Are Tetra[gold(I)]phosphonium Cations [(LAu)₄P]+ Non-obedient to the LeBel-van’t Hoff Rule?

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Recent theoretical studies of the molecular and electronic structure of tetra[(phosphine)gold(I)]-phosphonium cations, [(H₃PAu)₄P]+, gave contradictory results favoring either a classical tetrahedral or a unique square-pyramidal structure of the PAu₄ unit. A tetrahedral structure had previously been confirmed for the corresponding ammonium cations [(Ph₃PAu)₄N]+, while a square-pyramidal structure was discovered for the corresponding arsonium cations [(Ph₃PAu)₄As]+, but there is as yet no unequivocal experimental evidence for the structure of phosphonium cations like [(Ph₃PAu)₄P]+ in an innocent environment. – In this account the structural chemistry of this class of onium salts and related species is reviewed. The data accumulated to date provide virtually compelling evidence that the phosphonium cations should have a ground state with a square pyramidal PAu₄ core unit, provided that no external constraints are imposed. For large central elements (P, As), aurophilic interactions appear to drive the reorganization from tetrahedral to square-pyramidal skeletons in which a maximum number of short Au---Au contacts can be maintained. For the small central element N, similar interactions are already realized in the tetrahedral structure.

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