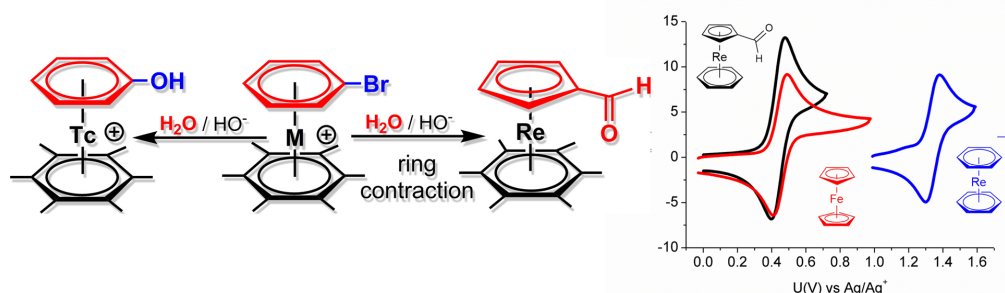


## A Mixed-Ring Sandwich Complex from Unexpected Ring Contraction in [Re( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Br)( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)](PF<sub>6</sub>)

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[M(arene)<sub>2</sub>]<sup>+</sup>-type complexes (M = Re, <sup>99(m)</sup>Tc) of rhenium and technetium came recently into the focus of our attention since their homologous metal complexes are an established matched-pair for radio diagnosis and (radio)therapy. Hence, the synthesis of [Re(arene)<sub>2</sub>]<sup>+</sup> type complexes was optimized and an efficient and applicable one-step synthesis for [<sup>99(m)</sup>Tc(arene)<sub>2</sub>]<sup>+</sup> compounds was developed.<sup>1,2</sup> Furthermore, novel synthetic pathways for the functionalization of this basic class of organometallic complexes was developed, which led to a variety of mono- and di-functionalized [Re(C<sub>6</sub>H<sub>5</sub>R)(C<sub>6</sub>H<sub>6-n</sub>R<sub>n</sub>)]<sup>+</sup> compounds (R = -COOH, -Br, -Cl, -F, -COC<sub>2</sub>H<sub>5</sub>, -CH(OH)Ph, -C(OH)Ph<sub>2</sub>). This type of complexes can be used as scaffolds in medicinal chemistry.<sup>3</sup> In contrast, the synthesis of mixed-ring sandwich complexes of Re<sup>I</sup> or Tc<sup>I</sup> is poorly reported in the literature. We report here on the conversion of a bromo-benzene, coordinated to a Re(I) center, into a cyclopentadienyl aldehyde [Re( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CHO)( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)] (R = -H, -CH<sub>3</sub>) under strong alkaline condition and in quantitative yield whereas the phenol complex of Re and <sup>99</sup>Tc was achieved under mild alkaline condition.<sup>4</sup> Such a ring contraction is unprecedented so far. We elucidated the mechanism of this reaction with <sup>1</sup>H and <sup>2</sup>H NMR and support the reaction path with DFT calculations. Following this strategy, new classes of organometallic compounds can be synthesized with high potential for therapeutic and diagnostic applications (inorganic drugs), in the future.



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