Gold Clustering at Dimethylsulfoximine Me₂S(O)NH

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Dedicated to Prof. Dr. Dr. h. c. Max Schmidt on the occasion of his 75th birthday

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Gold Clustering, Dimethylsulfoximine

Polyaurated complexes of the dimethylsulfoximide anion [Me₂S(O)N]⁻ have been prepared by reacting N-trimethylsilyl-dimethylsulfoximide with [(Ph₃P)Au]BF₄ in various molar ratios. With one or two equivalents of the gold(I) reagent only the dinuclear complex is obtained in high yield: \{[(Ph₃P)Au]₂NS(O)Me₂\}²⁺ BF₄⁻. With three or four equivalents only the trinuclear complex is produced: \{[(Ph₃P)Au]₃NS(O)Me₂\}²⁺ 2 BF₄⁻. No mono- or tetra-auration was observed, respectively. The composition of the compounds has been confirmed by analytical and spectroscopic data, and the crystal structure of the dinuclear compound has been determined by single crystal X-ray diffraction of the dichloromethane solvate. The two gold atoms are found to be coordinated to the nitrogen atom with a small Au-N-Au angle of only 92.3(3)° and a short Au–Au distance of 2.9900(5) Å. The nitrogen atom is in a distorted trigonal pyramidal configuration which allows an intramolecular SO–Au contact. For the trinuclear complex a structure with a tetracoordinate nitrogen atom [SNAu₃] is proposed which is analogous to the corresponding complexes of phosphinimines R₃P=NH. With the ditertiary phosphine Ph₂PCH₂Ch₂PPh₂ (dppe) a cyclic dinuclear complex (dppe)Au₂[NS(O)Me₂]BF₄ can be synthesized starting from (dppe)Au₂Cl₂. The reaction of the phosphine-rich precursor [(Ph₃P)₂Au]BF₄ with Me₃SiNS(O)Me₂ in the molar ratio 2:1 affords a binuclear complex \{[(Ph₃P)₂Au]₂NS(O)Me₂\}BF₄ of an as yet unknown structure.