Initial metal-metal bond breakage detected by fs X-ray scattering in the photolysis of Ru$_3$(CO)$_{12}$ in cyclohexane at 400 nm

Using femtosecond resolution X-ray solution scattering at a free electron laser we were able to directly observe metal-metal bond cleavage upon photolysis at 400 nm of Ru$_3$(CO)$_{12}$, a prototype for the photochemistry of transition metal carbonyls. This leads to the known single intermediate Ru$_3$(CO)$_{11}$(μ-CO)*, with a bridging ligand (μCO) and where the asterisk indicates an open Ru$_3$-ring. This loses a CO ligand on a picosecond time scale yielding a newly observed triple bridge intermediate, Ru$_3$(CO)$_8$(μ-CO)$_3*$, which returns to Ru$_3$(CO)$_{12}$ via the known single-bridge Ru$_3$(CO)$_{10}$(μ-CO). These results indicate that contrary to long standing hypotheses, metal-metal bond breakage is the only chemical reaction immediately following the photolysis of Ru$_3$(CO)$_{12}$ at 400 nm. Combined with previous picosecond resolution X-ray scattering data and time resolved infrared spectroscopy, these results yield a new mechanism for the photolysis of Ru$_3$(CO)$_{12}$.