

Neutral η -Arene Complexes of Rhodium(I); X-Ray Structure of η -Toluene(η -cyclo-octene)[bis{bis(trimethylsilyl)amido}chlorostannate(II)]rhodium(I)[†]

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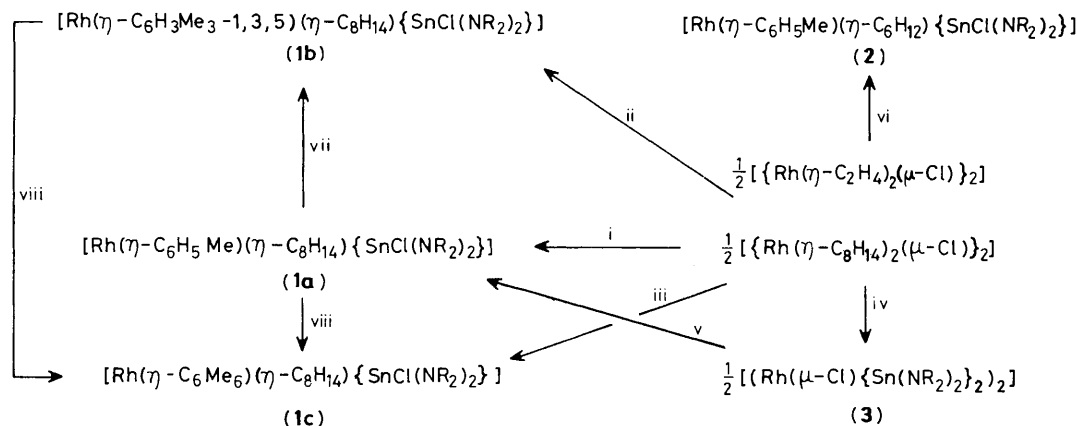
Stable, crystalline, neutral arene-Rh^I complexes, [Rh(η -ArH)(η -C₈H₁₄){SnCl(NR₂)₂}] [R = SiMe₃, C₈H₁₄ = cyclo-octene; and ArH = PhMe (**1a**), C₆H₃Me_{3-1,3,5} (**1b**), or C₆Me₆ (**1c**)] and [Rh(η -PhMe)(η -*trans*-hex-3-ene){SnCl(NR₂)₂}] (**2**), are obtained from [{Rh(alkene)₂(μ -Cl)}₂], 2Sn(NR₂)₂, and excess of ArH at 20 °C, or, for (**1a**), from Sn(NR₂)₂, C₈H₁₄, PhMe, and [(Rh(μ -Cl){Sn(NR₂)₂}₂)] (**3**), itself prepared from [{Rh(η -C₈H₁₄)₂Cl}]₂ and 4Sn(NR₂)₂ in *n*-C₆H₁₄ at 20 °C; unexpectedly facile arene displacement reactions convert (**1a**) into (**1b**) or (**1c**), and (**1b**) into (**1c**), and the X-ray structure of (**1a**) shows a planar Rh environment.

Although an η -arene-rhodium(II) salt, [Rh(η -C₆Me₆)₂]-[AlCl₄]₂, has been known for more than 20 years,¹ and there is now a plethora of cationic η^6 -arene-Rh^I or Rh^{III} complexes,² we now report the first *neutral η -arene-Rh^I complexes*; (**1a**), (**1b**), (**1c**), and (**2**). These 18-electron molecules have the general formula [Rh(η -arene)(η -alkene){SnCl(NR₂)₂}] (R = SiMe₃) and were obtained from [{Rh(η -alkene)₂(μ -Cl)}₂], Sn(NR₂)₂, and arene in high yield (70–80%) under remarkably mild conditions, Scheme 1.

The thermal stability of the crystalline complexes (**1a**)—(**1c**), and (**2**) may be attributable to the bulky, lipophilic ligand SnCl(NR₂)₂; four Pt^{II} complexes derived from this were previously known, made by Sn(NR₂)₂ insertion into Pt-Cl bonds,^{3,4} and for one of them, *trans*-[(Pt(μ -Cl)(PEt₃){SnCl(NR₂)₂}₂)]₂, there are X-ray data.⁴

It is likely that intermediate stannanediyl [:Sn(NR₂)₂] complexes are implicated in the reaction pathways (*cf.*, ref. 3) leading to the chlorostannate(II)s (**1a**)—(**1c**), and (**2**). As evidence, we point to (i) the isolation of [(Rh(μ -Cl){Sn(NR₂)₂}₂)] (**3**) from [{Rh(η -C₈H₁₄)₂(μ -Cl)}₂] (C₈H₁₄ = cyclo-octene) and Sn(NR₂)₂, and (ii) the conversion of (**3**) into

[†] No reprints available.



Scheme 1. Abbreviations: R = SiMe₃, C₈H₁₄ = cyclo-octene, C₆H₁₂ = *trans*-hex-3-ene. Reagents and solvents (all at 20 °C): i, Sn(NR₂)₂, PhMe; ii, Sn(NR₂)₂, C₆H₃Me₃-1,3,5; iii, Sn(NR₂)₂, C₆Me₆ (excess), OEt₂; iv, 2Sn(NR₂)₂, *n*-C₆H₁₄; v, Sn(NR₂)₂, 2C₈H₁₄, PhMe; vi, 2C₆H₁₂, PhMe, and then 2Sn(NR₂)₂; vii, C₆H₃Me₃-1,3,5; viii, C₆Me₆, *n*-C₆H₁₄.

Characterisation: Satisfactory ¹H n.m.r. spectra for the orange complexes (1a), (1b), and (2), the brown (1c), and the deep red (3) in C₆D₆ {or, for (2), in [²H₁₄]methylcyclohexane, in which the complex slowly changed to brown}; the new complexes decomposed before melting at 128–132 °C, except for (2) (95–99 °C).

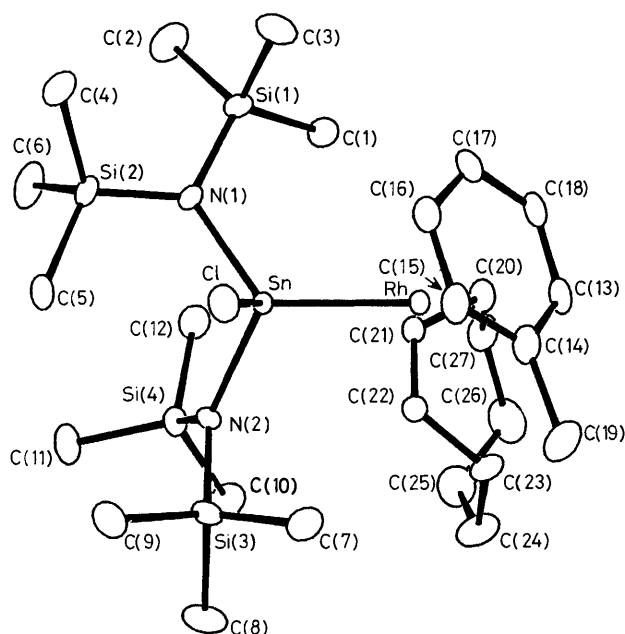


Figure 1. A view of the molecule [Rh(η-C₆H₅Me)(η-C₈H₁₄){SnCl(NR₂)₂}] (R = SiMe₃, C₈H₁₄ = cyclo-octene), (1a), with atoms drawn as 20% thermal vibration ellipsoids, showing the atom numbering scheme. Some dimensions are [L(1) represents the centroid of the aromatic ring and L(2) the mid-point of the C(21)–C(22) olefinic bond]: Rh–Sn 2.554(1), Rh–L(1) 1.833, Rh–L(2) 2.021, Sn–Cl 2.437(2), and <Sn–N> 2.086(9) Å; Rh–Sn–Cl 104.31(4), Rh–Sn–N(1) 125.0(2); Rh–Sn–N(2) 115.3(1), Sn–Rh–L(1) 128, L(1)–Rh–L(2) 141, and Sn–Rh–L(2) 90°.

[Rh(η-C₆H₅Me)(η-C₈H₁₄){SnCl(NR₂)₂}] (1a), Scheme 1. Complex (3) is the first rhodium complex having an Sn(NR₂)₂ ligand.

A further surprising aspect is the facility with which arene ligands are exchanged in neutral arene–rhodium complexes [(1c) ← (1a) → (1b)], Scheme 1, although the relative migratory aptitudes are unexceptional⁵ (C₆Me₆ > C₆H₃Me₃-1,3,5 > C₆H₅Me). By contrast, for other 18-electron η-arene-complexes, such as [Ru(η-arene)(η⁴-cod)] or [Ir(η-arene)(η⁴-cod)]⁺ (cod = cyclo-octa-1,5-diene), exchange is slow (M =

Ir) or negligible (M = Ru) in the absence of a co-ordinating solvent (e.g., Me₂SO or MeCN).⁶

X-Ray quality crystals of (1a) were grown from toluene–*n*-hexane at –30 °C. Crystal data for (1a):[‡] C₂₇H₅₈ClN₂RhSi₄Sn, triclinic, space group P $\bar{1}$, *a* = 11.103(2), *b* = 11.709(3), *c* = 16.469(3) Å, α = 102.77(2), β = 94.39(2), γ = 116.15(2)°, *U* = 1837.2 Å³, *Z* = 2, *D_c* = 1.41 g cm^{–3}, μ = 13.4 cm^{–1}. The structure was solved by routine heavy atom methods and refined to *R* = 0.037, *R'* = 0.059 for 4335 'observed' reflections [with *I* > σ(*I*)] measured on a CAD diffractometer, with Mo-*K*_α radiation, λ = 0.71069 Å.

The X-ray structure of complex (1a) is illustrated in Figure 1. Features of note include (i) the virtual coplanarity of Rh, Sn, L(1), and L(2); (ii) the considerable lengthening of the co-ordinated CC double bond to 1.532(10) Å; and (iii) slight folding of the Me group away from the metal centre.

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[‡] Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.