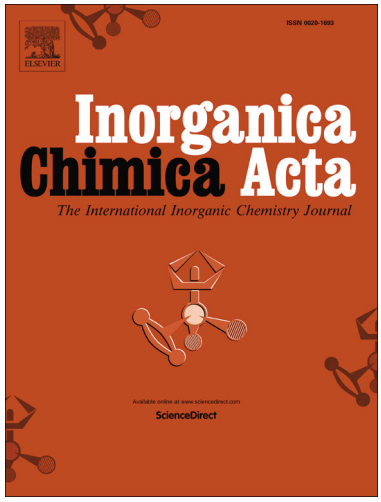

Research paper

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Binuclear Vanadium Dimethylphosphino Carbonyls: Vanadium-Vanadium Multiple Bonds and Four-Electron Donor Carbonyl Groups as Structural Features in Unsaturated Systems

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Abstract

The structures and energetics of the binuclear dimethylphosphido vanadium carbonyls $(Me_2P)_2V_2(CO)_n$ (n = 10, 9, 8, 7, 6) have been examined using density functional theory. The experimentally known $(Me_2P)_2V_2(CO)_8$ with two bridging Me_2P groups and all terminal CO groups is found to be the lowest energy structure by a substantial margin. The predicted V=V distance in this structure of 2.696 Å is close to the experimental distance of 2.733 Å as determined by X-ray crystallography. The Wiberg bond index (WBIs) of 0.94 supports the formulation of this V=V interaction as a formal double bond, consistent with the 18-electron rule. Decarbonylation of $(Me_2P)_2V_2(CO)_8$ is predicted to give a singly CO-bridged $(Me_2P)_2V_2(CO)_6(\mu\text{-CO})$ structure with a shorter V≡V distance of 2.374 Å corresponding to a WBI of 1.30 and suggesting a formal triple bond. Further decarbonylation to $(Me_2P)_2V_2(CO)_6$ is predicted to lead to structures with four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups rather than structures with formal V-V quadruple bond. For the carbonyl-richer system $(Me_2P)_2V_2(CO)_9$ the lowest energy structure retains two bridging Me_2P ligands and all terminal CO groups. Its V–V distance of 3.138 Å coupled with a WBI value of 0.23 suggests the formal single bond required by the 18-electron rule. The lowest energy $(Me_2P)_2V_2(CO)_{10}$ structure has a similar V–V single bond. However, only one of its Me_2P ligands bridges the central V–V bond; the other Me_2P group is a terminal ligand bonded to a single vanadium atom. Structures with intact $Me_2P\text{-}PMe_2$ ligands having direct P–P bonds are very high energy structures relative to their isomers with two separate Me_2P units lacking a direct P–P bond.

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