ROTATIONAL CONFORMERS OF GROUP VI (Cr, Mo, and W) METAL BIS(TOLUENE) $SANDWICH$ COMPLEXES

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Transition metal bis(arene) sandwich complexes may adopt eclipsed or staggered conformations due to the aromatic ring rotations about the metal-arene axis.[a,b] 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 $^1A_1$ (C_{2v}) and ^1A_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 (C_2), 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.

[a] B.S. Sohnlein, S. Li, and D.S. Yang, J. Chem. Phys. 123, 214306 (2005); B.S. Sohnlein and D.S. Yang, J. Chem. Phys. 124, 134305 (2006)

[b] S.Y. Ketkov, H.L. Sezle, and F.G.N. Cloke, Angew. Chem. Int. Ed. 46, 7072 (2007) and references therein.