Transition metal bis(arene) sandwich complexes may adopt eclipsed or staggered conformations due to the aromatic ring rotations about the metal-arene axis. In this study, the group VI (Cr, Mo, and W) metal bis(toluene) complexes are synthesized in a laser-ablation molecular beam source, and their rotational conformers are identified by pulsed-field-ionization zero-electron-kinetic-energy (ZEKE) spectroscopy. For Cr-bis(toluene), the ZEKE spectrum shows three distinctive vibrationless (0-0) transitions between the ground electronic states of the neutral and ionic complexes at 42739(5), 42745(5), and 42805(5) cm$^{-1}$, corresponding to ionization energies of 180°, 60°/120°, and 0° rotamers. In addition, the spectrum exhibits metal-toluene bending (164, 180, 196, and 223 cm$^{-1}$) and stretching (278 and 291 cm$^{-1}$) frequencies of these rotamers. The ground electronic states of the 0° and 180° rotamers are $^2A_1 (C_{2v})$ and $^2A_g (C_{2h})$ in the neutral form and $^2A_1 (C_{2v})$ and $^2A_g (C_{2h})$ in the ionized form, respectively. For the 60° and 120° rotamers, the ground states of the neutral molecules are $^1A_1 (C_3)$, and those of the corresponding ions are $^2A (C_2)$. Through the variation of the molecular beam conditions, the eclipsed conformer (0°) is determined to be more stable than the staggered ones (180°, 120°, and 60°). Similarly, multiple conformers are identified for the Mo and W complexes.

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