

## Preparation, X-Ray Crystal and Electronic Structure of the Novel Raft Cluster [NbAuH<sub>2</sub>{C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>

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The reaction of (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>NbH<sub>3</sub> with Au[N(SiMe<sub>3</sub>)<sub>2</sub>]PPh<sub>3</sub> produces the novel raft cluster [NbAuH<sub>2</sub>{C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> in high yield; the structure consists of a gold triangle surrounded by 3 Cp'<sub>2</sub>Nb groups (Cp' = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>) and 6 bridging hydrides [Au–Au 2.7635(20), 2.7571(18), and 2.7801(25) Å; Nb–Au 3.0321(25), 3.0326(25), and 2.9891(18) Å], MO calculations indicate a striking electronic stabilization of this geometry which may be of importance in other gold hydrides.

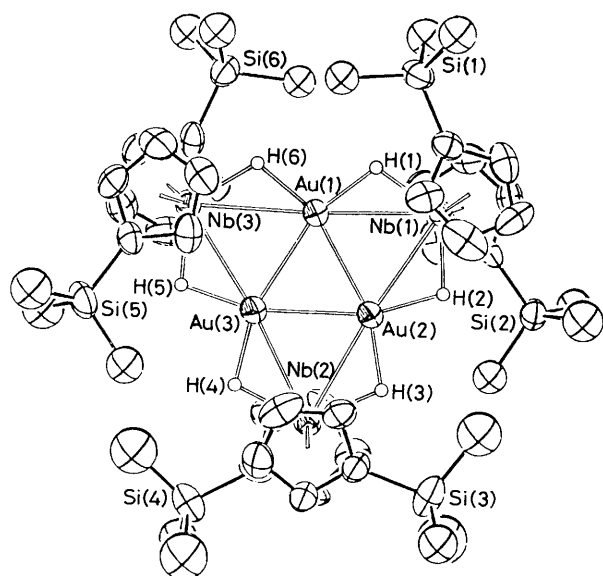
The isolobal analogy suggested between the 'AuPR<sub>3</sub>' and 'H<sup>1</sup>' fragments has recently stimulated the synthesis and study of gold-containing heterometallic derivatives.<sup>2</sup> After the discovery that niobium trihydrides containing silylated cyclopentadienyl groups show anomalous NMR behaviour,<sup>3</sup> observed too for Cp<sup>\*</sup>RuH<sub>3</sub>PR<sub>3</sub><sup>4</sup> (Cp<sup>\*</sup> = C<sub>5</sub>Me<sub>5</sub>) and [CpIrH<sub>3</sub>PR<sub>3</sub>]<sup>+</sup> (ref. 5) derivatives, we have attempted chemical characterization of the compounds by different methods. (The presence of exchange coupling in these compounds has been demonstrated recently by two groups,<sup>6,7</sup> but this does not explain the spectra modifications as a function of the electronic influence of the ligands.) The first approach used a Lewis acid with the hope of discriminating hydrides from co-ordinated H<sub>2</sub>,<sup>8</sup> the second was to selectively replace one hydrogen atom by the AuPR<sub>3</sub> fragment to see whether the formation of co-ordinated H<sub>2</sub> was still possible. Furthermore, the presence of gold in hydride compounds has been shown to increase their activity for hydrogen transfer reactions although the underlying

reason is not yet understood.<sup>2</sup> It is thus of interest to synthesize new species of this type.

We report the reaction of Cp'<sub>2</sub>NbH<sub>3</sub> (Cp' = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>) with Au[N(SiMe<sub>3</sub>)<sub>2</sub>]PPh<sub>3</sub> which leads to the first raft cluster containing gold. A few niobium–gold derivatives have been reported in the literature,<sup>9–11</sup> of which only one<sup>11</sup> has been structurally characterized.

The complex Cp'<sub>2</sub>NbH<sub>3</sub> reacts with one equivalent of Au[N(SiMe<sub>3</sub>)<sub>2</sub>]PPh<sub>3</sub> in a hydrocarbon solvent (hexane, toluene) at room temperature to give instantaneously a purple solution from which purple crystals, analysed as [Cp'<sub>2</sub>NbH<sub>2</sub>Au], were isolated after 2 h. No terminal M–H stretch is detected by IR spectroscopy but in the <sup>1</sup>H NMR spectrum a hydride signal is visible as a singlet at δ – 2.90 at all temperatures used (integration ratio, 2 hydrides: 2 Cp : 2 SiMe<sub>3</sub>). A measure of relaxation time as a function of temperature gives a minimum of *ca.* 100 ms at 228 K.<sup>12</sup> This value is fairly low but similar values have been found in polynuclear polyhydride derivatives.<sup>13</sup> The <sup>1</sup>H NMR also shows the SiMe<sub>3</sub> groups at δ 0.54 and the Cp protons as an AA'BB' pattern at δ 4.99 and 5.48 (J<sub>AB</sub> 2.2 Hz). The results of

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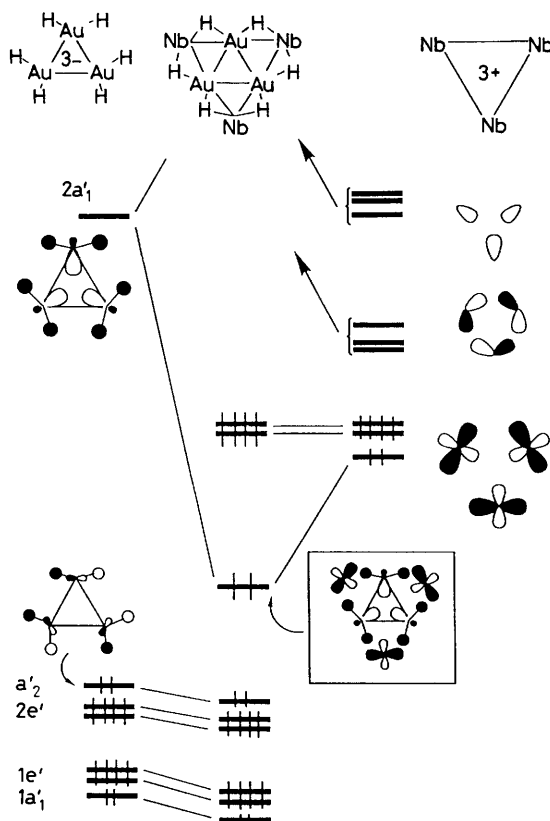


**Figure 1.** ORTEP view of  $\text{Nb}_3\text{Au}_3\text{H}_6(\text{C}_5\text{H}_4\text{SiMe}_3)_6$ , selected bond lengths (Å) and angles ( $^\circ$ ). Au(1)–Au(2) 2.764(2), Au(1)–Au(3) 2.757(2), Au(2)–Au(3) 2.780(3), Au(1)–Nb(1) 3.032(3), Au(1)–Nb(3) 3.033(3), Au(2)–Nb(1) 2.985(2), Au(2)–Nb(3) 2.989(2), Au(3)–Nb(2) 2.987(2), Au(3)–Nb(3) 2.967(2), H–Au  $\sim$ 1.88, H–Nb  $\sim$ 1.91; Au(2)–Au(1)–Au(3) 60.5(1), Au(1)–Au(2)–Au(3) 59.7(1), Au(1)–Au(3)–Au(2) 59.9(1), Au(2)–Au(1)–Nb(1) 61.8(1), Au(2)–Au(1)–Nb(3) 121.9(1), Au(3)–Au(1)–Nb(3) 61.4(1), Au(3)–Au(1)–Nb(1) 122.2(1), Au(1)–Au(2)–Nb(1) 63.5(1), Au(1)–Au(2)–Nb(2) 121.9(1), Au(3)–Au(2)–Nb(2) 62.2(1), Au(3)–Au(2)–Nb(1) 123.1(1), Au(1)–Au(3)–Nb(3) 63.9(1), Au(1)–Au(3)–Nb(2) 122.2(1), Au(2)–Au(3)–Nb(2) 62.3(1), Au(2)–Au(3)–Nb(3) 123.7(1), Nb(1)–Au(1)–Nb(3) 176.2(1), Nb(1)–Au(2)–Nb(2) 174.3(1), Nb(2)–Au(3)–Nb(3) 173.7(1), Au(1)–Nb(1)–Au(2) 54.7(1).

an X-ray structure determination are shown in Figure 1.† The structure consists of an almost equilateral triangle of gold surrounded by a similarly equilateral niobium triangle. The Au–Au distance is very short (near 2.77 Å), shorter than found for the metallic gold (2.8841 Å) but close to distances found for other clusters containing gold.<sup>2</sup> The placement of the hydrogen atoms in the positions shown is indicated by the residual electron density in the last Fourier difference. Location of hydrogen atoms in these sites is chemically reasonable and receives strong theoretical support below.

The niobium–gold distance (near 3.0 Å) is larger than that found for the other known niobium–gold cluster [2.9139(8) and 2.9098(8) Å]<sup>11</sup> and also larger than for other transition metal–gold clusters.<sup>2</sup> This reflects the relatively electron-poor character of the niobium centre. There are three precedents for a polyhydride cluster associated with both transition metal and coinage elements (Group 11)<sup>14–16</sup> and there is a recent report of the preparation of niobium(0) or tantalum(0) similarly located on the metal–metal bonds of a silver triangle.<sup>17</sup> However this is the first such gold cluster. Gold has been shown earlier to lead preferentially to *closo*-polyhedral bimetallic clusters.

† Crystal data:  $\text{C}_{48}\text{H}_{84}\text{Au}_3\text{Nb}_3\text{Si}_6$ ,  $M = 1699.326$ , triclinic, space group  $P_1$ ,  $a = 14.927(2)$ ,  $b = 15.083(2)$ ,  $c = 15.632(2)$  Å,  $\alpha = 103.81(1)$ ,  $\beta = 99.20(1)$ ,  $\gamma = 112.55(1)^\circ$ ,  $U = 3029.8(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.8627$  g cm<sup>-3</sup>, crystal size =  $0.06 \times 0.12 \times 0.61$  mm,  $\lambda = 0.71069$  Å,  $F(000) = 1632$ ,  $\mu = 78.94$  cm<sup>-1</sup>,  $R = 0.038$ ,  $R_w = 0.036$  for 4451 observed reflections with  $I \geq 4.0\sigma(I)$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 2.** Interaction of the  $\text{Au}_3\text{H}_6^{3-}$  raft with the  $(\text{Cp}_2\text{Nb}^+)_3$  unit. Only the  $a_1'$  combination of the  $\text{Nb}_3^{3+}$  low lying d orbitals is shown. The Cp labels have been omitted for clarity.

The electronic structure of the new species is both novel and simple. There are two obvious ways to assemble the molecule; from an  $\text{Au}_3$  triangle plus three  $\text{Cp}_2\text{NbH}_2$  units or from an  $\text{Au}_3\text{H}_6^{3-}$  moiety plus three  $\text{Cp}_2\text{Nb}^+$  fragments. The latter route is more instructive and shows an interesting orbital stabilization mechanism of the gold/hydrogen unit which we believe is important in other compounds where gold hydrides are attached to transition metal units. We have been aided in our analysis by the results of extended Hückel calculations<sup>18</sup> on an idealized version of the molecule of Figure 1 (Au–Au = 2.76 Å, Au–Nb = 3 Å, Au–H = Nb–H = 1.9 Å, Nb–Au–H = 37.9°).

The orbitals of  $\text{Au}_3\text{H}_6^{3-}$  are conveniently built by the assembly of three  $\text{AuH}_2^-$  fragments in which Au uses 6s and 6p valence orbitals.‡ The lowest  $\text{AuH}_2^-$  orbital ( $1a_1$ ) is strongly (6s)Au–H bonding and combines to give a ( $1a_1', 1e'$ ) set for  $\text{Au}_3\text{H}_6^{3-}$  in  $D_{3h}$  symmetry. The next higher bonding orbital of  $\text{AuH}_2^-$  ( $1b_2$ ) uses an Au 6p orbital to bond to the antisymmetric combination of the 1s H;  $1b_2$  is only weakly Au–H bonding, mostly located on H, and it combines to give a ( $2e', a_2'$ ) set of orbitals ( $a_2'$  is represented on Figure 2). These six orbitals house the twelve electrons of the raft. The next highest set is built from the  $\text{AuH}_2^-$   $2a_1$  orbital. Since  $2a_1$  points strongly away from the H centres, the overlap between the three fragments is large and the in-phase combination, strongly Au–Au bonding, lies at a low energy and is the LUMO of the raft (Figure 2). This orbital plays a vital role in the cluster energetics as we show below. The associated  $e'$

‡ The occupied d orbitals of gold would modify the strength of the various interactions but would not affect the qualitative description of the bonding.

combination is at significantly higher energy and does not participate significantly in the bonding scheme.

Figure 2 shows the interaction between the two fragments. On the left are the orbitals of the  $\text{Au}_3\text{H}_6^{3-}$  and on the right are the relevant linear combinations of the lowest lying orbitals of the  $\text{Cp}_2\text{Nb}^+$  unit. The orbitals of the two highest blocks find symmetry matches with appropriate filled orbitals of the  $\text{Au}_3\text{H}_6^{3-}$  unit; for clarity the tie lines to the lower orbitals are not shown. The highest set of these  $\text{Cp}_2\text{Nb}^+$  orbitals is made up of linear combinations of a metal hybrid orbital pointing toward the middle of the Au–Au bond (the  $a'_1$  combination is shown in Figure 2). This set of orbitals best overlaps with the lowest occupied ( $1a'_1, 1e'$ ) set of  $\text{Au}_3\text{H}_6^{3-}$  and the in-phase combination is thus responsible for the Nb–Au bonding interaction. The middle set of  $\text{Cp}_2\text{Nb}^+$  orbitals is composed of a metal based hybrid pointing toward the hydrogen atoms (Figure 2), which best overlaps with the higher set ( $2e'_1, a'_2$ ) of occupied orbitals of the  $\text{Au}_3\text{H}_6^{3-}$  unit. If we recall that these orbitals contain a large amount of hydrogen 1s character then these interactions lead to the generation of Nb–H 'bonds'. The most interesting interaction, and certainly from the calculations the most energetic, is that associated with the overlap of the  $a'_1$  combination of the  $\text{Cp}_2\text{Nb}^+$  lone pair orbitals with the  $2a'_1$  LUMO of the gold–hydrogen unit. The resulting strong interaction leads to an important contribution to Au–Au bonding which we believe accounts for the short Au–Au distance (we calculate an overlap population in the complex of 0.09, of which 0.07 comes from occupation of  $2a'_1$ ) and also strengthens Au–H and Nb–H bonding. Preliminary computations suggest that interactions of this type are important in stabilizing structures containing other polynuclear gold fragments bound to transition metals. The large HOMO–LUMO gap may account for the relative chemical inertness of the raft cluster.

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