The yields vary from 71 to 87% for the red to brown microcrystalline products. Notably, and in contrast to the COD complexes, the P*i*Pr$_3$ compound **4b** is isolated in 86% yield without detecting a π-arene byproduct. Its ^{31}P NMR signal is observed at δ = 43.5 ppm with a "normal" coupling constant for Rh^I square-planar complexes[11] of 157 Hz. In ^{119}Sn-NMR experiments the chemical shifts of the signals for the NBD complexes [**4a**: –111.7; **4b**: –149.5; **4c**: –103.1; **5a**: –113.0; **5c**: –102.2 ppm] are at lower field compared to their COD analogs in **2a**–**e** and **3a**–**e**.

Synthesis of an 18 Electron η^6-Arene Rh-Sn Heterodimetallic Complex

To obtain further support for the hypothesis of the formation of π-arene complexes as the byproducts in the synthesis of **2b** and **3b**, we aimed to prepare the 18e complex [MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(P*i*Pr$_3$)(η^6-toluene)] (**6**). To

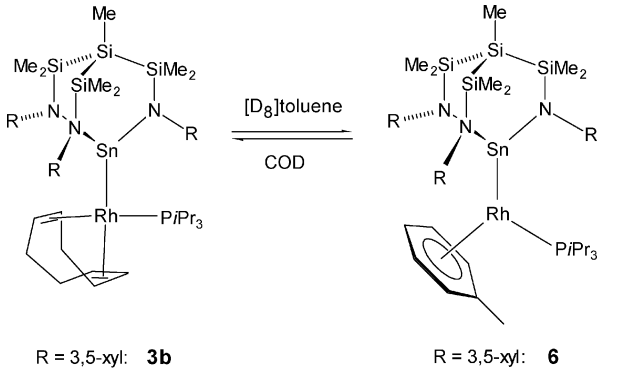


Scheme 2. Synthesis of the 18-electron Rh-Sn η^6-toluene complex **6**.

this end, the tris(xylylamido)stannate **1b** was treated with 1/2 equiv. of $[RhCl(C_2H_4)_2]_2$ and P*i*Pr$_3$ in toluene (Scheme 2). The possible formation of a square-planar bis-ethylene complex $[MeSi\{SiMe_2N(3,5\text{-xyl})\}_3SnRh(C_2H_4)_2(P\mathit{i}Pr_3)]$ was not observed, but the brown 18e complex **6** was formed with the concomitant evolution of gaseous ethylene.

A dramatic high field shift to –233.1 ppm is detected in ^{119}Sn-NMR spectrum with a large coupling constant to ^{103}Rh ($^1J_{SnRh}$ = 1331 Hz). The ^{31}P nuclei in **6** resonate at δ = 68.0 ppm which differs markedly from the observed shift of the square-planar COD compound **3b** (δ = 43.3 ppm). The spectroscopic data of this species are identical with thoses of the byproduct of **3b**, which establishes the π-toluene complex **6** as the second product.

Upon dissolution of the pure compounds **2b** or **3b** toluene the equilibrium with their corresponding π-toluene complexes is shifted towards the latter (Scheme 3). After equilibration, the product distribution between **3b** and **6** is 14:86 and **2b** and **7** is 45:55.



Scheme 3. Equilibrium between the 16-electron complexes **3b**, **2b** and the 18-electron complexes **3b**, **2b**, respectively.

Molecular Structures of $[MeSi\{SiMe_2N(aryl)\}_3SnRh(diolefin)(L)]$ [aryl = 3,5-xylyl, 4-tolyl; diolefin = COD, NBD; L = *t*BuNC, CyNC, Et$_3$P, (PhO)$_3$P]

In order to establish the details of the molecular structures of the Rh-Sn complexes, X-ray diffraction studies were carried out for **2c**, **3c**, **3d**, **3e** and **4a**. In general, two possible orientations of the rhodium fragment relative to the triamidostannate unit, conformers *syn* and *anti* in Figure 1 have been observed: whilst the *syn* conformation with respect to the ligand L is found for **3c**, **3d** and **3e**, the molecular structures of **2c** and **4a** adopt the *anti* conformation.

The molecular structures of the COD complexes **2c**, **3c**, **3d** and **3e** are displayed in Figure 2 (a–d) and selected bond lengths and angles listed in Table 1. The Rh–Sn bond lengths increase on going from **3d** [2.6004(3) Å] to **3c** [2.6096(3) Å] and further to **2c** [2.6241(3) Å], which may be explained by the increasing steric demand of the isocyanide substituents. Furthermore, the arrangement of stannate relative to the isocyanide ligands appears to play a role: The *syn* conformation favours a short Rh–Sn bond (for **3c** and **3d**) whereas the *anti* conformation leads to repulsion between the 4-tolyl group and COD in compound **2c** and, consequently, an elongation of the Rh–Sn bond.

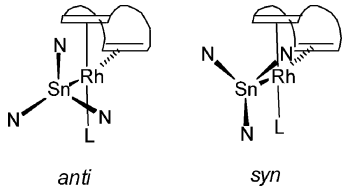


Figure 1. The two orientations (*anti* and *syn*) of the donor ligand L relative to the triamidostannate.

In contrast to this, the phosphite derivative **3e** is arranged in a *syn* conformation, but possesses a long Rh–Sn distance [2.6331(4) Å]. This is a result of the bulkiness of both stannate and phosphite, which are oriented the same direction. As a consequence, the stannate unit is bent backwards and pushed away from the Rh centre, leading to the elongation of the tin–rhodium bond.

The metric parameters of especially the isocyanide complexes **2c**, **3c** and **3d** are very similar. For example the bond length C(40)–Rh is essentially identical within the standard deviation [1.925(3) Å (**2c**), 1.924(2) Å (**3c**), 1.922(3) Å (**3d**)], while being slightly shorter than the corresponding Rh–C distances of Tejel's isocyanide complex $[\{Rh(\mu\text{-Pz})(Cl)(CN\mathit{t}Bu)_2\}_2(\mu\text{-}CHCO_2Me)]$ [Rh–C 1.950(3) Å][12] but longer than the one reported by Werner et al. [*trans*-$[RhCl(CNMe)(Sb\mathit{i}Pr_3)_2]$ [Rh–C 1.854(7) Å]].[13] Whilst the latter two examples display almost linear arrangements of the coordinated isonitriles, these are slightly bent in the stannate complexes reported in this work, as reflected in the angles N(4)–C(40)–Rh [171.9(3)° (**2c**), 167.0(2)° (**3c**), 172.3(3)° (**3d**)] and C(40)–N(4)–C(41) [175.2(3)° (**2c**), 168.3(2)° (**3c**), 175.1(3)° (**3d**)]. This is thought to be the result of steric repulsion by the stannate moiety and the isocyanide.

It has also been possible to obtain crystals of the NBD compound **4a** suitable for X-ray diffraction. Its molecular structure is displayed in Figure 3 and is found to adopt the *anti* conformation of $[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(PEt_3)(NBD)]$ (**4a**). Here the rhodium–phosphorus distance [2.2988(14) Å] is longer than in the phosphite complex **3e** [2.2048(9) Å] discussed above, which we attribute to the weaker π-acceptor properties of the trialkylphosphane as compared to the phosphite.

In comparison to the previously characterized PPh_3 derivatives $[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(PPh_3)(diolefin)]$ (diolefin = NBD, COD)[10b] [2.6522(6) Å and 2.6391(6) Å] a shorter Rh–Sn bond for **4a** [2.6211(6) Å] is found, which is due to the decrease in steric demand of the smaller PEt_3. This also leads to a less distorted (tilted) stannate unit which is reflected in the angle Si(4)–Sn–Rh [**4a**: 170.84(3)°; NBD: 155.67(3)°, COD: 167.81°].

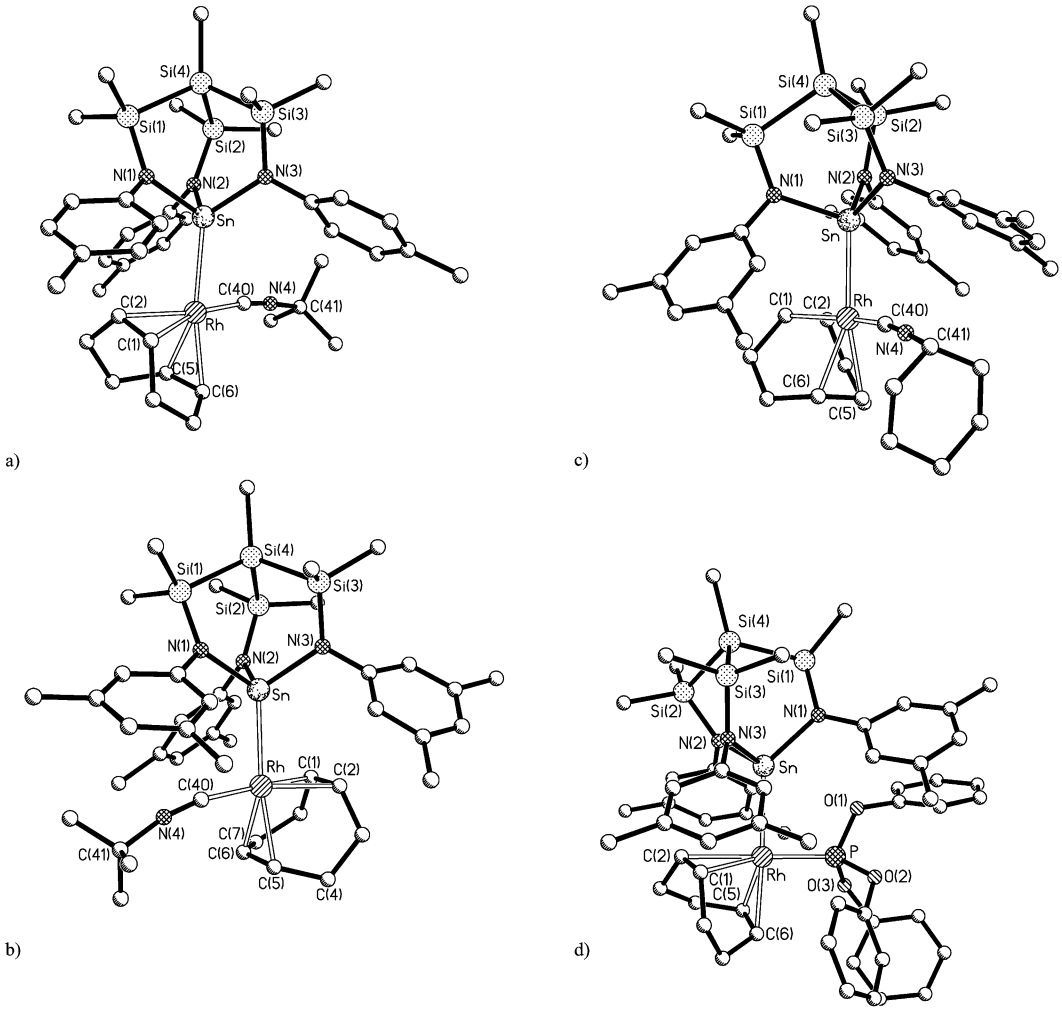


Figure 2. Molecular structures of complexes **2c** (a), **3c** (b), **3d** (c) and **3e** (d). A comparative listing of the principal bond lengths and angles is given in Table A.

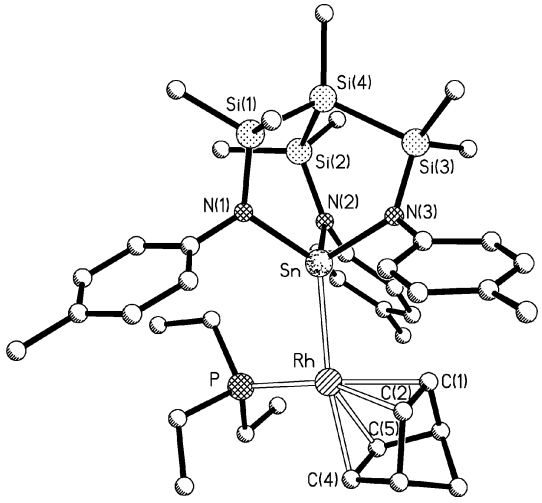


Figure 3. Molecular structure of complex **4a**. Principal bond lengths (Å) and angles (°): C(1)–C(2) 1.362(8), C(1)–Rh 2.222(5), C(2)–Rh 2.242(5), C(4)–C(5) 1.374(7), C(4)–Rh 2.173(5), C(5)–Rh 2.150(5), N(1)–Sn 2.116(4), N(2)–Sn 2.119(4), N(3)–Sn 2.109(4), P–Rh 2.2988(14), Rh–Sn 2.6211(6); P–Rh–Sn 92.43(4), N(3)–Sn–N(1) 100.7(2), N(3)–Sn–N(2) 97.3(2), N(1)–Sn–N(2) 98.7(2), N(3)–Sn–Rh 116.1(1), N(1)–Sn–Rh 126.9(1), N(2)–Sn–Rh 112.1(1), Si(4)–Sn–Rh 170.84(3).

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2c**, **3c**, **3d** and **3e**.

	2c	**3c**	**3d**	**3e**
Rh–Sn	2.6241(3)	2.6096(3)	2.6004(3)	2.6331(4)
C(40)/P–Rh	1.925(3)	1.924(2)	1.922(3)	2.2048(9)
C(40)–N(4)	1.155(4)	1.158(3)	1.134(5)	
C(41)–N(4)	1.460(4)	1.457(3)	1.535(7)	
C(1)–C(2)	1.367(5)	1.366(3)	1.372(5)	1.367(5)
C(5)–C(6)	1.378(5)	1.374(4)	1.363(6)	1.398(5)
C(1)–Rh	2.224(3)	2.240(2)	2.229(3)	2.252(3)
C(2)–Rh	2.227(3)	2.231(2)	2.246(3)	2.298(3)
C(5)–Rh	2.180(3)	2.196(2)	2.191(3)	2.171(3)
C(6)–Rh	2.191(3)	2.181(2)	2.194(3)	2.214(3)
N(1)–Sn	2.102(2)	2.108(2)	2.107(3)	2.118(3)
N(2)–Sn	2.102(2)	2.110(2)	2.092(2)	2.114(3)
N(3)–Sn	2.091(2)	2.096(2)	2.110(2)	2.109(3)
C(40)/P–Rh–Sn	86.81(9)	93.38(6)	89.32(10)	92.87(2)
N(4)–C(40)–Rh	171.9(3)	167.0(2)	172.3(3)	
C(40)–N(4)–C(41)	175.2(3)	168.3(2)	175.1(5)	
Si(4)–Sn–Rh	167.45(2)	166.59(1)	169.24(2)	160.81(2)
N(1)–Sn–Rh	119.90(7)	124.17(5)	107.95(7)	131.64(8)
N(2)–Sn–Rh	107.65(7)	105.96(5)	122.60(7)	101.33(7)
N(3)–Sn–Rh	127.61(7)	122.86(5)	122.40(7)	118.72(7)

Conclusions

The combination of thermodynamic stabilization of the triamidostannates by their integration into a rigid molecular cage structure along with the well-defined orientation and high variability of the peripheral N-substituents has established these systems as a new class of ancillary ligands in the coordination chemistry of rhodium. To which extent they tolerate other transformations in the coordination sphere of rhodium, is currently being studied and will determine their usefulness as spectator ligands in catalytic applications.

Experimental Section

General: All manipulations were performed under an inert gas atmosphere of dried argon (desiccant P_4O_{10}, Granusic®, J.T. Baker) in standard (Schlenk) glassware or by working in a glove box. All reaction flasks were heated prior to use using three evacuation–refill cycles. Solvents and solutions were transferred by cannula/septa techniques. Solvents were dried according to standard methods and saturated with argon and stored over potassium mirror. $MeSi\{SiMe_2N(4\text{-tol})\}_3SnLi(OEt_2)$ (**1a**),[6c] $MeSi\{SiMe_2N(3,5\text{-xyl})\}_3SnLi(OEt_2)$ (**1b**),[10] $[RhCl(COD)]_2$,[14] $[RhCl(NBD)]_2$ [15] and $[RhCl(C_2H_4)_2]_2$ [16] were synthesized according to literature procedures. Rhodium precursors were dried with $MgSO_4$ as solutions in dichloromethane. The solutions were reduced in vacuo and the complexes were precipitated by adding hexane. All other reagents were commercially available and used as received. ^1H, ^7Li, ^{13}C, ^{29}Si, ^{31}P and ^{119}Sn-NMR spectra were recorded on a Bruker DRX 200, Avance II 400 or Avance III 600. NMR spectra are quoted in ppm relative to tetramethylsilane (^1H and ^{13}C); ^7Li, ^{29}Si, ^{31}P and ^{119}Sn NMR spectroscopic data are listed in ppm relative to an external standard (^7Li: $LiCl_{aq.}$ ^{29}Si: $Si(CH_3)_4$, ^{31}P: 85% H_3PO_4 and ^{119}Sn: $Sn(CH_3)_4$). ^1H and ^{13}C NMR spectra were referenced internally using the residual protonated solvent peak (^1H) or the carbon resonance (^{13}C). Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer. Elemental analyses were carried out in the microanalytical laboratory of the chemistry department (University of Heidelberg).

General Synthetic Procedure for $[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(L)(COD)]$: A mixture of $MeSi\{SiMe_2N(4\text{-tol})\}_3SnLi(OEt_2)$ (**1a**) (200 mg, 0.273 mmol) and $[RhCl(COD)]_2$ (67 mg, 0.136 mmol) was cooled to –78 °C and suspended with cold toluene. After stirring for 10 min 0.278 mmol of the ligand L were added dropwise to the orange reaction mixture. After warming to room temperature over a period of 2 h, and a concomitant change of colour from yellow to to red/brown, all insolubilities were removed by centrifugation. The solvent was was subsequently removed from the centrifugate by distillation under reduced pressure, the orange to red residue was washed with pentane and dried in vacuo.

$[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(PEt_3)(COD)]$ (2a): Yield 216 mg (81%). ^1H NMR (399.9 MHz, C_6D_6, 295 K): δ = 7.26 (d, $^3J_{HH}$ = 8.2 Hz, 6 H, tol), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, tol), 5.52 (br. s, 2 H, CH_{COD}), 3.63 (br. s, 2 H, CH_{COD}), 2.22 (s, 9 H, $C_6H_4CH_3$), 1.87 (br. s, 2 H, $CH_{2\ COD}$), 1.75 (br. s, 2 H, $CH_{2\ COD}$), 1.64 (br. s, 2 H, $CH_{2\ COD}$), 1.41 (br. s, 2 H, $CH_{2\ COD}$), 1.10 (vq, N = 7.5 Hz, $P(CH_2CH_3)_3$), 0.65 (s, 18 H, $Si(CH_3)_2$), 0.48 (dt, J = 7.3 Hz, $P(CH_2CH_3)_3$), 0.32 (s, 3 H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 295 K): δ = 152.2 (s, tol), 129.5 (s, tol), 128.9 (s, tol), 127.1 (s, tol), 89.3 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 9.3 Hz, CH_{COD}), 83.5 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 9.7 Hz, CH_{COD}), 31.2 (s, $CH_{2\ COD}$), 30.2 (d, $^2J(^{103}Rh\text{-}^{13}C)$ = 2.9 Hz, $CH_{2\ COD}$), 20.9 (s, $C_6H_4CH_3$), 17.3 (d, $^2J(^{31}P\text{-}^{13}C)$ = 23 Hz, $P(CH_2CH_3)_3$), 8.6 (d, $^3J(^{31}P\text{-}^{13}C)$ = 2.8 Hz, $P(CH_2CH_3)_3$), 4.0 (s, $Si(CH_3)_2$), –14.2 (s, $SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 295 K): δ = –2.7 (s, $SiMe_2$), –91.0 (s, SiMe) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 295 K): δ = 9.6 (d, $^1J(^{103}Rh\text{-}^{31}P)$ = 137, $^2J(^{117}Sn\text{-}^{31}P)$ = 347, $^2J(^{119}Sn\text{-}^{31}P)$ = 363 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6, 295 K): δ = –140.5 (dd, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 846, $^2J(^{119}Sn\text{-}^{31}P)$ = 368 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3012 (w), 2939 (w), 2873 (w), 2825 (w), 1604 (w), 1497 (s), 1232 (s), 1219 (s), 1104 (w), 1032 (w), 913 (s), 846 (m), 778 (m), 708 (m), 510 (m) cm^{-1}. $C_{42}H_{69}N_3PRhSi_4Sn$ (980.9): calcd. C 51.42, H 7.09, N 4.28; found C 51.38, H 7.18, N 4.43.

$[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(P\mathit{i}Pr_3)(COD)]$ (2b): The reaction time was shortened to 30 min and the red residue was recrystallized from toluene at –30 °C. Yield 106 mg (38%). ^1H NMR (399.9 MHz, CD_2Cl_2, 295 K): δ = 6.98 (s, 12 H, tol), 5.37 (br. s, 2 H, CH_{COD}), 4.07 (br. s, 2 H, CH_{COD}), 2.31 (s, 9 H, $C_6H_4CH_3$), 1.77–1.62 (m, 3 H, $P[CH(CH_3)_3]_3$), 1.60–1.51 (m, 2 H, $CH_{2\ COD}$), 1.50–1.41 (m, 2 H, $CH_{2\ COD}$), 1.34–1.26 (m, 2 H, $CH_{2\ COD}$), 1.25–1.18 (m, 2 H, $CH_{2\ COD}$), 1.12 (dd, $^3J_{PH}$ = 12.9, $^3J_{HH}$ = 7.1 Hz, 18 H, $P[CH(CH_3)_3]_3$), 0.27 (s, 18 H, $Si(CH_3)_2$), 0.14 (s, 3 H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 295 K): δ = 151.9 (s, tol), 129.0 (s, tol), 128.9 (s, tol), 128.4 (s, tol), 93.1 (br. s, CH_{COD}), 79.0 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 10.9 Hz, CH_{COD}), 31.1 (s, $CH_{2\ COD}$), 30.5 (s, $CH_{2\ COD}$), 28.2 (d, $^2J(^{31}P\text{-}^{13}C)$ = 17.0 Hz, $P(CH_2CH_3)_3$), 21.4 (s, $P(CH_2CH_3)_3$), 20.8 (s, $C_6H_4CH_3$), 3.8 (s, $Si(CH_3)_2$), –14.0 (s, $SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, CD_2Cl_2, 295 K): δ = –3.8 (s, $SiMe_2$), –89.6 (s, SiMe) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 295 K): δ = 43.0 (d, $^1J(^{103}Rh\text{-}^{31}P)$ = 142, $^2J(^{117}Sn\text{-}^{31}P)$ = 224, $^2J(^{119}Sn\text{-}^{31}P)$ = 233 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, CD_2Cl_2, 295 K): δ = –187.4 (dd, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 829, $^2J(^{119}Sn\text{-}^{31}P)$ = 244 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2959 (w), 2877 (w), 1604 (w), 1497 (s), 1235 (s), 1217 (m), 1103 (w), 939 (m), 911 (s), 844 (m), 815 (m), 777 (m), 708 (w), 649 (w), 542 (w), 509 (w) cm^{-1}. $C_{45}H_{75}N_3PRhSi_4Sn$ (1023.0): calcd. C 52.83, H 7.39, N 4.11; found C 52.62, H 7.11, N 3.93.

$[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(CN\mathit{t}Bu)(COD)]$ (2c): Yield 228 mg (88%). ^1H NMR (600.1 MHz, C_6D_6, 295 K): δ = 7.23 (d, $^3J_{HH}$ = 8.2 Hz, 6 H, tol), 6.98 (d, $^3J_{HH}$ = 8.2 Hz, 6 H, tol), 5.12 (m, 2 H, CH_{COD}), 4.00 (m, 2 H, CH_{COD}), 2.20 (s, 9 H, $C_6H_4CH_3$), 1.70–1.52 (m, 6 H, $CH_{2\ COD}$), 1.50–1.40 (m, 2 H, $CH_{2\ COD}$), 0.88 (s, 9 H, $C(CH_3)_3$), 0.70 (s, 18 H, $Si(CH_3)_2$), 0.35 (s, 3 H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6, 295 K): δ = 152.1 (s, 1-C_{tol}), 129.4 (s, 3,5-C_{tol}), 127.9 (s, 4-C_{tol}), 126.8 (s, 2,6-C_{tol}), 94.4 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 7.0 Hz, CH_{COD}), 86.3 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 8.5 Hz, CH_{COD}), 56.8 (s, $CNC(CH_3)_3$), 31.4 (s, $CH_{2\ COD}$), 30.2 (s, $CNC(CH_3)_3$), 29.7 (s, $CH_{2\ COD}$), 20.9 (s, $C_6H_4CH_3$), 4.0 (s, $Si(CH_3)_2$), –14.2 (s, $SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 295 K): δ = –3.0 (s, $SiMe_2$), –89.9 (s, SiMe) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6, 295 K): δ = –112.2 (d, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 832 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3013 (w), 2940 (w), 2890 (w), 2152 (s), 1604 (w), 1498 (s), 1243 (s), 912 (s), 846 (m), 812 (m), 775 (m), 708 (w), 544 (w), 510 (m) cm^{-1}. $C_{41}H_{63}N_4RhSi_4Sn$ (945.9): calcd. C 52.06, H 6.71, N 5.92; found C 52.29, H 6.81, N 6.02.

$[MeSi\{SiMe_2N(4\text{-tol})\}_3SnRh(CNCy)(COD)]$ (2d): The reaction time was extended to 3 h. Yield 240 mg (90%). ^1H NMR (600.1 MHz, C_6D_6, 295 K): δ = 7.24 (d, $^3J_{HH}$ = 7.9 Hz, 6 H, tol), 6.99 (d, $^3J_{HH}$ = 7.9 Hz, 6 H, tol), 4.97 (br. s, 2 H, CH_{COD}), 4.21 (br. s, 2 H, CH_{COD}), 3.22 (br. s, 1 H, CNC*H*), 2.20 (s, 9 H, $C_6H_4CH_3$), 1.60–1.40 (m, 10 H, $CH_{2\ COD}$), 1.38–1.20 (m, 4 H, $CH_{2\ Cy}$), 1.15–1.05 (m, 2 H, $CH_{2\ Cy}$), 1.00–0.90 (m, 2 H, $CH_{2\ Cy}$),

0.71 (s, 18 H, Si(CH_3)$_2$), 0.35 (s, 3 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 295 K): δ = 152.0 (s, tol), 129.2 (s, tol), 127.9 (s, tol), 126.6 (s, tol), 95.8 (d, ^1J(^{103}Rh-^{13}C) = 7.2 Hz, *C*H$_{COD}$), 85.2 (d, ^1J(^{103}Rh-^{13}C) = 8.9 Hz, *C*H$_{COD}$), 53.4 (s, CN*C*H), 32.3 (s, CN*Cy*), 31.0 (s, *C*H$_{2\ COD}$), 29.5 (s, *C*H$_{2\ COD}$), 24.8 (s, CN*Cy*), 22.8 (s, CN*Cy*), 20.7 (s, C_6H_4*C*H$_3$), 3.8 (s, Si(*C*H$_3$)$_2$), –14.3 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 295 K): δ = –2.7 (s, SiMe$_2$), –88.9 (s, SiMe) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 295 K): δ = –113.0 (d, ^1J(^{119}Sn-^{103}Rh) = 831 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3012 (w), 2940 (m), 2875 (w), 2164 (s), 1604 (w), 1498 (s), 1240 (s), 914 (s), 845 (m), 778 (m), 707 (w), 544 (w), 510 (m) cm^{-1}. $C_{43}H_{65}N_4RhSi_4Sn$ (972.0): calcd. C 53.14, H 6.74, N 5.76; found C 53.34, H 6.77, N 5.75.

[MeSi{SiMe$_2$N(4-tol)}$_3$SnRh{P(OPh)$_3$}(COD)] (2e): Yield 164 mg (51%). ^{1}H NMR (399.1 MHz, C_6D_6, 295 K): δ = 7.41 (d, $^3J_{HH}$ = 8.1 Hz, 6 H, 3,5-*H*$_{tol}$), 7.01 (d, $^3J_{HH}$ = 8.1 Hz, 6 H, 2,6-*H*$_{tol}$), 6.93–6.98 (m, 15 H, P(O*Ph*)$_3$), 5.73 (br. s, 2 H, C*H*$_{COD}$), 3.95 (br. s, 2 H, C*H*$_{COD}$), 2.22 (s, 9 H, C_6H_4C*H*$_3$), 1.48–1.40 (m, 4 H, C*H*$_{2\ COD}$), 1.39–1.15 (m, 4 H, C*H*$_{2\ COD}$), 0.64 (s, 18 H, Si(C*H*$_3$)$_2$), 0.29 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 295 K): δ = δ = 152.3 (s, 1-*C*$_{tol}$), 151.9 (d, J(^{31}P-^{13}C) = 10.6 Hz, P(O*Ph*)$_3$), 129.4 (d, J(^{31}P-^{13}C) = 26 Hz, P(O*Ph*)$_3$), 129.2 (d, J(^{31}P-^{13}C) = 43 Hz, P(O*Ph*)$_3$), 128.6 (s, 3,5-*C*$_{tol}$), 127.1 (s, 2,6-*C*$_{tol}$), 124.5 (s, 4-*C*$_{tol}$), 121.3 (d, J(^{31}P-^{13}C) = 4.9 Hz, P(O*Ph*)$_3$), 101.7 (d, ^1J(^{103}Rh-^{13}C) = 13.1 Hz, *C*H$_{COD}$), 88.3 (d, ^1J(^{103}Rh-^{13}C) = 8.6 Hz, *C*H$_{COD}$), 30.4 (s, *C*H$_{2\ COD}$), 29.6 (s, *C*H$_{2\ COD}$), 20.9 (s, C_6H_4*C*H$_3$), 4.1 (s, Si-(*C*H$_3$)$_2$), –14.1 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 295 K): δ = –1.9 (s, *Si*Me$_2$), –90.7 (s, *Si*Me) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 295 K): δ = 110.6 (d, ^1J(^{103}Rh-^{31}P) = 275, ^2J(^{117}Sn-^{31}P) = 322, ^2J(^{119}Sn-^{31}P) = 339 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 295 K): δ = –146.3 (d, ^1J(^{119}Sn-^{103}Rh) = 790, ^2J(^{119}Sn-^{31}P) = 339 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3024 (w, br.), 2952 (w, br.), 1591 (s), 1489 (s), 1302 (m), 1220 (m), 1195 (s), 1161 (s), 1098 (w, br.), 1026 (m), 890 (s), 846 (m), 826 (m), 771 (s), 690 (m), 647 (w), 596 (w) cm^{-1}. $C_{54}H_{69}N_3O_3PRhSi_4Sn$ (1173.1): calcd. C 55.29, H 5.93, N 3.58; found C 55.03, H 5.89, N 3.25.

General Synthetic Procedure for [MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(L)-(COD)]: A mixture of 200 mg (0.258 mmol) MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnLi(OEt$_2$) (**1b**) and 64 mg (0.130 mmol) [RhCl(COD)]$_2$ was cooled to –78 °C and suspended in cold toluene. After stirring for 15 min 0.258 mmol of L was added dropwise to the orange reaction mixture. Over a period of 2 h, the colour changed to red and, subsequently, the suspension was warmed to room temperature. All insolubilities were removed by centrifugation and the solvent of the centrifigate was distilled of under reduced pressure. The red residue was washed with pentane and dried in vacuo.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(PEt$_3$)(COD)] (3a): Yield 223 mg (84%). ^{1}H NMR (399.9 MHz, C_6D_6, 295 K): δ = 7.03 (s, 6 H, 2,6-*H*$_{xyl}$), 6.56 (s, 3 H, 4-*H*$_{xyl}$), 5.57 (br. s, 2 H, C*H*$_{COD}$), 3.57 (br. s, 2 H, C*H*$_{COD}$), 2.30 (s, 18 H, C_6H_3(C*H*$_3$)$_2$), 1.95–1.80 (m, 2 H, C*H*$_{2\ COD}$), 1.75–1.55 (m, 4 H, C*H*$_{2\ COD}$), 1.45–1.35 (m, 2 H, C*H*$_{2\ COD}$), 1.13 (vq, N = 7.5 Hz, P(C*H*$_2$CH$_3$)$_3$), 6 H, 0.68 (s, 18 H, Si(C*H*$_3$)$_2$), 0.55 (dt, $^3J_{HH}$ = 7.6, ^3J(^{31}P-^{1}H) = 14 Hz, 9 H, P(CH$_2$C*H*$_3$)$_3$), 0.33 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 295 K): δ = 154.6 (s, 1-*C*$_{xyl}$), 137.5 (s, 3,5-*C*$_{xyl}$), 125.7 (s, 2,6-*C*$_{xyl}$), 122.0 (s, 4-*C*$_{xyl}$), 89.2 (d, ^1J(^{103}Rh-^{13}C) = 9.6 Hz, *C*H$_{COD}$), 83.1 (d, ^1J(^{103}Rh-^{13}C) = 9.7 Hz, *C*H$_{COD}$), 31.2 (s, *C*H$_{2\ COD}$), 29.9 (s, *C*H$_{2\ COD}$), 21.6 (s, C_6H_4*C*H$_3$), 17.2 (d, ^2J(^{31}P-^{13}C) = 24 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.7 (d, ^3J(^{31}P-^{13}C) = 2.8 Hz, P(CH$_2$*C*H$_3$)$_3$), 4.0 (s, Si(*C*H$_3$)$_2$), –14.4 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 295 K): δ = –3.1 (s, SiMe$_2$), –91.8 (s, SiMe) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 295 K): δ = 10.2 (d, ^1J(^{103}Rh-^{31}P) = 138, ^2J(^{117}Sn-^{31}P) = 349, ^2J(^{119}Sn-^{31}P) = 365 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 295 K): δ = –146.4 (dd, ^1J(^{119}Sn-^{103}Rh) = 858, ^2J(^{119}Sn-^{31}P) = 363 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3023 (w), 2938 (w), 2879 (w), 1582 (s), 1459 (w), 1302 (m), 1236 (w), 1162 (m), 1036 (m), 960 (w), 898 (m), 850 (s), 828 (m), 777 (m), 704 (m), 646 (m) cm^{-1}. $C_{45}H_{75}N_3PRhSi_4Sn$ (1023.0): calcd. C 52.83, H 7.39, N 4.11; found C 52.88, H 7.47, N 4.34.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(P*i*Pr$_3$)(COD)] (3b): The reaction time was shortened to 30 min and the red residue was recrystallized from toluene at –30 °C. Yield 102 mg (37%). ^{1}H NMR (399.9 MHz, $CH_3C_6D_5$, 253 K): δ = 7.26 (s, 6 H, 2,6-*H*$_{xyl}$), 6.72 (s, 3 H, 4-*H*$_{xyl}$), 5.55 (br. s, 2 H, C*H*$_{COD}$), 3.62 (br. s, 2 H, C*H*$_{COD}$), 2.51 (s, 18 H, C_6H_3(C*H*$_3$)$_2$), 1.82–1.70 (m, 2 H, C*H*$_{2\ Cy}$), 1.64–1.50 (m, 2 H, C*H*$_{2\ Cy}$), 1.48–1.36 (m, 3 H, P[C*H*(CH$_3$)$_2$]$_3$), 1.30–1.16 (m, 4 H, 2× C*H*$_{2\ Cy}$), 1.13–0.96 (m, 6 H, P[CH(C*H*$_3$)$_2$]$_3$), 0.87 (s, 18 H, Si(C*H*$_3$)$_2$), 0.49 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 293 K): δ = 154.7 (s, 1-*C*$_{xyl}$), 137.1 (s, 3,5-*C*$_{xyl}$), 127.1 (s, 2,6-*C*$_{xyl}$), 122.3 (s, 4-*C*$_{xyl}$), 93.7 (d, ^1J(^{103}Rh-^{13}C) = 6.9 Hz, *C*H$_{COD}$), 79.2 (d, ^1J(^{103}Rh-^{13}C) = 11 Hz, *C*H$_{COD}$), 31.4 (s, *C*H$_{2\ COD}$), 30.4 (s, *C*H$_{2\ COD}$), 27.6 (d, ^2J(^{31}P-^{13}C) = 17.5 Hz, P[*C*H(CH$_3$)$_3$]$_3$), 21.7 (s, C_6H_4*C*H$_3$), 20.2 (s, P[CH(*C*H$_3$)$_3$]$_3$), 4.4 (s, Si(*C*H$_3$)$_2$), –13.7 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, $CH_3C_6D_5$, 253 K): δ = –3.1 (s, SiMe$_2$), –90.0 (s, SiMe) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CH_3C_6D_5$, 253 K): δ = 43.3 (d, ^1J(^{103}Rh-^{31}P) = 144, ^2J(^{117}Sn-^{31}P) = 235, ^2J(^{119}Sn-^{31}P) = 247 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –192.8 (d, ^1J(^{119}Sn-^{103}Rh) = 831, ^2J(^{119}Sn-^{31}P) = 238 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3022 (w), 2959 (w), 2936 (w), 2888 (w), 1595 (m), 1582 (s), 1459 (w), 1301 (m), 1242 (m), 1163 (m), 1093 (w), 1034 (m), 958 (w), 901 (m), 851 (s), 793 (m), 777 (m), 707 (w), 645 (m) cm^{-1}. $C_{48}H_{81}N_3PRhSi_4Sn$ (1065.1): calcd. C 54.13, H 7.67, N 3.95; found C 54.34, H 7.87, N 3.87.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(CN*t*Bu)(COD)] (3c): The reaction time was extended to 8 h. Yield 206 mg (81%). ^{1}H NMR (399.9 MHz, C_6D_6, 293 K): δ = 6.99 (s, 6 H, 2,6-*H*$_{xyl}$), 6.52 (s, 3 H, 4-*H*$_{xyl}$), 5.08 (br. s, 2 H, C*H*$_{COD}$), 4.04 (br. s, 2 H, C*H*$_{COD}$), 2.26 (s, 18 H, C_6H_3(C*H*$_3$)$_2$), 1.65–1.45 (m, 8 H, 4× C*H*$_{2\ COD}$), 0.90 (s, 9 H, C(C*H*$_3$)$_3$), 0.72 (s, 18 H, Si(C*H*$_3$)$_2$), 0.34 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 293 K): δ = 154.5 (s, 1-*C*$_{xyl}$), 137.4 (s, 3,5-*C*$_{xyl}$), 125.0 (s, 2,6-*C*$_{xyl}$), 121.6 (s, 4-*C*$_{xyl}$), 94.8 (d, ^1J(^{103}Rh-^{13}C) = 7.2 Hz, *C*H$_{COD}$), 86.0 (d, ^1J(^{103}Rh-^{13}C) = 9.0 Hz, *C*H$_{COD}$), 56.8 (s, CN*C*(CH$_3$)$_3$), 31.2 (s, *C*H$_{2\ COD}$), 29.9 (s, C-(*C*H$_3$)$_3$), 29.8 (s, *C*H$_{2\ COD}$), 21.8 (s, C_6H_4*C*H$_3$), 4.1 (s, Si(*C*H$_3$)$_2$), –14.3 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –3.2 (s, SiMe$_2$), –90.7 (s, SiMe) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –113.9 (d, ^1J(^{119}Sn-^{103}Rh) = 839 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3022 (w), 2942 (m), 2889 (w), 2135 (s), 1583 (s), 1467 (w), 1304 (s), 1241 (m), 1173 (s), 1041 (m), 962 (m), 895 (m), 879 (m), 847 (s), 777 (m), 702 (m), 647 (m) cm^{-1}. $C_{44}H_{69}N_4RhSi_4Sn$·1/4 $C_6H_5CH_3$ (1011.0): calcd. C 54.35, H 7.08, N 5.54; found C 54.17, H 7.01, N 5.25.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(CNCy)(COD)] (3d): Yield 182 mg (70%). ^{1}H NMR (600.1 MHz, C_6D_6, 293 K): δ = 7.01 (s, 6 H, 2,6-*H*$_{xyl}$), 6.51 (s, 3 H, 4-*H*$_{xyl}$), 5.00 (br. s, 2 H, C*H*$_{COD}$), 4.19 (br. s, 2 H, C*H*$_{COD}$), 3.06 (br. s, 1 H, CN*CH*), 2.27 (s, 18 H, C_6H_3(C*H*$_3$)$_2$), 1.63–1.40 (m, 12 H, 4× C*H*$_{2\ COD}$, 2× C*H*$_{2\ Cy}$), 1.35–1.25 (m, 2 H, C*H*$_{2\ Cy}$), 1.15–1.05 (m, 2 H, C*H*$_{2\ Cy}$), 1.00–0.90 (m, 2 H, C*H*$_{2\ Cy}$), 0.74 (s, 18 H, Si(C*H*$_3$)$_2$), 0.35 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 293 K): δ = 154.6 (s, 1-*C*$_{xyl}$), 137.6 (s, 3,5-*C*$_{xyl}$), 124.8 (s, 2,6-*C*$_{xyl}$), 121.5 (s, 4-*C*$_{xyl}$), 95.5 (d, ^1J(^{103}Rh-^{13}C) = 7.0 Hz, *C*H$_{COD}$), 86.0 (d, ^1J(^{103}Rh-^{13}C) = 8.6 Hz, *C*H$_{COD}$), 53.7 (s, CN*CH*), 32.8 (s, CN*Cy*), 31.1 (s, *C*H$_{2\ COD}$), 30.0 (s, *C*H$_{2\ COD}$), 25.0

(s, CN*Cy*), 23.4 (s, CN*Cy*), 21.8 (s, $C_6H_4CH_3$), 4.0 (s, Si(CH_3)$_2$), –14.1 (s, SiCH_3) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –2.8 (s, $SiMe_2$), –89.6 (s, SiMe) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –115.1 (d, ^1J(^{119}Sn-^{103}Rh) = 838 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3021 (w), 2938 (m), 2859 (w), 2151 (s), 1595 (m), 1582 (s), 1451 (w), 1351 (w), 1303 (s), 1240 (m), 1173 (s), 1040 (m), 961 (m), 879 (m), 850 (s), 777 (m), 703 (w), 649 (m) cm^{-1}. $C_{46}H_{71}N_4RhSi_4Sn$·1/2 $C_6H_5CH_3$ (1060.1): calcd. C 56.08, H 7.13, N 5.29; found C 55.84, H 7.14, N 5.34.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh{P(OPh)$_3$}(COD)] (3e): Yield 121 mg (47%). ^{1}H NMR (399.9 MHz, C_6D_6, 293 K): δ = 7.23 (s, 6 H, 2,6-H_{xyl}), 7.10–7.00 (m, 3 H, P(O*Ph*)$_3$), 6.94 (t, $^3J_{HH}$ = 7.9 Hz, 6 H, P(O*Ph*)$_3$), 6.76 (d, $^3J_{HH}$ = 8.3 Hz, 6 H, P(O*Ph*)$_3$), 6.61 (s, 3 H, 4-H_{xyl}), 5.95 (br. s, 2 H, CH_{COD}), 3.84 (br. s, 2 H, CH_{COD}), 2.30 (s, 18 H, $C_6H_3(CH_3)_2$), 1.63–1.40 (m, 4 H, C$H_{2\ COD}$), 1.37–1.15 (m, 4 H, C$H_{2\ COD}$), 0.64 (s, 18 H, Si(CH_3)$_2$), 0.29 (s, 3 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 293 K): δ = 155.1 (s, 1-C_{xyl}), 151.8 (d, J(^{31}P-^{13}C) = 11.2 Hz, P(O*Ph*)$_3$), 137.6 (s, 3,5-C_{xyl}), 129.3 (d, J(^{31}P-^{13}C) = 1.9 Hz, P(O*Ph*)$_3$), 126.1 (s, 2,6-C_{xyl}), 124.5 (s, P(O*Ph*)$_3$), 122.5 (s, 4-C_{xyl}), 121.6 (d, J(^{31}P-^{13}C) = 4.6 Hz, P(O*Ph*)$_3$), 100.5 (d, ^1J(^{103}Rh-^{13}C) = 13.1 Hz, *C*H$_{COD}$), 87.8 (d, ^1J(^{103}Rh-^{13}C) = 8.0 Hz, *C*H$_{COD}$), 30.6 (s, *C*H$_{2\ COD}$), 29.5 (s, *C*H$_{2\ COD}$), 21.8 (s, $C_6H_3(CH_3)_2$), 4.3 (s, Si(CH_3)$_2$), –14.3 (s, SiCH_3) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –2.4 (s, *Si*Me$_2$), –93.0 (s, *Si*Me) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): δ = 113.4 (d, ^1J(^{103}Rh-^{31}P) = 277, ^2J(^{117}Sn-^{31}P) = 324, ^2J(^{119}Sn-^{31}P) = 338 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –152.7 (d, ^1J(^{119}Sn-^{103}Rh) = 1148, ^2J(^{119}Sn-^{31}P) = 432 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3012 (w, br.), 2942 (w, br.), 2918 (w), 2889 (w, br.), 1590 (m), 1497 (s), 1287 (w), 1236 (s), 1196 (m), 1160 (m), 1025 (w), 910 (s), 848 (m), 814 (m), 774 (m), 711 (m), 670 (m), 512 (w) cm^{-1}. $C_{57}H_{75}N_3O_3PRhSi_4Sn$ (1215.2): calcd. C 56.34, H 6.22, N 3.46; found C 55.99, H 6.15, N 3.23.

General Synthetic Procedure for [MeSi{SiMe$_2$N(4-tol)}$_3$SnRh(L)-(NBD)]: A mixture of 200 mg (0.273 mmol) MeSi{SiMe$_2$N(4-tol)}$_3$SnLi(OEt$_2$) (**1a**) and 63 mg (0.137 mmol) [RhCl(NBD)]$_2$ was cooled to –78 °C and suspended with cold toluene. After stirring for 10 min, 0.278 mmol of L were added dropwise to the orange reaction mixture. While warming to room temperature over a period of 90 min, the colour changed to red. All insolubilities were removed by centrifugation and the solvent of the centrifugate was removed by distillation under reduced pressure. The brown to red residue was washed with pentane and dried in vacuo.

[MeSi{SiMe$_2$N(4-tol)}$_3$SnRh(PEt$_3$)(NBD)] (4a): Yield 229 mg (87%). ^{1}H NMR (600.1 MHz, $C_6D_5CD_3$, 263 K): δ = 7.24 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, tol), 7.02 (d, $^3J_{HH}$ = 7.9 Hz, 6 H, tol), 4.98 (br., 2 H, 2/3/5/6-NBD C*H*), 3.47 (br., 2 H, 2/3/5/6-NBD C*H*), 3.25 (s, 2 H, 1/4-NBD C*H*), 2.27 (s, 9 H, $C_6H_4CH_3$), 1.25–0.95 (m, 2 H, C$H_{2\ NBD}$), 0.78 (vq, N = 7.6 Hz, 6 H, P(CH_2CH_3)$_3$), 0.70 (s, 18 H, Si(CH_3)$_2$), 0.49 (dt, $^3J_{HH}$ = 7.6, ^3J(^{31}P-^{1}H) = 15 Hz, 9 H, P(CH_2CH_3)$_3$), 0.34 (s, 3 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $C_6D_5CD_3$, 263 K): δ = 152.0 (s, tol), 129.3 (s, tol), 128.0 (s, tol), 125.9 (s, tol), 76.3 (br. s, 2/3/5/6-NBD *C*H), 66.5 (s, *C*H$_{2\ NBD}$), 65.0 (br. s, 2/3/5/6-NBD *C*H), 53.1 (s, 1/4-NBD *C*H), 20.6 (s, $C_6H_4CH_3$), 16.4 (d, ^2J(^{31}P-^{13}C) = 25 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.2 (d, ^3J(^{31}P-^{13}C) = 1.6 Hz, P(CH_2CH_3)$_3$), 3.4 (s, Si(CH_3)$_2$), –14.4 (s, SiCH_3) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –3.0 (s, $SiMe_2$), –89.7 (s, SiMe) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): δ = 15.3 (d, ^1J(^{103}Rh-^{31}P) = 150, ^2J(^{117}Sn-^{31}P) = 363, ^2J(^{119}Sn-^{31}P) = 380 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –111.7 (dd, ^1J(^{119}Sn-^{103}Rh) = 925, ^2J(^{119}Sn-^{31}P) = 376 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2992 (w), 2959 (w), 2933 (w), 2880 (w), 1604 (w), 1497 (s), 1458 (w), 1239 (s), 1216 (s), 1179 (w), 1105 (w), 1034 (w), 911 (s), 844 (s), 813 (m), 780 (s), 707 (m), 542 (w), 509 (m) cm^{-1}. $C_{41}H_{65}N_3PRhSi_4Sn$ (964.9): calcd. C 51.03, H 6.79, N 4.35; found C 51.00, H 6.90, N 4.40.

[MeSi{SiMe$_2$N(4-tol)}$_3$SnRh(P*i*Pr$_3$)(NBD)] (4b): Yield 194 mg (86%). ^{1}H NMR (600.1 MHz, $C_6D_5CD_3$, 263 K): δ = 7.29 (d, $^3J_{HH}$ = 8.0 Hz, 6 H, tol), 7.02 (d, $^3J_{HH}$ = 7.5 Hz, 6 H, tol), 4.42 (br., 2 H, 2/3/5/6-NBD C*H*), 3.28 (br., 4 H, 2/3/5/6-NBD C*H*), 3.11 (s, 2 H, 1/4-NBD C*H*), 2.28 (s, 9 H, $C_6H_4CH_3$), 1.24–1.16 (m, 3 H, P[C*H*(CH_3)$_3$]$_3$), 0.98–0.88 (m, 2 H, C$H_{2\ NBD}$), 0.80 (dd, $^3J_{PH}$ = 13.2, $^3J_{HH}$ = 7.1 Hz, 18 H, P[CH(CH_3)$_3$]$_3$), 0.73 (s, 18 H, Si(CH_3)$_2$), 0.39 (s, 3 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $C_6D_5CD_3$, 263 K): δ = 152.1 (s, tol), 128.9 (s, tol), 128.0 (s, tol), 126.9 (s, tol), 72.4 (br. s, 2/3/5/6-NBD *C*H), 64.8 (s, *C*H$_{2\ NBD}$), 58.5 (br. s, 2/3/5/6-NBD *C*H), 51.7 (s, 1/4-NBD *C*H), 26.4 (d, ^2J(^{31}P-^{13}C) = 17 Hz, P[*C*H(CH_3)$_3$]$_3$), 20.6 (s, $C_6H_4CH_3$), 19.8 (s, P[CH(*C*H$_3$)$_3$]$_3$), 3.9 (s, Si(*C*H$_3$)$_2$), –14.1 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –3.1 (s, $SiMe_2$), –88.9 (s, SiMe) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): δ = 43.5 (d, ^1J(^{103}Rh-^{31}P) = 157, ^2J(^{117}Sn-^{31}P) = 255, ^2J(^{119}Sn-^{31}P) = 266 Hz) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –149.5 (dd, ^1J(^{119}Sn-^{103}Rh) = 928, ^2J(^{119}Sn-^{31}P) = 268 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2959 (w), 2891 (w), 1605 (w), 1498 (s), 1366 (w), 1235 (s), 1106 (w), 1030 (w), 912 (s), 839 (m), 813 (s), 776 (m), 706 (w), 648 (w), 542 (w), 510 (m) cm^{-1}. $C_{44}H_{71}N_3PRhSi_4Sn$ (1007.0): calcd. C 52.48, H 7.11, N 4.17; found C 52.19, H 7.20, N 4.42.

[MeSi{SiMe$_2$N(4-tol)}$_3$SnRh(CN*t*Bu)(NBD)] (4c): Yield 200 mg (79%). ^{1}H NMR (399.1 MHz, C_6D_6, 293 K): δ = 7.20 (d, $^3J_{HH}$ = 8.1 Hz, 6 H, 3,5-H_{tol}), 7.01 (d, $^3J_{HH}$ = 8.1 Hz, 6 H, 2,6-H_{tol}), 4.22 (br. s, 4 H, 2,3,5,6-CH_{NBD}), 3.01 (br. s, 2 H, 1,4-CH_{NBD}), 2.21 (s, 9 H, $C_6H_4CH_3$), 0.87 (s, 9 H, C(CH_3)$_3$), 0.82 (s, 2 H, C$H_{2\ NBD}$), 0.71 (s, 18 H, Si(CH_3)$_2$), 0.34 (s, 3 H, SiCH_3) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 293 K): δ = 152.5 (s, 1-C_{tol}), 129.5 (s, 3,5-C_{tol}), 127.9 (s, 4-C_{tol}), 125.5 (s, 2,6-C_{tol}), 66.2 (s, *C*H$_{2\ NBD}$), 56.6 (s, *C*(CH$_3$)$_3$), 53.2 (d, ^1J(^{103}Rh-^{13}C) = 2.1 Hz, 1,4-*C*H$_{NBD}$), 45.1 (d, ^1J(^{103}Rh-^{13}C) = 1.6 Hz, 2,3,5,6-*C*H$_{NBD}$), 37.3 (d, ^1J(^{103}Rh-^{13}C) = 6.3 Hz, 2,3,5,6-*C*H$_{NBD}$), 30.0 (s, C(*C*H$_3$)$_3$), 20.8 (s, $C_6H_4CH_3$), 3.9 (s, Si(*C*H$_3$)$_2$), –14.1 (s, Si*C*H$_3$) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 293 K): δ = –2.8 (s, *Si*Me$_2$), –88.3 (s, *Si*Me) ppm. ^{119}Sn{^{1}H} NMR (149.1 MHz, C_6D_6, 293 K): δ = –103.1 (d, ^1J(^{119}Sn-^{103}Rh) = 910 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3007 (w), 2944 (w), 2915 (w), 2362 (w), 1605 (m), 1499 (s), 1369 (w), 1237 (s), 1178 (w), 1109 (w), 913 (s), 840 (s), 813 (s), 777 (s), 958 (m), 742 (m), 708 (w), 649 (w), 545 (w), 512 (m) cm^{-1}. $C_{40}H_{59}N_4RhSi_4Sn$ (929.9): calcd. C 51.67, H 6.40, N 6.03; found C 51.31, H 6.35, N 6.09.

General Synthetic Procedure for [MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(L)-(NBD)]: A mixture of 200 mg (0.258 mmol) MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnLi(OEt$_2$) (**1b**) and 59 mg (0.120 mmol) [RhCl(NBD)]$_2$ was cooled to –78 °C and suspended in pre-cooled toluene. After stirring for 15 min 0.258 mmol of L were added dropwise to the orange reaction mixture. While warming to room temperature over a period of 90 min, the colour changed to red. All insolubilities were removed by centrifugation and the solvent of the centrifugate was removed by distillation under reduced pressure. The red/brown residue was washed with pentane and dried in vacuo.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(PEt$_3$)(NBD)] (5a): Yield 202 mg (78%). ^{1}H NMR (399.9 MHz, C_6D_6, 293 K): δ = 7.00 (s, 6 H, 2,6-H_{xyl}), 6.56 (s, 3 H, 4-H_{xyl}), 5.02 (br. s, 2 H, 2/3/5/6-NBD C*H*), 3.47 (br. s, 2 H, 2/3/5/6-NBD C*H*), 3.34 (br. s, 2 H, C$H_{2\ NBD}$), 2.32 (s, 18 H, $C_6H_3(CH_3)_2$), 1.16 (br. s, 1 H, 1/4-NBD C*H*), 1.04 (br. s, 1 H, 1/4-NBD C*H*), 0.90 (m, 6H P(CH_2CH_3)$_3$), 0.69 (s, 18 H, Si(CH_3)$_2$), 0.46 (dt, $^3J_{HH}$ = 7.6, ^3J(^{31}P-^{1}H) = 15 Hz, 9 H, P(CH_2CH_3)$_3$), 0.33

(s, 3 H, SiCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ = 154.9 (s, 1-C_{xyl}), 137.8 (s, 3,5-C_{xyl}), 124.7 (s, 2,6-C_{xyl}), 121.9 (s, 4-C_{xyl}), 74.7 (br. s, 2/3/5/6-NBD *C*H), 67.1 (s, *C*$H_{2\ NBD}$), 65.4 (br. s, 2/3/5/6-NBD *C*H), 53.4 (s, 1/4-NBD *C*H), 21.8 (s, $C_6H_4CH_3$), 16.6 (d, $^2J(^{31}P\text{-}^{13}C)$ = 23 Hz, P(*C*$H_2CH_3)_3$), 8.3 (d, $^3J(^{31}P\text{-}^{13}C)$ = 2.6 Hz, P($CH_2CH_3)_3$), 3.9 (s, Si(*C*$H_3)_2$), –14.3 (s, Si*C*H_3) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 293 K): δ = –3.1 (s, $SiMe_2$), –91.1 (s, SiMe) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 293 K): δ = 14.4 (d, $^1J(^{103}Rh\text{-}^{31}P)$ = 151, $^2J(^{117}Sn\text{-}^{31}P)$ = 363, $^2J(^{119}Sn\text{-}^{31}P)$ = 379 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6, 293 K): δ = –113.0 (dd, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 934, $^2J(^{119}Sn\text{-}^{31}P)$ = 383 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3019 (w), 2955 (m), 2859 (w), 1595 (m), 1582 (s), 1459 (m), 1301 (s), 1242 (m), 1174 (m), 1160 (s), 1036 (m), 960 (m), 901 (m), 844 (s), 826 (m), 775 (m), 700 (m), 647 (m) cm^{-1}. $C_{44}H_{71}N_3PRhSi_4Sn{\cdot}1/4\ C_6H_5CH_3$ (1030.0): calcd. C 53.35, H 7.14, N 4.08; found C 53.22, H 7.20, N 4.26.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(CN*t*Bu)(NBD)] (5c): Yield 178 mg (71%). ^1H NMR (399.1 MHz, C_6D_6, 293 K): δ = 7.43–6.98 (m, 2,6-H_{xyl}), 6.55 (s, 3 H, 4-H_{xyl}), 4.31 (br. s, 4 H, 2,3,5,6-CH_{NBD}), 3.1 (br. s, 2 H, 1,4-CH_{NBD}), 2.29 (s, 18 H, $C_6H_3(CH_3)_2$), 1.29–1.17 (m, 2 H, C$H_{2\ NBD}$),0.83 (s, 9 H, C(C$H_3)_3$), 0.73 (s, 18 H, Si(C$H_3)_2$), 0.33 (s, 3 H, SiCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ = 154.9 (s, 1-C_{xyl}), 138.8 (s, 3,5-C_{xyl}), 123.8 (s, 2,6-C_{xyl}), 121.4 (s, 4-C_{xyl}), 72.5 (br. s, 2/3/5/6-NBD *C*H), 66.8 (s, *C*$H_{2\ NBD}$), 56.7 (s, *C*$(CH_3)_3$), 53.3 (s, 1/4-NBD *C*H), 29.8 (s, C(*C*$H_3)_3$), 21.9 (s, $C_6H_3(CH_3)_2$), 4.1 (s, Si(*C*$H_3)_2$), –14.2 (s, Si*C*H_3) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 293 K): δ = –2.5 (s, *Si*Me_2), –89.8 (s, *Si*Me) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6, 293 K): δ = –102.2 (d, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 910 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2981 (w), 2944 (m), 2860 (w), 2142 (s), 1582 (s), 1467 (m), 1304 (s), 1238 (m), 1171 (s), 1039 (m), 963 (m), 902 (m), 881 (m), 842 (s), 778 (m), 703 (m), 649 (m) cm^{-1}. $C_{43}H_{65}N_4RhSi_4Sn$ (972.0): calcd. C 53.14, H 6.74, N 5.76; found C 52.97, H 6.58, N 5.82.

[MeSi{SiMe$_2$N(3,5-xyl)}$_3$SnRh(P*i*Pr3)(η^6-C$_6$H$_5$CH$_3$)] (6): A mixture of 200 mg (0.258 mmol) MeSi{$SiMe_2N$(4-tol)}$_3$SnLi(OEt_2) (**1a**) and 50 mg (0.129 mmol) $[RhCl(C_2H_4)_2]_2$ was cooled to –78 °C and suspended with cold toluene. After stirring for 15 min P*i*Pr_3 (50 μL, 0.261 mmol) was added and the yellow suspension was stirred for another 15 min at –78 °C. Upon subsequent warming to room temperature, the colour changed to brown. All insolubilities were removed by centrifugation and solvent of the centrifugate was removed by distillation under reduced pressure to yield complex **6** as a brown microcrystalline powder. Yield 104 mg (38%). ^1H NMR (399.9 MHz, C_6D_6, 293 K): δ = 7.11 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, η^6-$C_6H_5CH_3$), 7.05 (m, 7 H, η^6-$C_6H_5CH_3$, 2,6-H_{xyl}), 7.00 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, η^6-$C_6H_5CH_3$), 6.60 (s, 3 H, 4-H_{xyl}), 2.32 (s, 18 H, $C_6H_3(CH_3)_2$), 2.18 (s, 3 H, η^6-$C_6H_5CH_3$), 1.20–1.10 (m, 3 H, P[C$H(CH_3)_3]_3$), 0.79 (dd, $^3J_{PH}$ = 13.5, $^3J_{HH}$ = 7.1 Hz, 18 H, P[CH(C$H_3)_3]_3$), 0.70 (s, 18 H, Si(C$H_3)_2$), 0.32 (s, 3 H, SiCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 293 K): δ = 154.5 (s, 1-C_{xyl}), 137.8 (s, η^6-$C_6H_5CH_3$), 137.2 (s, 3,5-C_{xyl}), 129.3 (s, η^6-$C_6H_5CH_3$), 128.5 (s, η^6-$C_6H_5CH_3$), 127.3 (s, 2,6-C_{xyl}), 125.6 (s, η^6-$C_6H_5CH_3$), 122.1 (s, 4-C_{xyl}), 29.5 (d, $^2J(^{31}P\text{-}^{13}C)$ = 22 Hz, P[*C*$H(CH_3)_3]_3$), 21.6 (s, $C_6H_3(CH_3)_2$), 21.4 (s, η^6-$C_6H_5CH_3$), 20.2 (s, P[CH(*C*$H_3)_3]_3$), 4.6 (s, Si(*C*$H_3)_2$), –14.8 (s, Si*C*H_3) ppm. $^{29}Si\{^1H\}$ NMR (79.4 MHz, C_6D_6, 293 K): δ = –2.9 (s, $SiMe_2$), –90.6 (s, SiMe) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 293 K): δ = 68.0 (d, $^1J(^{103}Rh\text{-}^{31}P)$ = 205, $^2J(^{117}Sn\text{-}^{31}P)$ = 247, $^2J(^{119}Sn\text{-}^{31}P)$ = 259 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6, 293 K): δ = –233.1 (dd, $^1J(^{119}Sn\text{-}^{103}Rh)$ = 1331, $^2J(^{119}Sn\text{-}^{31}P)$ = 261 Hz) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2959 (m), 2891 (m), 1597 (s), 1582 (s), 1466 (m), 1299 (m), 1241 (m), 1158 (m), 1035 (m), 959 (m), 903 (m), 845 (s), 776 (m), 704 (w), 645 (m) cm^{-1}.

Table 2. Details of the crystal structure determinations of the complexes **2c**, **3c**–**3e** and **4a**.

	2c	**3c**	**3d**	**3e**	**4a**
Formula	$C_{44.50}H_{67}N_4RhSi_4Sn$	$C_{51}H_{77}N_4RhSi_4Sn$	$C_{53}H_{79}N_4RhSi_4Sn$	$C_{57}H_{75}N_3O_3PRhSi_4Sn$	$C_{41}H_{65}N_3PRhSi_4Sn$
Crystal system	triclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a [Å]	12.3797(9)	12.6140(8)	12.7606(9)	12.327(1)	12.5805(11)
b [Å]	14.0140(10)	14.0559(9)	13.8360(10)	12.871(1)	18.2854(15)
c [Å]	17.1831(12)	30.3683(19)	31.050(2)	20.651(2)	19.5699(17)
α [°]	107.019(1)	90	90	72.170(1)	90
β [°]	90.888(1)	92.525(1)	91.829(1)	89.627(1)	90
γ [°]	115.597(1)	90	90	87.669(2)	90
V [Å^3]	2535.7(3)	5379.1(6)	5479.3(7)	3116.4(4)	4501.8(7)
Z	2	4	4	2	4
M_r	991.98	1080.13	1106.16	1215.13	964.89
d_c [Mg m^{-3}]	1.299	1.334	1.341	1.295	1.424
F(000)	1026	2248	2304	1256	1992
μ(Mo-K_α) [mm^{-1}]	0.944	0.896	0.882	0.809	1.095
Max., min. transmission	0.7453, 0.5874	0.7461, 0.5765	0.7457, 0.6251	0.7454, 0.6324	0.7464, 0.5345
ϑ range [°]	1.8 to 30.0	2.0 to 31.0	2.0 to 31.0	2.0 to 28.3	2.0 to 29.1
Index ranges	–17 to 17,	–18 to 18,	–18 to 18,	–16 to 16,	–17 to 17,
Independent set; h,k,l	–19 to 18; 0 to 24	0 to 20; 0 to 44	0 to 20; 0 to 44	–16 to 17; 0 to 27	0 to 25; 0 to 26
Reflections measured	59026	131323	133095	64764	37104
Refl. unique, R_{int}	14794, 0.0630	17109, 0.0645	17388, 0.0694	15461, 0.0740	12125, 0.0827
Refl. observed [$I \geq 2\sigma(I)$]	10041	13075	12545	10302	9130
Parameters refined	510	598	582	644	473
R indices	$R1$ = 0.0410,	$R1$ = 0.0352,	$R1$ = 0.0465,	$R1$ = 0.0418,	$R1$ = 0.0490,
$I > 2\sigma(I)$	wR_2 = 0.0930	wR_2 = 0.0736	wR_2 = 0.1079	wR_2 = 0.0907	wR_2 = 0.0944
R indices	$R1$ = 0.0712,	$R1$ = 0.0545,	$R1$ = 0.0728,	$R1$ = 0.0740,	$R1$ = 0.0786,
All data	wR_2 = 0.1032	wR_2 = 0.0794	wR_2 = 0.1197	wR_2 = 0.1011	wR_2 = 0.1052
GooF on F^2	1.02	1.10	1.10	1.01	1.05
Absolute structure parameter					–0.02(2)
Largest residual peaks [e Å^{-3}]	1.24, –0.94	0.71, –1.13	1.88, –1.27	1.02, –0.85	0.94, –1.09

$C_{47}H_{77}N_3PRhSi_4Sn$ (1049.1): calcd. C 53.81, H 7.40, N 4.01; found C 53.59, H 7.01, N 4.11.

X-ray Crystallographic Study of 2c, 3c, 3d, 3e and 4a: Crystal data and details of the structure determinations are listed in Table 1 and Table 2. Intensity data were collected at 100 K with a Bruker AXS Smart 1000 CCD diffractometer (Mo-Ka radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for Lorentz, polarization and absorption effects (semiempirical, SADABS).[17] The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (DIRDIF)[18] or by direct methods[19] (complex **3e**) and refined by full-matrix least-squares methods based on F^2.[20] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data (complex **3c** only) the positions of some hydrogen atoms (those on the carbon atoms involved in coordination to Rh) were taken from difference Fourier syntheses and refined. Due to heavy disorder and fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures (and the corresponding F_{obs}) of **2c** (one of two half molecules of toluene per molecule of **2c**) and **3e** (pentane and/or ether) with the SQUEEZE procedure,[21] as implemented in PLATON.[22] The absolute structure of 4a was success refined with respect to Flack's inverted twin parameter.[23]

CCDC-667701 (for **2c**), -667702 (for **3c**), -667704 (for **3d**), -667705 (for **3e**) and -667703 (for **4a**) contain the crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the University of Heidelberg and the Fonds der Chemischen Industrie for support.

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Received: November 19, 2007
Published Online: February 21, 2008

