

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF THE MIXED-METAL CLUSTER CATION $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+$ WITH $\text{R} = \text{H}$ OR $\text{Si}(\text{CH}_3)_3$ *

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Summary

Triangular “NbAu₂” cluster compounds have been prepared by the reaction of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{H}_3]$ ($\text{R} = \text{H}, \text{Si}(\text{CH}_3)_3$) with gold(I) salts and the structure of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2] \text{PF}_6$ has been determined by X-ray diffraction.

The complexes $[\text{Nb}(\text{AuPPh}_3)(\text{CO})_5\text{L}]$ ($\text{L} = \text{CO}, \text{PPh}_3$) [1] and $[\text{Et}_4\text{N}][\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{AuPPh}_3)(\text{CO})_3]$ [2] are thought to be examples of niobium derivatives containing niobium–gold bonds but there is no X-ray evidence for the metal–metal bond in these compounds.

In this communication we report the synthesis and characterisation of new niobium–gold cluster compounds $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+ \text{X}^-$ ($\text{R} = \text{H}, \text{Si}(\text{CH}_3)_3$; $\text{X} = \text{ClO}_4, \text{PF}_6$), which were obtained, in accord with Mingo’s isolobal principles [3], by the reaction of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{H}_3]$ ($\text{R} = \text{H}, \text{Si}(\text{CH}_3)_3$) with a solution of $[\text{AuPPh}_3]^+ \text{X}^-$ ($\text{X} = \text{ClO}_4$ or PF_6), itself obtained from $[\text{Au}(\text{PPh}_3)\text{Cl}]$ and $[\text{TiX}]$ ($\text{X} = \text{ClO}_4, \text{PF}_6$) (1/2 molar ratio) in tetrahydrofuran. As far as we know these compounds are the first examples of triangular “NbAu₂” metal frameworks, and they represent a previously unknown class of heteronuclear niobium–gold clusters.

The IR spectra of the complexes indicate the presence of the cyclopentadienyl, trimethylsilyl, and triphenylphosphine groups in the cations, and perchlorate and hexafluorophosphate groups for the anions. The ¹H NMR spectra show the char-

* Dedicated to Prof. R. Usón on the occasion of his 60th birthday.

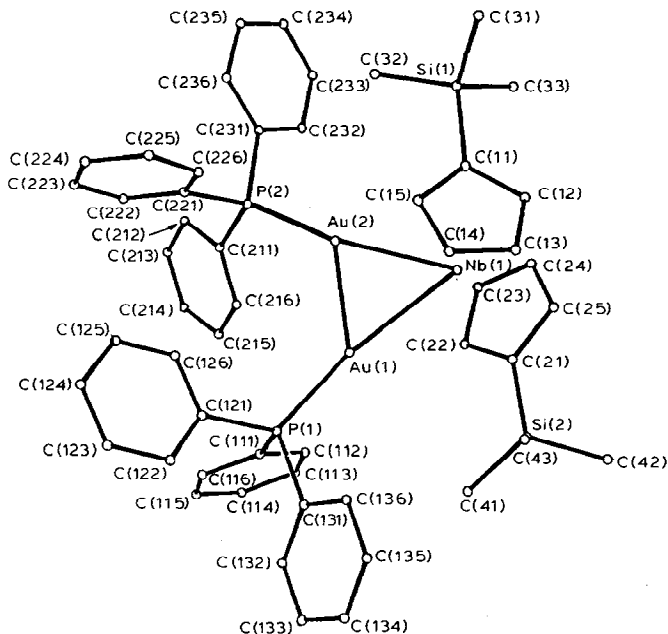


Fig. 1. The molecular structure of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+$ Important bond lengths (Å): Nb(1)–Au(1), 2.9139(8); Nb(1)–Au(2), 2.9098(8); Au(1)–Au(2), 2.7359(5); Au(1)–P(1), 2.294(2); Au(2)–P(2), 2.306(2); Nb(1)…C(11), 2.403(7); Nb(1)…C(12), 2.371(7); Nb(1)…C(13), 2.393(7); Nb(1)…C(14), 2.413(7); Nb(1)…C(15), 2.388(7); Nb(1)…C(21), 2.415(8); Nb(1)…C(22), 2.409(7); Nb(1)…C(23), 2.416(8); Nb(1)…C(24), 2.403(9); Nb(1)…C(25), 2.378(8); important bond angles (°): Au(1)–Nb(1)–Au(2), 56.04(2); Au(1)–Au(2)–Nb(1), 61.91(2); Au(1)–Au(2)–P(2), 125.80(6); Au(2)–Au(1)–P(1), 126.00(6); Nb(1)–Au(1)–P(1), 169.31(6); Nb(1)–Au(2)–P(2), 171.39(7).

Crystal data $\text{C}_{52}\text{H}_{56}\text{F}_6\text{P}_3\text{Au}_2\text{NbSi}_2$. $M = 1403.9$, triclinic, space group $P\bar{1}$ (No. 2), a 17.2295(4), b 14.0335(4), c 12.9686(3) Å, α 107.13(1), β 91.36(1), γ 92.35(1)°, U 2991.9 Å³, $Z = 2$, D_c 1.58 g cm⁻³, $F(000) = 1388$, $(\text{Mo-K}\alpha)$ 52.29 cm⁻¹.

Data recorded on an Enraf–Nonius CAD-4 4-circle diffractometer using graphite monochromated Mo- $K\alpha$ radiation; 2θ range 2–60°, 8004 unique observed ($I > 2\sigma(I)$), absorption corrected reflections, $R = 0.035$, $R_w = 0.036$.

acteristic resonances of cyclopentadienyl and phenyl groups, and the ¹³C NMR spectra indicate symmetrical environments for the cyclopentadienyl groups [4] *.

The conductivity measurements show the expected values for 1/1 electrolytes in acetone [5].

The structure of the cation of $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+ \text{PF}_6^-$, as determined by a single-crystal X-ray analysis is shown in Fig. 1 the caption of which includes some important bond parameters *. The metal framework consists of a triangle with rather similar and large Nb(1)–Au(1) (2.9139(8)) and Nb(1)–Au(2)

* Spectroscopic data: (a) for $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+$. ¹H NMR (chloroform- d_1): 5.3 s (cyclopentadienyl); 7.32(m), 7.20 m (phenyl) ppm. ¹³C NMR (THF): 94.52 s (cyclopentadienyl); 135.05, 134.20, 132.40, 130.22, 129.75 q (Phenyl) ppm.

For $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2]^+$. ¹H NMR (acetone- d_6): 0.07 (trimethylsilyl); 5.19 m, 5.53 m (cyclopentadienyl); 7.31 m, 7.24 m (phenyl) ppm. ¹³C NMR (THF): 0.47 s (trimethylsilyl); 92.89(2), 94.25(2), 99.82(1) t (cyclopentadienyl); 135.15, 134.44, 132.41, 130.44, 129.89 q (phenyl).

(2.9098(8) Å) distances and a short Au(1)–Au(2) distance (2.7359(5) Å), which indicates that there is a strong bonding between the two Au atoms. Similar Au–Au distances have been previously reported for analogous compounds [6]. The Au(1)–Nb(1)–Au(2) angle is 56.04(2)°. The Nb(1)–Au(1)–Au(2) atoms define the molecular plane, and the angles with centroids of the cyclopentadienyl rings are 24.4(2)° and 22.8(2)° for Cp(1) and Cp(2), respectively.

The behaviour of the cluster is being studied in reactions with various amounts of chlorine. Preliminary results reveal that the first molecule of chlorine is incorporated into the gold–gold system without decomposition of the cluster, whereas the second cleaves the Au–Au bond.

Atomic coordinates and bond parameter data for the compound $[\text{Nb}\{\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3\}_2\{\text{AuP}(\text{C}_6\text{H}_5)_3\}_2][\text{PF}_6]$ have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain). Requests for them should state the full literature citation for this communication.

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