The microwave spectra of van der Waals complexes of difluoromethane (DFM) and 1,1-difluoroethene (DFE) trifluoroethene (TFE) CH₂F₂ CF₂=CH₂ and CH₂F₂ CF₂=CHF have been observed using a Fourier transform microwave spectrometer from 5 to 19 GHz. The samples of 1% DFM and DFE/TFE in Ar were used to form the complexes in a super sonic expansion. For DFM-DFE, 48 α-type transitions were assigned and 72 α- and β-type transitions were assigned for DFM-TFE. The rotational and centrifugal distortion constants have been determined, leading to the molecular structures of DFM-DFE and DFM-TFE complexes. Both complexes were found to be C₂ symmetry and bound with triple hydrogen bonds: One is the strong F-HC type and two are the weaker CH-F type. Molecular structures of these complexes are, however, quite different from each other. For DFM-DFE, the out-of-plane atoms are two hydrogens which are bonded to a fluorine in DFE and a fluorine in DFM is bonded to a hydrogen in DFE. For DFM-TFE, the out-of-plane atoms are two fluorines which attach to a hydrogen in DFE and a fluorine in DFM is bonded to the hydrogen in the same carbon of DFE. Ab initio MO calculations of MP2/6-311+G(d,p) lebel have supported these experimental results.