

# A *triangulo* palladium cluster consisting of $\mu^3$ -capping silyl ligands $\dagger\dagger$

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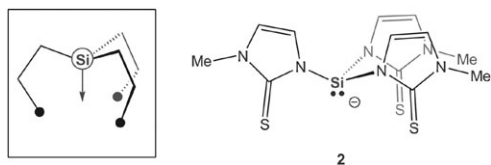
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We report on the utility of multifunctional,  $\kappa^1\text{Si}:\kappa^3\text{S}$ -coordinated tris(methimazolyl)silanide ligands  $[\text{Si}(\text{mt}^{\text{Me}})_3]^-$  for the stabilisation of a *triangulo* palladium cluster  $[\text{Pd}_3\{\text{Si}(\text{mt}^{\text{Me}})_3\}_2]$  (**3**) consisting of very unusual  $\mu^3$ -capping  $\text{SiR}_3$  donors. Differences to the corresponding platinum chemistry were supported by NMR spectroscopy and DFT calculations.

There is a growing interest in multidentate ligand systems featuring dual functionality.<sup>1</sup> Among tripodal shaped ligands, one important subgroup of intramolecularly coordinating, tetradentate ligands is based on chelating donors which are coupled by an additional Lewis-basic coordination site. In most cases, these chelating sets of donors are coordinated to a single metal atom to produce mononuclear complexes with well-defined coordination geometries.

Although relatively rare compared to other well-established systems,<sup>2</sup> strongly *trans* influencing, anionic silanide donors connected to three ancillary donor buttresses have attracted considerable recent interest. Seminal work was published by Hendriksen *et al.*<sup>3</sup> and Stobart *et al.*<sup>4</sup> in the late 1980s on rhodium and iridium complexes consisting of tetradentate  $[\kappa^1\text{Si}:\kappa^3\text{P}_3]^-$  ligands. Most recently, Peters *et al.*<sup>5</sup> reported inspiring work on 3d transition metal complexes of closely related tris(phosphino)silanides. In extension to our studies on ambidentate tris(pyrazolyl)methanides<sup>6</sup> and -silanides<sup>7</sup> we became interested in intramolecularly coordinating ligands for the stabilisation of small metal clusters and/or reactive species. Herein, we report the synthesis and characterisation of a trinuclear Pd cluster (**3**) stabilised by two  $\mu^3$ -capping tris(methimazolyl)silanide ligands  $[\text{Si}(\text{mt}^{\text{Me}})_3]^-$  (**2**).



Scheme 1 Synthesis of **3**.

The ligand precursor  $\text{HSi}(\text{mt}^{\text{Me}})_3$  (**2H**) was synthesised as analytically pure, colourless powder by reacting  $\text{Me}_3\text{Si}(\text{mt}^{\text{Me}})$  (**1**) with  $\text{HSiCl}_3$  in toluene at 70 °C in a closed reaction vessel. **2H** is only hardly soluble in most organic solvents, preventing a full NMR spectroscopic characterisation. Nevertheless, the elemental analysis and EI mass spectroscopic data were consistent with the composition  $\text{HSi}(\text{mt}^{\text{Me}})_3$ . The Si–H moiety was detected at a characteristic frequency of  $\nu = 2322 \text{ cm}^{-1}$  in the IR spectrum.

In a second step, 2 equiv. of **2H** were reacted with 3 equiv. of the palladium precursor  $[\text{Pd}(\text{PtBu}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  at room temperature (Scheme 1). The ligand gradually dissolved and the reaction mixture became intensively yellow in colour. Furthermore, the evolution of  $\text{H}_2$  could be observed (confirmed by  $^1\text{H}$  NMR). After *ca.* 2 minutes, stirring was stopped and the reaction vessel was kept at room temperature over night. Air-stable, orange crystals of  $[\text{Pd}_3\{\text{Si}(\text{mt}^{\text{Me}})_3\}_2]$  (**3**) were isolated by filtration and washed with hexane in analytically pure form in 56% yield. The NMR spectra of **3** were consistent with the structure proposed in Scheme 1. One set of resonances for  $\text{mt}^{\text{Me}}$  groups were observed in the  $^1\text{H}$  NMR ( $d_6$ -dmsO) in the ratio 1H : 1H : 3H at  $\delta^{\text{H}}$  7.13, 6.26 (each CH) and 3.48 ppm (Me), consistent with  $\kappa^1\text{Si}:\kappa^3\text{S}$ -coordinated ligands (**2**) and an overall highly symmetric constitution. No signals for SiH or PdH entities could be observed, further supporting the proposed loss of  $\text{H}_2$  during the complexation. The  $^{29}\text{Si}$  NMR chemical shift of  $\delta^{\text{Si}}$  0.56 ppm was detected by acquiring a  $^1\text{H}$ ,  $^{29}\text{Si}$  gHMQC 2D experiment (see ESI $\ddagger$ ). As expected, two nitrogen chemical shifts were observed by  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC at  $\delta^{\text{N}} = 157$  and 207 ppm. The structural integrity of **3** in solution was supported by pulsed field gradient spin-echo (PGSE) measurements. The hydrodynamic radius ( $r_{\text{H}} = 6.9 \text{ \AA}$ ) and volume ( $V_{\text{H}} = 1375 \text{ \AA}^3$ ) of **3** in  $d_6$ -dmsO solutions were obtained by using the experimental diffusion coefficient ( $D = 1.466 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) together with the Stokes–Einstein equation.  $V_{\text{H}}$  is in very good agreement with the volume for an

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