Synthesis and Crystal Structure of a Novel Tetranuclear Complex of Gold(I) with *o*-Carborane Derivatives as Ligands

Olga Crespo,[a] **M. Concepción Gimeno,**[a] **Peter G. Jones**[b] **and Antonio Laguna***[a]

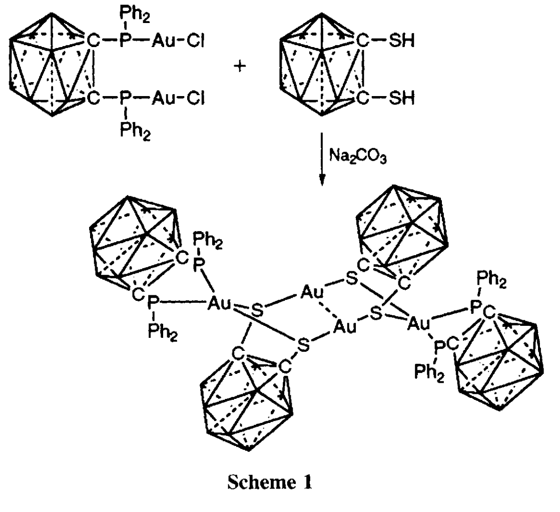
[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

[b] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany*

Treatment of the dinuclear complex $[(AuCl)_2\{B_{10}H_{10}C_2(PPh_2)_2\}]$ in dichloromethane with 1,2-dimercapto-1,2-dicarba-*closo*-dodecarborane and Na_2CO_3 results in the formation of the tetranuclear complex $[Au_4(S_2C_2B_{10}H_{10})_2\{(PPh_2)_2C_2B_{10}H_{10}\}_2]$; the structure was confirmed by X-ray studies and shows an eight-membered Au_4S_4 ring with a short transannular gold–gold interaction.

1,2-Dicarba-*closo*-dodecarborane (*o*-carborane) forms a great variety of derivatives as a consequence of the high resistance of the *o*-carborane cage to chemical attack.[1] The 1,2-bis(diphenylphosphino)- and 1,2-dimercapto-*o*-carborane[2,3] derivatives have been little studied; only a few complexes of Co^{II} and Ni^{II} have been previously described,[4,5] although related systems such as diphosphine or dithiol ligands have been extensively studied and numerous transition metal complexes reported.[6] In these ligands the phosphorus or the sulfur donor atoms are not only attached to a highly electronegative moiety but also constrained in a system of rigid geometry. This can facilitate the preparation of gold(I) complexes with unusual coordination numbers. In a previous paper we have described the synthesis of 1,2-bis(diphenylphosphino)-*o*-carborane gold(I) complexes with the gold atom in various geometries.[7] In the course of our studies with *o*-carborane derivatives we have now synthesised a novel tetranuclear complex by the reaction in Scheme 1.†

Although the most commonly observed geometry for gold(I) is linear two-coordinate, also present in dinuclear bridged complexes, the reaction does not afford the expected complex $[Au_2\{\mu\text{-}(PPh_2)_2C_2B_{10}H_{10}\}(\mu\text{-}S_2C_2B_{10}H_{10})]$ analogously to the synthesis of the complex $[Au_2\{\mu\text{-}S(CH_2)_3S\}(\mu\text{-}dppm)]$ [dppm = bis(diphenylphosphino)methane][8] from the dithiolate $(CH_2)_3S_2^{2-}$. Instead a tetranuclear complex is



Scheme 1

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† To a solution of $[(AuCl)_2]\{B_{10}H_{10}C_2(PPh_2)_2\}$ (0.146 g, 0.15 mmol) in dichloromethane (25 cm^3), $B_{10}H_{10}C_2(SH)_2$ (0.031 g, 0.15 mmol) and excess of Na_2SO_3 were added. The suspension was stirred for 30 min and then filtered off to eliminate excess of Na_2CO_3. The solvent was evaporated to *ca.* 5 cm^3 and addition of *n*-hexane (15 cm^3) gave a yellow solid of $[Au_4(S_2C_2B_{10}H_{10})_2\{(PPh_2)_2C_2B_{10}H_{10}\}_2]$ (71% yield). Elemental analyses were satisfactory. Λ_M 10 Ω^{-1} cm^2 mol^{-1}.

formed; it displays short gold–gold contacts and has two tetrahedrally coordinated gold atoms (see X-ray comments below). This fact could be attributed to the presence of rigid *o*-carborane backbones which should promote chelation.

The compound was characterized by elemental analysis, IR and $^{31}P\{^1H\}$ NMR spectroscopy, fast atom bombardment mass spectrometry and single-crystal X-ray diffraction. The IR spectrum exhibits ν(B–H) bands at 2587 s, br cm^{-1}. Its $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at δ 54.8. In the mass spectrum (FAB^+) the parent ion appears at m/z = 2226 with very low intensity (4%), the dinuclear species at m/z = 1113 being the most abundant mass ion.

The complex crystallizes from dichloromethane-*n*-hexane. Its crystal structure was determined by single-crystal X-ray diffraction analysis (Fig. 1).‡ The molecule has a crystallographic inversion centre. The four gold atoms form short contacts, 3.131(1) Å (transannular), 3.568(1) and 3.751(1) Å. The central gold atoms in the eight-membered ring display essentially linear co-ordination S(2i)–Au(1)–S(1) 172.06(7)°, while the peripheral gold atoms show distorted tetrahedral geometry, P(1)–Au(2)–P(2) 95.52(8), P(2)–Au(2)–S(2) 110.09(7), P(2)–Au(2)–S(1) 111.91(7) and S(2)–Au(2)–S(1) 82.85(7), the bite of the two carboranyl ligands being responsible for the deviations. The P–P bite is wider than in the trigonal planar gold complex $[Au\{B_{10}H_{10}C_2(PPh_2)_2\}(PPh_3)]ClO_4$ [90.2(1)°][7] whereas the S–S bite of the 1,2-dithiolate-*o*-carborane ligand is very narrow. We cannot make any comparison with other complexes because no crystal structures were determined for the above mentioned Co^{II} and Ni^{II} complexes. The Au–S bond lengths are very different. Firstly there are very short bonds at the central gold atoms, Au(1)–S(1) 2.299(2), Au(1)–S(2i) 2.298(2) Å; these values compare well with other Au–S distances found in linear complexes.[9–11] In contrast the Au(2)–S(2), 2.584(2), and Au(2)–S(1), 2.614(2) Å, bonds are longer, associated with the higher coordination number at Au(2). In the compound $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$,[12] where one of the gold atoms is bonded to two sulfur atoms and two PPh_3 groups, the Au–S distances are 2.604(2) and 2.684(2) Å, still longer than those in our complex. The Au–P bond lengths, 2.307(2) and 2.427(2) Å, are different, the longer being similar to those in the three-coordinate complex $[Au\{B_{10}H_{10}C_2(PPh_2)_2\}(PPh_3)]ClO_4$, 2.405(1) and 2.417(1) Å,[7] while the shorter approaches values typical for two-coordinate gold. The eight-membered ring adopts a chair conformation.

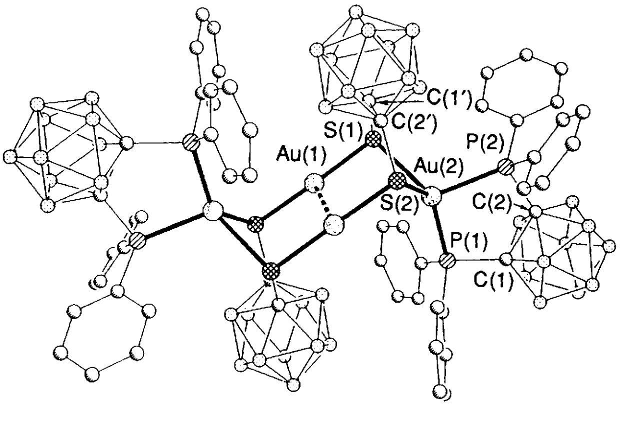

Fig. 1 Molecular structure of $[Au_4(S_2C_2B_{10}H_{10})_2\{(PPh_2)_2C_2B_{10}H_{10}\}_2]$ in the crystal showing the atom numbering scheme. Radii are arbitrary; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.299(2), Au(2)–S(2) 2.584(2), Au(1)–S(2i) 2.298(2), Au(2)–S(1) 2.614(2), Au(1)–Au(1i) 3.1311(12), Au(2)–P(1) 2.307(2), Au(2)–P(2) 2.427(2) Å; S(2i)–Au(1)–S(1) 172.06(7), P(1)–Au(2)–P(2) 95.52(8), P(2)–Au(2)–S(2) 110.09(7), P(2)–Au(2)–S(1) 111.91(7), S(2)–Au(2)–S(1) 82.85(7)°. Symmetry operator (i), 1 − *x*, 1 − *y*, 1 − *z*. Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 380006. Atomic coordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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‡ *Crystal data*: $C_{56}H_{80}Au_4B_{40}P_4S_4$, M_r = 2225.59, monoclinic, space group $P2_1/n$, a = 18.486(3), b = 10.274(2), c = 26.370(5) Å, β = 101.47(2)°, U = 4908.3(16) Å^3, Z = 2, D_c = 1.506 Mg m^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 6.2 mm^{-1}, F(000) = 2112, T = −100 °C, yellow tablet 0.65 × 0.30 × 0.15 mm. 11489 intensities were recorded to $2\theta_{max}$ 50° (Siemens R3 diffractometer, Mo-Kα radiation), of which 8666 were unique (R_{int} 0.023) after absorption corrections. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-92);[13] Au, P, S and C atoms were refined anisotropically. H atoms were included using a riding model. The structure contains large regions of featureless (<2 e Å^{-3}) electron density, probably corresponding to disordered light petroleum components. This is consistent with the rapid disintegration of the crystals on exposure to air. Since no discrete molecules of solvent could be identified, none were refined. No solvent is included in the formula and in dependent quantities such as M, F(000), density. Refinement proceeded to $wR(F^2)$ 0.134, conventional $R(F)$ 0.039 for 387 parameters and 238 restraints, $S(F^2)$ = 1.08; maximum Δρ 1.82 e Å^{-3}.

References

1 R. N. Grimes, *Carboranes*, Academic Press, New York, 1970.
2 R. P. Alexander and H. Schroeder, *Inorg. Chem.*, 1963, **2**, 1107.
3 H. D. Smith, Jr., C. O. Obenland and S. Papetti, *Inorg. Chem.*, 1966, **5**, 1013.
4 H. D. Smith, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 1817.
5 H. D. Smith, Jr., M. A. Robinson and S. Papetti, *Inorg. Chem.*, 1967, **6**, 1014.
6 R. J. Puddephatt, in *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1985, vol. 5, p. 861.
7 O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1601.
8 R. M. Dávila, A. Elduque, T. Grant, R. J. Staples and J. P. Fackler, Jr., *Inorg. Chem.*, 1993, **32**, 1749.
9 R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.
10 P. G. Jones, C. Lensch and G. M. Sheldrick, *Z. Naturforsch, Teil B*, 1982, **37**, 141.
11 M. Nakamoto, W. Hiller and H. Schmidbaur, *Chem. Ber.*, 1993, **126**, 605.
12 J. M. Charnock, S. Bristow, J. R. Nicholson, C. D. Garner and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1987, 303.
13 G. M. Sheldrick, SHELXL-93, a program for crystal structure refinement (pre-release version 1992), University of Göttingen, Germany, 1992.