Structural re-entrant phase transitions or a series of transitions where there is a sequence of transitions in which earlier and some subsequent phases are effectively identical are exceptionally rare in crystalline materials with very few examples. The temperature dependent phase behaviour of Malonitrile is one of the most studied examples of such behaviour.[1] Using single crystal high pressure X-ray diffraction we report unique pressure induced re-entrant behaviour in tris(µ₂-3,5-diisopropyl-1,2,4-triazolato-N,N')-tri-gold(I).[2] The gold (I) trimer complex is found to undergo multiple phase transitions, 4 in total, before returning to a compressed form of an earlier low pressure phase, a process that may be followed directly from axial diffraction images. In addition to a complete study of the re-entrant behaviour we also report a study into the effect of high pressure on a previously unreported polytype of the same compound that displays drastically different behaviour at high pressure and investigate both materials using high pressure luminescence spectroscopy and cutting edge computational techniques to reveal new insights into the high pressure behaviour of gold (I) complexes and unusual phase transformations.