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EFFICIENT CYCLOPROPANATION AND INTERMOLECULAR C-H BOND ACTIVATION VIA CARBENE INSERTION CATALYSED BY THIOSEMICARBAZONE COPPER COMPLEXES.

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Cyclopropane derivatives are an important family of chemical compounds that plays a prominent role in organic chemistry.<sup>1</sup> As a result, great efforts have been made to develop efficient methods for their synthesis.<sup>2</sup> A particularly versatile method is the metal-catalysed cyclopropanation of olefins with diazo compounds, for which several efficient homogeneous catalysts have been developed. We have recently reported that Schiff bases derived from the condensation of hydrazinecarbothioamide or phenyl thiosemicarbazone with 3-acetyl-2H-chromen-2-one are suitable ligands for the synthesis of copper(II) complexes very active as cyclopropanation catalysts.<sup>3</sup> We herein report that Schiff bases derived from the condensation reaction of hydrazinecarbothioamide with substituted salicylaldehydes are suitable ligands for copper and that the derived complexes are competent catalysts for the cyclopropanation of olefins and for the intermolecular C-H bond activation by using ethyldiazoacetate (EDA) as carbene source. Different ligands have been synthesized and characterized. Their copper complexes have been prepared by employing Cu(II) acetate, but analytical and spectroscopical data for the isolated complexes revealed that in most cases a reduction to copper (I) occurred. Cyclopropanation reactions of several olefins by EDA in the presence of catalytic amounts of the complexes were examined. Cyclopropanes were obtained in high yields (up to 97 %, TON up to 18,400) with moderate to excellent diastereoselectivities (up to >99%). The catalytic capabilities of this copper-based system has also been tested toward the activation of cycloalkanes and cyclic ethers and we have found moderate-to-good degrees of conversion.

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