Reactions of acetylene \((\text{C}_2\text{H}_2)\) with laser-vaporized La atoms produced \(\text{La} (\text{C}_6\text{H}_4)\) and \(\text{La} (\text{C}_{10}\text{H}_8)\) in supersonic molecular beams. The organic fragments in these complexes were benzyne and naphthalene. The benzyne species was produced by the La-mediated cyclotrimerization of three acetylene molecules, whereas naphthalene was formed likely by the cyclization of the transient benzyne with two additional acetylene molecules. These cyclized products were identified by mass-analyzed threshold ionization mass spectroscopy, which measured adiabatic ionization energies and several vibrational frequencies. The measured ionization energies were 40875 (5) cm\(^{-1}\) for \(\text{La} (\text{C}_6\text{H}_4)\) and 36767 (5) cm\(^{-1}\) for \(\text{La} (\text{C}_{10}\text{H}_8)\). The most active vibrational transitions of both complexes were metal-ligand stretching with 326 cm\(^{-1}\) for \(\text{La} (\text{C}_6\text{H}_4)\) and 286 cm\(^{-1}\) for \(\text{La} (\text{C}_{10}\text{H}_8)\). By combining the spectra with theoretical calculations, the ground electronic states of the neutral complexes were determined to be \(2^2\text{A}_1\) \((\text{C}_2\text{v})\) and \(2^2\text{A}'\) \((\text{C}_s)\) and those of the corresponding ions were \(^1\text{A}_1\) \((\text{C}_2\text{v})\) and \(^1\text{A}'\) \((\text{C}_s)\) for \(\text{La} (\text{C}_6\text{H}_4)\) and \(\text{La} (\text{C}_{10}\text{H}_8)\), respectively.