

# Synthesis and characterization of $\{(\text{diene})\text{Rh}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_2$ , a precursor to silica-bound rhodium

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Reaction of  $[(\text{diene})\text{RhCl}]_2$  with 2 equiv of  $\text{KOSi}(\text{O}^t\text{Bu})_3$  afforded  $\{(\text{diene})\text{Rh}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_2$ , where diene = cod (**1**) and nbd (**2**). Multinuclear NMR studies reveal that **1** and **2** have a dimeric structure with bridging tris(*tert*-butoxy)siloxy ligands. These dimers are folded along the O...O axis. Complexes **1** and **2** reacted with  $\text{PR}_3$  (R = Me, Ph) to give monomeric products, the formulae of which depend on the amount of  $\text{PR}_3$  added ( $(\text{diene})\text{Rh}[\text{OSi}(\text{O}^t\text{Bu})_3](\text{PR}_3)$  and  $\text{Rh}[\text{OSi}(\text{O}^t\text{Bu})_3](\text{PMe}_3)_3$ ). The behavior of **1** towards water and methanol is discussed. Thermogravimetric analyses (TGAs) of **1** and **2** reveal rather sharp conversions to rhodium-containing materials. Thermolysis of **1** in toluene at 180 °C resulted in formation of a black precipitate, which contained rhodium nanoparticles with an average diameter of 22 nm, as determined by powder X-ray diffraction (PXRD), after calcination at 300 °C for 1 h.

## Introduction

The study of rhodium complexes is of increasing interest because of their remarkable reactivity<sup>1</sup> and their participation in catalytic reactions.<sup>2</sup> Also, the useful catalytic properties of rhodium have attracted considerable attention to the surface chemistry of this metal.<sup>3</sup> Silica-supported rhodium complexes and particles were found to be effective catalysts for the hydroformylation of alkenes,<sup>4</sup> the hydrogenation of arenes,<sup>5</sup> and the hydrogenolysis of alkanes.<sup>6</sup> There has therefore been considerable interest in the characterizations of the structures of catalytically active rhodium-bound species, and the nature of metal-support interactions.<sup>7</sup> Although many spectroscopic techniques are now available, the synthesis and characterization of molecular models are essential for gaining insights into the nature of rhodium–silica interactions at the molecular level. Molecular complexes incorporating Rh–O–Si bonds constitute good models for rhodium complexes supported on a silica surface. Rhodium–silicon molecular model compounds studied previously are  $[(\text{diene})\text{Rh}(\mu\text{-OSiMe}_3)]_2$ , where diene = 1,5-cyclooctadiene (cod)<sup>8a,b</sup> and norborna-2,5-diene (nbd),<sup>9</sup>  $[(\text{cod})\text{Rh}(\mu\text{-OSiPh}_3)]_2$ ,<sup>8a,c</sup>  $[(\text{CO})\text{Rh}(\mu\text{-OSiR}_3)]_2$ , where R = Ph,<sup>8c</sup> Me,<sup>10</sup> and monomeric  $[\text{Rh}(\text{cod})(\text{PR}'_3)(\text{OSiR}_3)]$ , where R = Me, <sup>i</sup>Pr, O<sup>t</sup>Bu; R' = Cy, Ph.<sup>11</sup>

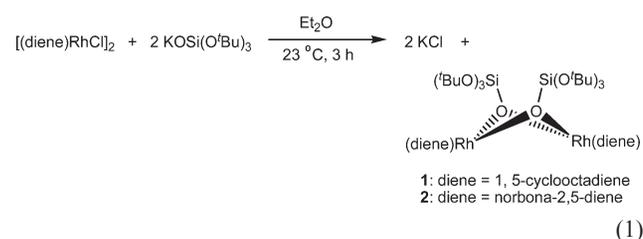
Over the past decade, we have been exploring a single-source molecular precursor approach to metal silicate materials based on tris(alkoxy)siloxy complexes of the type  $\text{M}[\text{OSi}(\text{O}^t\text{Bu})_3]_n$ .<sup>12</sup> This approach provides molecular-level control over the stoichiometry of the resulting materials, and low-temperature (100–200 °C) pathways to homogeneous, metal oxide–silica or metal silicate materials. However, relatively few late-transition metal (alkoxy)siloxy complexes have been reported, and these are limited to copper<sup>13</sup> and nickel derivatives.<sup>14</sup> We are interested in further investigating the generality of the single-source molecular precursor method by examining the behavior of related precursors containing electron-rich metal centers. Here we report the synthesis, characterization, and reactivity of the rhodium(I) siloxide complexes,  $\{(\text{diene})\text{Rh}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_2$ , where diene = cod (**1**), nbd (**2**). The thermolytic conversion of **1** to rhodium-containing materials, and reactions of **1** and **2** toward tertiary phosphines, water and methanol are also described.

## Results and discussion

### Synthesis of the molecular precursors $\{(\text{diene})\text{Rh}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_2$ (diene = cod, nbd)

Reaction of  $[(\text{diene})\text{RhCl}]_2$  with 2 equiv of  $\text{KOSi}(\text{O}^t\text{Bu})_3$ <sup>15</sup> in diethyl ether at room temperature for 3 h produced the Rh(I) *tert*-butoxysiloxy complexes  $\{(\text{diene})\text{Rh}[\mu\text{-OSi}(\text{O}^t\text{Bu})_3]\}_2$ , according to eqn. (1).

The products were isolated from cold (–30 °C) pentane as yellow–orange crystals in high yield (82% for **1** and 76% for **2**); however, attempts to obtain X-ray quality crystals for structure analysis have so far proven futile. Both **1** and **2** are dimeric in benzene solution (by the Signer method<sup>16</sup>). These electron-rich Rh(I) compounds are air- and moisture-sensitive.



The <sup>1</sup>H NMR spectrum of **1** exhibits two slightly broadened singlets at 4.74 and 4.56 ppm, corresponding to chemically inequivalent vinylic protons. The broadening of these resonances is presumably due to unresolved coupling, and not to chemical exchange. The allylic proton resonances were observed as four broadened multiplets at 2.83, 2.42, 1.82, and 1.66 ppm. The *tert*-butoxy resonance is a sharp singlet at 1.54 ppm. Given that **1** is a dimer in benzene solution, these <sup>1</sup>H NMR results suggest that the Rh<sub>2</sub>O<sub>2</sub> core of the dimer is not planar but is bent in a butterfly fashion resulting in a fold angle of <180° between the two RhO<sub>2</sub> planes. Overall, the geometry of **1** resembles that previously reported for the dimeric compounds  $[(\text{cod})\text{Rh}(\mu\text{-OSiR}_3)]_2$ , R = Ph,<sup>8a</sup> Me,<sup>8b</sup> which are bent along the O–O axis (fold angles 109.6 and 120.4°, respectively). This proposed structure is further substantiated by the NMR spectroscopic characterizations of **2** (*vide infra*). The <sup>13</sup>C NMR spectrum of **1** is also consistent with a dimeric, folded structure. The vinylic carbon resonances are not equivalent and appear at 76.06 ppm ( $J_{\text{RhC}} = 15.1$  Hz) and 71.96 ppm ( $J_{\text{RhC}} = 14.7$  Hz). The allylic carbon resonances appear as two singlets at 31.80 and 30.53 ppm. The *tert*-butoxy carbon resonances appear as singlets at 72.46 and 32.45 ppm.

Palyi *et al.* suggested that the geometry of  $[\text{L}_2\text{Rh}(\mu\text{-X})_2]$  complexes was affected not by the strengths of Rh–Rh interactions, but rather by the bridging ligands (X) in terms of interactions between filled p orbitals on X and d orbitals of Rh.<sup>8a</sup> In addition, the electronic structure of the folded dimer  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-OMe})_2]$  investigated by using Fenske–Hall molecular orbital calculations indicated that the folded structure is due to electronic preferences of the bridging alkoxide ligands.<sup>18</sup> The folding allows the lone-pair orbitals of appropriate symmetry on the bridging oxygen atoms to

maximize their donation into the unoccupied Ru orbitals. A similar structure was also observed for the tris(*tert*-butoxy)siloxy-bridged dimer  $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}]_2$ .<sup>14</sup>

The <sup>1</sup>H NMR spectrum of **2** in benzene-*d*<sub>6</sub> exhibits broad, overlapping resonances in the 3.4–4.6 ppm region which are assigned to vinylic and allylic protons. The bridgehead CH<sub>2</sub> chemical shift is observed as a singlet at 1.12 ppm, and the *tert*-butoxy resonance is a sharp singlet at 1.52 ppm. The <sup>13</sup>C NMR spectrum of **2** also reveals broad resonances for the vinylic and allylic carbons. These broadened resonances may be attributed to a fluxional process (*vide infra*), which may correspond to a rotation of the nbd ligand around an imaginary Rh–Rh axis. Such dynamic behavior has been proposed for many other transition-metal complexes with a cyclodiene ligand.<sup>17</sup> In addition, a butterfly-like inversion (flapping) of the Rh<sub>2</sub>O<sub>2</sub> ring may be responsible for this fluxional process. Such broadening was not apparent in the room temperature <sup>1</sup>H NMR spectrum of **1**, indicating a higher coalescence temperature for the analogous process.

Variable-temperature <sup>1</sup>H NMR studies of **2** in toluene-*d*<sub>8</sub> were performed (Fig. 1). The room temperature spectrum shows only small differences compared to that in benzene-*d*<sub>6</sub> ( $\Delta\delta < 0.02$  ppm). All resonances were temperature dependent. The *tert*-butoxy and bridgehead CH<sub>2</sub> resonances shifted to lower fields as the temperature decreased, and appeared as sharp singlets down to –80 °C. The broad, overlapping resonances for the allylic and vinylic protons were eventually resolved at –20 °C into four singlets at 4.40, 4.00, 3.93, and 3.58 ppm with an integral ratio of 2 : 1 : 2 : 1. These results are consistent with the folded structure proposed for **1**. Further cooling led to a collapse of the peaks in the 4.0 ppm region (Fig. 1). In addition, the <sup>13</sup>C NMR spectrum of **2** in toluene-*d*<sub>8</sub> at –60 °C reveals two types of allylic and vinylic carbon atoms, in agreement with the proposed structure. The inequivalency of the allylic and vinylic resonances recorded in the <sup>1</sup>H and <sup>13</sup>C NMR spectra is apparently due to the folded angle about the edge formed by the intersection of the two square planar rhodium fragments in dimeric **1** and **2**.

As expected, the <sup>29</sup>Si NMR spectra of **1** and **2** in benzene-*d*<sub>6</sub> reveal only one resonance at very high field (–94.59 ppm for **1** and –91.06 ppm for **2**). For comparison, the <sup>29</sup>Si NMR spectrum of [(*cod*)Rh( $\mu$ -OSiPh<sub>3</sub>)<sub>2</sub>] appears at 10.46 ppm.<sup>8a</sup>

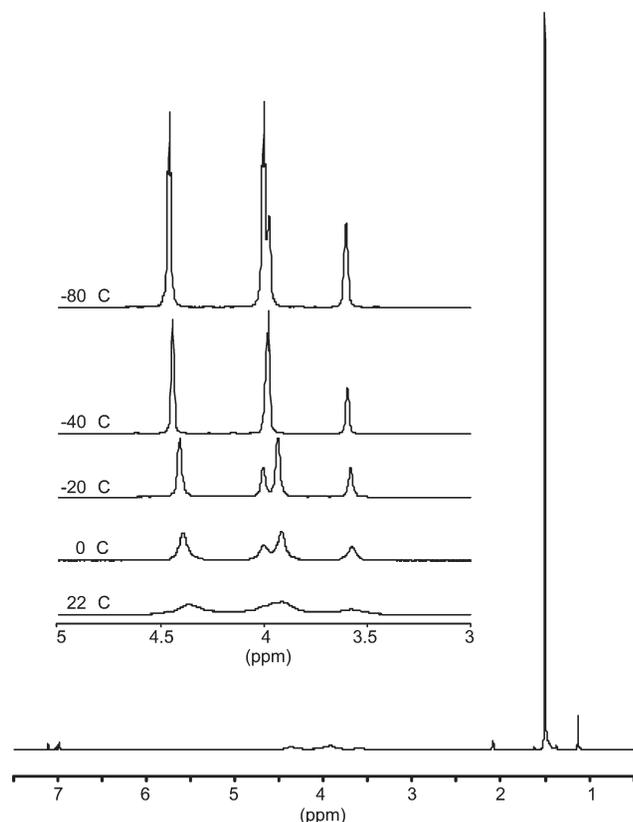
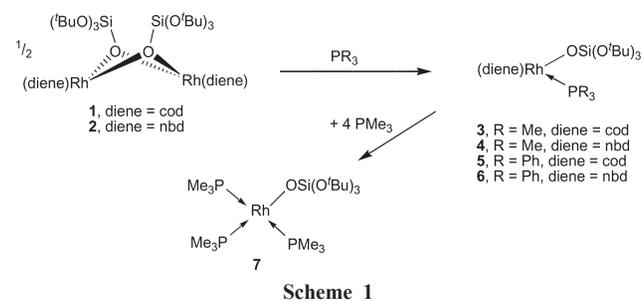


Fig. 1 Variable-temperature <sup>1</sup>H NMR spectra of **2** in toluene-*d*<sub>8</sub>.

## Reactions of **1** and **2** with phosphines

A commonly observed reactivity pattern for bridged rhodium(I) dimers is bridge cleavage by a Lewis base. Both **1** and **2** react readily with 2 equiv of PR<sub>3</sub> (R = Me, Ph) to give sixteen-electron complexes of the type (diene)Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PR<sub>3</sub>) (**3–6**; Scheme 1). The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra of these rhodium compounds support a monomeric square planar structure. The complexes (diene)Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PR<sub>3</sub>) exhibited only one doublet in their <sup>31</sup>P NMR spectra, with rhodium–phosphorus coupling constants in the range observed for monomeric rhodium(I) species.<sup>9a,19</sup> An increase in  $\pi$  back-bonding between Rh and the diene double bonds is observed when the other ligands become better  $\sigma$  donors.<sup>20</sup> Substitution of one of the  $\mu$ -OSi(O<sup>*t*</sup>Bu)<sub>3</sub> ligands in **1** or **2** with PR<sub>3</sub> increases the electron density on the rhodium atom; as a result, the metal–diene  $\pi$  back-bonding character is increased and a deshielding of the *trans*-P vinylic carbon is observed. In addition, we found that the shielding of the *trans*-P vinylic carbons increases slightly on decreasing the basicity of the phosphine<sup>21</sup> from PMe<sub>3</sub> to PPh<sub>3</sub> ( $\delta$  105.2 for **3** vs. 104.6 for **5** and  $\delta$  89.3 for **4** vs. 86.4 for **6**). These are opposite to the results reported by Platzer and coworkers for complexes (*cod*)Rh(Cl)PR<sub>3</sub> (R = Ph, Cy),<sup>20</sup> but are similar to those observed by Bodner *et al.* for carbonyl derivatives.<sup>22</sup> Additionally, compounds **3–6** exhibited  $J_{\text{RhP}}$  coupling constant values of 158, 162, 162, and 184, respectively. Thus, the  $J_{\text{RhP}}$  value increases as the basicity of the phosphine decreases.<sup>23</sup>

The addition of 1 equiv of PMe<sub>3</sub> to a benzene-*d*<sub>6</sub> solution of (diene)Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PMe<sub>3</sub>) (**3** or **4**; Scheme 1) led to a 1 : 1 mixture of the starting complex (diene)Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PMe<sub>3</sub>) and the new tris(trimethyl)phosphinerhodium(I) complex Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PMe<sub>3</sub>)<sub>3</sub> (**7**). No evidence for the dimeric species {(PMe<sub>3</sub>)<sub>2</sub>Rh(OSi(O<sup>*t*</sup>Bu)<sub>3</sub>)<sub>2</sub>} was observed. In contrast, Marciniak and coworkers reported that the rhodium silyloxy complexes (diene)Rh[OSiMe<sub>3</sub>](PPh<sub>3</sub>) react with PPh<sub>3</sub> to form dimeric [(PPh<sub>3</sub>)<sub>2</sub>Rh( $\mu$ -OSiMe<sub>3</sub>)<sub>2</sub>].<sup>9</sup> The reaction of **1** with 6 equiv of PMe<sub>3</sub> in pentane afforded **7** in quantitative yield. The <sup>31</sup>P NMR spectrum of **7** consists of four lines at high field ( $\delta$  –13.9) due to the mutually *trans* phosphorus atoms, and six lines at lower field ( $\delta$  5.59) due to the *cis* phosphorus atom. The structure of these lines arises from a large rhodium–phosphorus coupling ( $J_{\text{RhPc}} = 164$  Hz,  $J_{\text{RhPt}} = 144$  Hz) superimposed upon the smaller phosphorus–phosphorus coupling of the nonequivalent phosphorus atoms ( $J_{\text{PP}} = 50.2$  Hz). These chemical shifts are in close agreement with those observed for surface-bound rhodium–phosphine complexes. Scott *et al.* have reported that the surface species ( $\equiv$ SiO)Rh(PMe<sub>3</sub>)<sub>3</sub> prepared by grafting CH<sub>3</sub>Rh(PMe<sub>3</sub>)<sub>3</sub> onto silica exhibits two <sup>31</sup>P resonances at –1.4 and –12.0 ppm, which were assigned to *cis* and *trans* phosphine ligands, respectively.<sup>24</sup>



The addition of equimolar amounts of PPh<sub>3</sub> to a benzene-*d*<sub>6</sub> solution of (diene)Rh[OSi(O<sup>*t*</sup>Bu)<sub>3</sub>](PPh<sub>3</sub>) (**5** or **6**; Scheme 1) led to no reaction even after prolonged heating at 110 °C. In contrast, rhodium silyloxy complexes of the type (diene)Rh[OSiMe<sub>3</sub>](PPh<sub>3</sub>) react with PPh<sub>3</sub> to form dimeric [(PPh<sub>3</sub>)<sub>2</sub>Rh(OSiMe<sub>3</sub>)<sub>2</sub>].<sup>9</sup> The absence of reaction between **5** or **6** and PPh<sub>3</sub> may result from the steric bulk of the phenyl and *tert*-butoxy groups, and/or the lower donating nature of PPh<sub>3</sub> (compared to PMe<sub>3</sub>).

## Hydrolysis and alcoholysis of **1**

Most alkoxy(siloxy) derivatives of transition metals are hydrolyzed irreversibly by even traces of moisture. To characterize the

hydrolytic stability of the Rh–O–Si linkages in **1**, we examined its reaction with water. A sample of **1** and a ferrocene standard were dissolved in benzene-*d*<sub>6</sub> and hydrolyzed by the addition of 5 μL of water. The hydrolysis products, identified by <sup>1</sup>H NMR spectroscopy, were HOSi(O*t*Bu)<sub>3</sub><sup>25</sup> (2.0 equiv) and the hydroxo-bridged complex [(cod)Rh(μ-OH)]<sub>2</sub>.<sup>26</sup> The facile hydrolysis of the Rh–O–Si bonds suggests that the presence of water could influence the stability of highly dispersed rhodium species on a silica surface. This tendency is also supported by the reported behavior of the hydroxo complex Cp\*Ir(OH)(Ph)(PMe<sub>3</sub>),<sup>27</sup> which easily binds to a silica surface by a reversible interaction with a surface silanol group.

Reaction of **1** with excess MeOH (0.02 mL) in benzene-*d*<sub>6</sub> led to a complete displacement of –OSi(O*t*Bu)<sub>3</sub> by –OMe ligands, and formation of [(cod)Rh(μ-OMe)]<sub>2</sub><sup>28</sup> and HOSi(O*t*Bu)<sub>3</sub>.<sup>25</sup> This is interesting in light of the enhanced acidity of silanols over alcohols, which has been demonstrated theoretically and experimentally.<sup>29</sup> In addition, some metal *tert*-butoxysiloxy complexes were synthesized from silanolysis reactions of metal alkoxide complexes and HOSi(O*t*Bu)<sub>3</sub>. For example, [CuOSi(O*t*Bu)<sub>3</sub>]<sub>4</sub> was prepared from [Cu(μ-O*t*Bu)]<sub>4</sub>,<sup>13a</sup> and (iBuO)<sub>3</sub>CrOSi(O*t*Bu)<sub>3</sub> was synthesized from Cr(O*t*Bu)<sub>4</sub>.<sup>12b</sup> Moreover, the –OMe ligands in [(cod)Rh(μ-OMe)]<sub>2</sub> are known to be labile and susceptible to exchange reactions with other alcohols (<sup>n</sup>PrOH, <sup>n</sup>BuOH and <sup>t</sup>BuOH) under mild conditions.<sup>30</sup> Thus, the facile reaction of **1** with methanol may be the result of the excess amount of methanol, which drives the reaction towards the formation of [(cod)Rh(μ-OMe)]<sub>2</sub>.

### Thermolytic conversions of **1** and **2**

Thermolyses of **1** and **2** were initially examined by thermogravimetric analysis (TGA). Complexes **1** and **2** exhibit a rather high thermal stability relative to most other *tert*-butoxysiloxy complexes, perhaps due to the presence of strong Rh–C bonds. The TGA trace for **1** under a flow of nitrogen (Fig. 2) reveals an onset temperature at *ca.* 180 °C. This decomposition resulted in a dark-gray solid in a yield of 22.1% at 1000 °C. This solid was determined by powder X-ray diffraction to contain crystallites of Rh. For comparison, the theoretical ceramic yields for RhO<sub>0.5</sub>·SiO<sub>2</sub>, Rh·SiO<sub>2</sub>, RhO<sub>0.5</sub>, and Rh are 36.0, 34.4, 23.4, and 21.7%, respectively. The reduction in the observed yield may involve the loss of silanol from the precursor during the thermolysis.

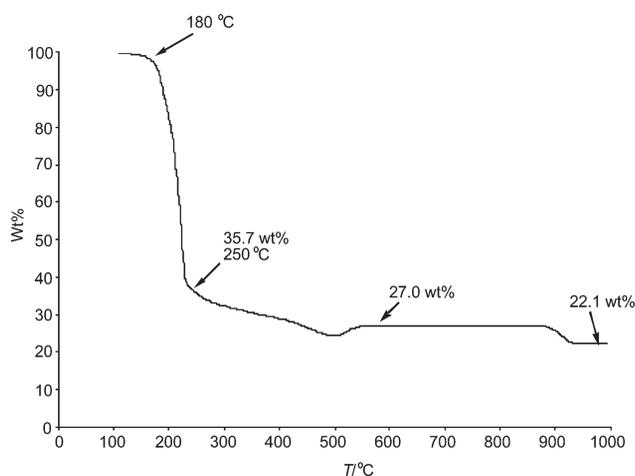


Fig. 2 TGA trace of **1** under N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>.

The chemistry of thermolysis for **1** was further studied by <sup>1</sup>H NMR spectroscopy. The compound was heated at 200 °C under vacuum in a J-Young tube, and the volatile decomposition products were then vacuum-transferred to another NMR tube. Analysis of these products by <sup>1</sup>H NMR spectroscopy revealed the presence of HOSi(O*t*Bu)<sub>3</sub> and HO*t*Bu in a ratio of 6:1. These results suggest that **1** undergoes pyrolytic elimination to rhodium-containing materials by a different pathway from those responsible for the clean conversions of electropositive metal *tert*-butoxysiloxy complexes *via* isobutylene elimination.<sup>12</sup> Analysis of **1** by differential

scanning calorimetry (DSC) under flowing nitrogen revealed the presence of two endotherms at 210 and 230 °C followed by a broad exotherm above 250 °C. The first endotherm is attributed to the decomposition of **1**, but the second one has not been characterized. The broad exotherm is probably associated with elimination of the organic components in **1**.

As might be expected, thermolysis of **2** proceeded similarly to that of **1**. The TGA trace for **2** under a flow of nitrogen (Fig. 3) reveals an abrupt weight loss above 190 °C and a yield of 41.4% at 260 °C corresponding to the loss of silanol. Further heating led to a gradual weight loss and a final yield of 24.0% at 1000 °C, which is considerably less than the theoretical yield for RhO<sub>0.5</sub>·SiO<sub>2</sub> (37.3%), but lies between those for RhO<sub>0.5</sub> and Rh (24.2 and 22.5%, respectively). Under oxygen, the decomposition is more gradual with precipitous weight loss initiating at *ca.* 180 °C. This decomposition is complete by 400 °C, resulting in a yield of 24.2% corresponding to the formation of RhO<sub>0.5</sub>. Further heating under oxygen to 1000 °C led to a weight gain with a final yield of 27.3%, which is in good agreement with the theoretical yield for RhO<sub>1.5</sub> (27.7%). The differential thermal analysis (DTA) curve for **2** reveals a highly exothermic reaction associated with decomposition under oxygen. This phenomenon may be explained by the combustion of organic residues under oxygen, catalyzed by the presence of Rh species.

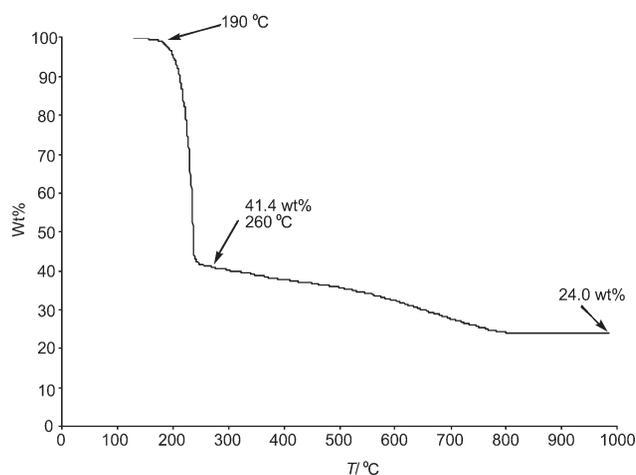
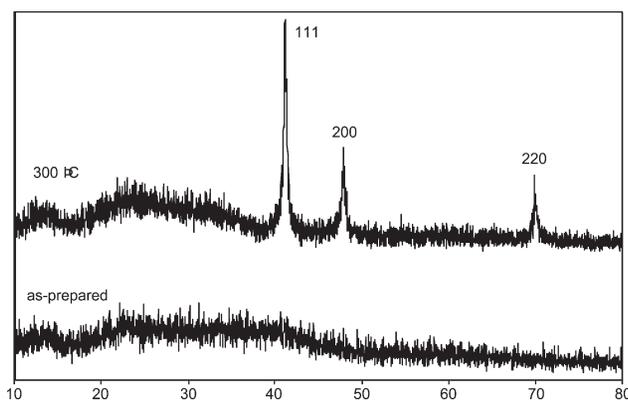


Fig. 3 TGA trace of **2** under N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>.

Thermolysis of **1** in toluene solution was carried out at 180 °C in a sealed Parr reactor under a nitrogen atmosphere. Heating the solution for 20 h led to formation of a black solid precipitate in a brownish solution. The brownish solution contained HOSi(O*t*Bu)<sub>3</sub> (*ca.* 1.5 equiv), cod (*ca.* 0.2 equiv), and unidentified compound(s). These results suggest that some of the silicon may be incorporated into the solid precipitate. The solid precipitate was washed with pentane and air-dried for 3 days. The solid was then ground into a fine powder and placed under vacuum overnight at 120 °C to provide the as-prepared material, which is amorphous as determined by powder X-ray diffraction (PXRD; Fig. 4). This as-prepared material has a very low surface area (6 m<sup>2</sup> g<sup>-1</sup>). Elemental analysis revealed the rhodium to silicon ratio to be 1.23, which is consistent with the loss of some silanol during the thermolysis. The organic content of the as-prepared sample was relatively high (C: 14.5; H: 1.34%). Calcination of this material under a flow of oxygen at 300 °C (10 °C min<sup>-1</sup>) for 1 h removed most of the organic material and induced the crystallization of cubic rhodium with an average particle size of 22 nm, as approximated by the Scherrer equation.<sup>31</sup>

At this point, it is difficult to speculate insightfully about the mechanism by which **1** and **2** undergo thermolytic elimination to rhodium-containing materials. This process clearly involves the elimination of silanol as it is formed as a byproduct in the thermolyses of **1** and **2**. These results indicate the distinct nature of **1** and **2** compared to that of *tert*-butoxysiloxy complexes of early-transition metals such as Zr<sup>12b</sup> and Cr,<sup>12b</sup> which convert cleanly to metal silicates *via* isobutylene elimination. Furthermore, the presence of



**Fig. 4** Room temperature PXRD patterns of Rh/Si/O materials derived from **1**, before and after calcination for 1 h under a flow of oxygen at 300 °C.

rhodium–carbon bonds may complicate the pyrolytic conversion. The appearance of both rhodium metal and silanol indicates that Rh–O homolysis may be involved. This mechanistic step was also suggested by Terry *et al.* in studies of copper *tert*-butoxysiloxo complexes.<sup>13a</sup>

## Concluding remarks

We have described the syntheses of the rhodium(I) siloxide complexes,  $\{(diene)Rh[\mu-O\text{Si}(\text{O}^i\text{Bu})_3]\}_2$ , where diene = cod (**1**), nbd (**2**). These compounds provide good models for dinuclear rhodium(I) species on silica. Both **1** and **2** are dimeric and their  $\text{Rh}_2\text{O}_2$  cores are bent in a butterfly fashion along the O–O axis as inferred from their NMR spectroscopic data. The monomeric siloxide complexes **3–7** were also prepared by reactions of **1** or **2** with various tertiary phosphines. These compounds may also serve as useful models for mononuclear rhodium(I) complexes on a silica surface, owing to their Rh–O–Si linkage. The behavior of **1** towards water and methanol was also studied. The facile hydrolysis of the Rh–OSi bond suggests that the presence of water could greatly influence the stability of highly dispersed rhodium particles on the silica surface.

The high-yielding, convenient syntheses of **1** and **2** make these complexes good candidates for single-source molecular precursors, *via* thermolytic molecular precursor conversions, to Rh/Si/O materials. However, the thermolyses of **1** and **2** led to Rh–O–Si cleavage and formation of rhodium metal at low temperature. Even though **1** and **2** appear to be poor single-source precursors for highly dispersed mixed-element materials, they may prove useful for deposition of rhodium onto silica surfaces. Preliminary results suggested that **1** reacted with the hydroxyl groups on mesoporous SBA-15 surface *via* siloxide displacement to give a 2.6 wt.% Rh loading, or 0.19 Rh nm<sup>-2</sup>. Much of the interest in materials of this type centers around their use in catalysts. Further investigations on the nature of these rhodium surface species, and their catalytic properties, are ongoing.

## Experimental

All manipulations were performed under an atmosphere of nitrogen with standard Schlenk techniques and/or in a Vacuum Atmospheres dry-box. Dry oxygen-free solvents were used throughout. Calcinations were performed with a Lindberg 1200 °C three-zone tube furnace. NMR spectra were recorded on Bruker AVQ400 and DRX500 instruments. Infrared spectra were acquired as Nujol mulls with CsI cells on a Mattson Infinity Series FTIR spectrometer. Surface area and pore volume analyses were measured by using the BET method on a QuantaChrome Autosorb-1 surface area analyzer with all samples heated at 120 °C, under vacuum, for a minimum of 2 h immediately prior to data collection. Powder X-ray diffraction was performed on a Siemens D5000 diffractometer with Cu  $\alpha$  radiation of wavelength 1.54056 Å. Elemental analyses were performed by Galbraith Laboratories (Rh, Si) or by the College of Chemistry's Microanalytical Facility at the University of California, Berkeley

(C, H). The starting material  $\text{KOSi}(\text{O}^i\text{Bu})_3$  was prepared according to the literature procedure.<sup>15</sup>  $[(\text{cod})\text{RhCl}]_2$  and  $[(\text{nbd})\text{RhCl}]_2$  were purchased from Strem and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  before use. All other reagents were purchased from Aldrich and used as received, unless stated otherwise.

## Preparation of the siloxide complexes

**$\{(\text{cod})\text{Rh}[\mu\text{-OSi}(\text{O}^i\text{Bu})_3]\}_2$  (**1**)**. A solid mixture of  $[(\text{cod})\text{RhCl}]_2$  (0.500 g, 1.01 mmol) and  $\text{KOSi}(\text{O}^i\text{Bu})_3$  (0.614 g, 2.03 mmol) was dissolved in  $\text{Et}_2\text{O}$  (50 mL). The reaction mixture was stirred at ambient temperature for 3 h. The volatile materials were removed under vacuum and the product was extracted from the KCl with pentane ( $3 \times 20$  mL). Concentration and cooling to  $-30$  °C afforded **1** as orange crystals (0.790 g, 82%). Anal. found: C, 50.8; H, 8.47.  $\text{C}_{40}\text{H}_{78}\text{O}_8\text{Rh}_2\text{Si}_2$  requires: C, 50.6; H, 8.28%. IR (Nujol mull, CsI,  $\text{cm}^{-1}$ ): 1363s, 1327m, 1300m, 1242s, 1213s, 1196s, 1157sh, 1056br s, 1038br s, 1001s, 968br s, 914sh, 893w, 879w, 872sh, 823m, 804w, 783w, 721sh, 696s, 621w, 588w, 517s, 501s, 465sh, 432m.  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ , 20 °C):  $\delta$  4.74 (s, 4H, =CH), 4.56 (s, 4H, =CH), 2.83 (m, 4H, *exo*  $\text{CH}_2$ ), 2.42 (m, 4H, *exo*  $\text{CH}_2$ ), 1.82 (m, 4H, *endo*  $\text{CH}_2$ ), 1.66 (m, 4H, *endo*  $\text{CH}_2$ ), 1.54 (s, 54H,  $\text{OCMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, benzene- $d_6$ , 20 °C):  $\delta$  76.1 (d,  $J_{\text{RhC}} = 15.1$  Hz, =CH), 72.5 (s,  $\text{OCMe}_3$ ), 72.0 (d,  $J_{\text{RhC}} = 14.7$  Hz, =CH), 32.5 (s,  $\text{OCMe}_3$ ), 31.8 (s,  $\text{CH}_2$ ), 30.5 (s,  $\text{CH}_2$ ).  $^{29}\text{Si}$  NMR (99.35 MHz, benzene- $d_6$ , 20 °C):  $\delta$   $-94.59$  (s,  $\text{OSi}(\text{O}^i\text{Bu})_3$ ).

**$\{(\text{nbd})\text{Rh}[\mu\text{-OSi}(\text{O}^i\text{Bu})_3]\}_2$  (**2**)**. A solid mixture of  $[(\text{nbd})\text{RhCl}]_2$  (0.250 g, 0.543 mmol) and  $\text{KOSi}(\text{O}^i\text{Bu})_3$  (0.329 g, 1.09 mmol) was dissolved in  $\text{Et}_2\text{O}$  (50 mL). The reaction mixture was stirred at ambient temperature for 3.5 h. The volatile materials were removed under vacuum and the product was extracted from the KCl with pentane ( $3 \times 20$  mL). Concentration and cooling to  $-30$  °C afforded **2** as orange crystals (0.378 g, 76%). Anal. found: C, 49.9; H, 7.82.  $\text{C}_{38}\text{H}_{70}\text{O}_8\text{Rh}_2\text{Si}_2$  requires: C, 49.8; H, 7.70%. IR (Nujol mull, CsI,  $\text{cm}^{-1}$ ): 1362s, 1302m, 1240s, 1215s, 1196s, 1174s, 1155m, 1060br s, 1028s, 991sh, 966br s, 918m, 887w, 854w, 823m, 795m, 775w, 721sh, 696s, 623w, 569m, 522m, 492m, 476sh, 461sh, 434m.  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ , 20 °C):  $\delta$  4.36–3.40 (br m, 12H, =CH, –CH), 1.52 (s, 54H,  $\text{OCMe}_3$ ), 1.12 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, benzene- $d_6$ , 20 °C):  $\delta$  72.0 (s,  $\text{OCMe}_3$ ), 60.2 (d,  $J_{\text{RhC}} = 7.55$  Hz, =CH), 49.4 (br, CH,  $\text{CH}_2$ ), 44.9 (br, =CH), 32.3 (s,  $\text{OCMe}_3$ ).  $^{29}\text{Si}$  NMR (99.35 MHz, benzene- $d_6$ , 20 °C):  $\delta$   $-91.06$  (s,  $\text{OSi}(\text{O}^i\text{Bu})_3$ ).  $^1\text{H}$  NMR (500 MHz, toluene- $d_8$ ,  $-20$  °C):  $\delta$  4.40 (s, 4H, =CH), 4.00 (s, 2H, CH), 3.93 (s, 4H, =CH), 3.58 (s, 2H, CH), 1.53 (s, 54H,  $\text{OCMe}_3$ ), 1.15 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, toluene- $d_8$ ,  $-60$  °C):  $\delta$  71.8 (s,  $\text{OCMe}_3$ ), 60.1 (m, =CH), 49.9 (m,  $\text{CH}_2$ ), 49.7 (s, CH), 48.8 (s, CH), 44.7 (m, =CH), 32.0 (s,  $\text{OCMe}_3$ ).

**$(\text{cod})\text{Rh}[\text{OSi}(\text{O}^i\text{Bu})_3](\text{PMe}_3)$  (**3**)**. To a 25 mL pentane solution of **1** (0.188 g, 0.198 mmol) was added 0.040 mL (0.39 mmol) of  $\text{PMe}_3$ . The mixture was stirred at room temperature for 1 h. The volatile materials were removed *in vacuo* to afford a yellow powder, which was redissolved in pentane. Concentration and cooling to  $-78$  °C afforded **3** as yellow crystals (0.165 g, 77%). Anal. found: C, 50.4; H, 8.87.  $\text{C}_{23}\text{H}_{48}\text{O}_4\text{PRhSi}$  requires: C, 50.2; H, 8.79%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 20 °C):  $\delta$  6.00 (s, 2H, =CH), 2.82 (s, 2H, =CH), 2.27 (m, 2H, *exo*  $\text{CH}_2$ ), 2.24 (m, 2H, *endo*  $\text{CH}_2$ ), 1.82 (m, 2H, *exo*  $\text{CH}_2$ ), 1.80 (m, 2H, *endo*  $\text{CH}_2$ ), 1.59 (s, 27H,  $\text{OCMe}_3$ ), 0.90 (d,  $J_{\text{PH}} = 9.50$  Hz, 9H,  $\text{PMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, benzene- $d_6$ , 20 °C):  $\delta$  105.2 (m, =CH), 70.9 (s,  $\text{OCMe}_3$ ), 61.0 (d,  $J_{\text{RhC}} = 14.1$  Hz, =CH), 33.8 (s,  $\text{CH}_2$ ), 32.3 (s,  $\text{OCMe}_3$ ), 28.6 (s,  $\text{CH}_2$ ), 12.9 (d,  $J_{\text{PC}} = 25.2$  Hz,  $\text{PMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz, benzene- $d_6$ , 20 °C):  $\delta$   $-8.60$  (d,  $J_{\text{RHP}} = 158$  Hz,  $\text{PMe}_3$ ).

**$(\text{nbd})\text{Rh}[\text{OSi}(\text{O}^i\text{Bu})_3](\text{PMe}_3)$  (**4**)**. To a 25 mL pentane solution of **2** (0.089 g, 0.097 mmol) was added 0.020 mL (0.19 mmol) of  $\text{PMe}_3$ . The mixture was stirred at room temperature for 3 h. The volatile materials were removed *in vacuo* to afford a yellow powder

(0.075 g, 73%).  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ , 20 °C):  $\delta$  5.78 (s, 2H, =CH), 3.49 (s, 2H, CH), 2.73 (s, 2H, =CH), 1.58 (s, 27H, OCM $e_3$ ), 1.42 (br, 2H, CH $_2$ ), 0.74 (d,  $J_{\text{PH}} = 9.00$  Hz, 9H, PMe $_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, benzene- $d_6$ , 20 °C):  $\delta$  89.3 (m, =CH), 70.8 (s, OCM $e_3$ ), 63.3 (s, CH), 50.8 (s, CH $_2$ ), 41.9 (m, =CH), 32.3 (s, OCM $e_3$ ), 12.5 (d,  $J_{\text{PC}} = 25.2$  Hz, PMe $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz, benzene- $d_6$ , 20 °C):  $\delta$  -6.78 (d,  $J_{\text{RHP}} = 162$  Hz, PMe $_3$ ).

**(cod)Rh[OSi(O $^i$ Bu) $_3$ ](PPh $_3$ ) (5).** A solid mixture of **1** (0.048 g, 0.050 mmol) and PPh $_3$  (0.026 g, 0.100 mmol) was dissolved in pentane (30 mL), and the resulting mixture was stirred at room temperature for 3 h. The volatile materials were removed *in vacuo*. The resulting product was then dissolved in pentane. Concentration and cooling to -78 °C afforded **5** as a yellow powder (0.053 g, 72%). Anal. found: C, 61.8; H, 7.52. C $_{38}$ H $_{54}$ O $_4$ PRhSi requires: C, 61.9; H, 7.39%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 20 °C):  $\delta$  7.93 (m, 6H, PPh $_3$ ), 7.07 (m, 9H, PPh $_3$ ), 6.47 (br m, 2H, =CH), 2.76 (br s, 2H, =CH), 2.41 (m, 2H, exo CH $_2$ ), 2.26 (m, 2H, endo CH $_2$ ), 1.87 (m, 2H, exo CH $_2$ ), 1.66 (m, 2H, endo CH $_2$ ), 1.41 (s, 27H, OCM $e_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz, benzene- $d_6$ , 20 °C):  $\delta$  135.8 (d,  $J_{\text{PC}} = 12.1$  Hz, PPh $_3$ ), 133.1 (d,  $J_{\text{PC}} = 38.2$  Hz, PPh $_3$ ), 130.0 (s, PPh $_3$ ), 104.6 (m, =CH), 70.8 (s, OCM $e_3$ ), 64.4 (d,  $J_{\text{RHC}} = 14.1$  Hz, =CH), 33.5 (s, CH $_2$ ), 32.2 (s, OCM $e_3$ ), 29.2 (s, CH $_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz, benzene- $d_6$ , 20 °C):  $\delta$  27.1 (d,  $J_{\text{RHP}} = 162$  Hz, PPh $_3$ ).

**(nbd)Rh[OSi(O $^i$ Bu) $_3$ ](PPh $_3$ ) (6).** A solid mixture of **2** (0.098 g, 0.107 mmol) and PPh $_3$  (0.057 g, 0.219 mmol) was dissolved in pentane (30 mL), and the resulting mixture was stirred at room temperature for 3 h. The volatile materials were removed *in vacuo*. Recrystallization in pentane at -78 °C afforded **6** as a bright-yellow powder (0.107 g, 69%). Anal. found: C, 61.9; H, 7.21. C $_{37}$ H $_{50}$ O $_4$ PRhSi requires: C, 61.7; H, 6.99%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 20 °C):  $\delta$  7.81 (m, 6H, PPh $_3$ ), 7.05 (m, 9H, PPh $_3$ ), 6.12 (s, 2H, =CH), 3.43 (s, 2H, CH), 2.49 (s, 2H, =CH), 1.51 (s, 27H, OCM $e_3$ ), 1.13 (d,  $J_{\text{HH}} = 8.4$  Hz, 1H, CH $_2$ ), 1.01 (d,  $J_{\text{HH}} = 8.4$  Hz, 1H, CH $_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz, benzene- $d_6$ , 20 °C):  $\delta$  135.0 (d,  $J_{\text{PC}} = 12.1$  Hz, PPh $_3$ ), 132.8 (d,  $J_{\text{PC}} = 39.2$  Hz, PPh $_3$ ), 129.9 (s, PPh $_3$ ), 86.4 (m, =CH), 70.9 (s, OCM $e_3$ ), 63.0 (s, CH), 52.1 (s, CH $_2$ ), 44.4 (d,  $J_{\text{RHC}} = 11.1$ , =CH), 32.3 (s, OCM $e_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz, benzene- $d_6$ , 20 °C):  $\delta$  28.7 (d,  $J_{\text{RHP}} = 184$  Hz, PPh $_3$ ).

**Rh[OSi(O $^i$ Bu) $_3$ ](PMe $_3$ ) $_3$  (7).** To a 30 mL pentane solution of **1** (0.090 g, 0.095 mmol) was added 0.060 mL (0.58 mmol) of PMe $_3$ . The mixture was stirred at room temperature for 3 h. The volatile materials were removed *in vacuo*. The resulting product was then redissolved in pentane. Concentration and cooling to -78 °C afforded orange crystals (0.121 g, 91%). Anal. found: C, 42.6; H, 9.39. C $_{21}$ H $_{54}$ O $_4$ P $_3$ RhSi requires: C, 42.4; H, 9.15%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 20 °C):  $\delta$  1.68 (s, 27H, OCM $e_3$ ), 1.31 (m, 18H, PMe $_3$ ), 1.01 (d,  $J_{\text{PH}} = 8.00$  Hz, 9H, PMe $_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz, benzene- $d_6$ , 20 °C):  $\delta$  70.5 (s, OCM $e_3$ ), 32.7 (s, OCM $e_3$ ), 22.2 (d,  $J_{\text{PC}} = 25.2$  Hz, PMe $_3$ ), 18.2 (d,  $J_{\text{PC}} = 26.4$  Hz, PMe $_3$ ), 17.6 (d,  $J_{\text{PC}} = 69.2$  Hz, PMe $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz, benzene- $d_6$ , 20 °C):  $\delta$  5.59 (td,  $J_{\text{PP}} = 50.2$ ,  $J_{\text{RHP}} = 164$  Hz, *cis*-PMe $_3$ ), -13.9 (dd,  $J_{\text{PP}} = 50.2$ ,  $J_{\text{RHP}} = 144$  Hz, *trans*-PMe $_3$ ).

### Solution thermolysis of **1**

A 20 mL Parr reactor was charged with a toluene (5.0 mL) solution of **1** (0.401 g, 0.423 mmol) in a dry-box. The reactor was then placed in a preheated oven at 180 °C for 20 h. The resulting precipitate was isolated by filtration, washed with pentane (3  $\times$  25 mL) and air-dried for 3 days, yielding 0.120 g (30%) of a solid powder.

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