Rhodium-Catalyzed Directed Halogenation of \( \pi \)-Excessive Heterocycles

**Significance:** The bromination and iodination of \( \pi \)-excessive heterocycles 1 under directed rhodium(III) catalysis is reported. The reaction provides an orthogonal approach to electrophilic halogenation, overriding the inherent reactivity of the starting materials. Additionally, the method is complementary to directed *ortho* metalation, which can afford similar products (2 and 3) without the need for a heavy metal catalyst, but under strongly basic conditions (e.g., see: E. G. Doedt, V. Snieckus *Tetrahedron Lett.* 1985, 26, 1149). Bis-halogenated products 3 were also obtained from compounds 2 in a one-pot process by addition of a second equivalent of the electrophile. The reaction was reported to proceed efficiently under air and without special precautions to exclude moisture.

**Comment:** The scope and functional group tolerance of the reported reaction were demonstrated to be broad, with a range of substituted five- and six-membered heterocycles being demonstrated. However, the viability of directing groups other than dialkyl amides would have provided welcome generality. Kinetic studies demonstrated a dual role for the rhodium(III) catalyst, whereby it additionally functions to suppress the inherent reactivity of the heterocycle. AgSbF₆ was also observed to suppress the innate reactivity, and in its presence, the catalyst loading could be decreased to 0.1%. Additional mechanistic evidence showed that C–H bond activation is turnover limiting but electrophilic aromatic substitution and concerted *metalation–deprotonation* mechanisms could not be distinguished.

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