Mechanistic Insights in Transition-Metal Catalyzed Cross-Coupling Reactions

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Transition-metal catalyzed cross-coupling reactions have revolutionized organic synthesis. Although palladium still is the most commonly applied catalyst, the use of earth-abundant 3d metals is highly advantageous for economic reasons. Currently, the rational development of 3d-metal catalyzed cross-coupling reactions is severely hampered by a lack of mechanistic understanding, however. To change this situation and to obtain insight into these reactions at the molecular level, we analyze reaction mixtures by electrospray-ionization mass spectrometry. Thus, we have been able to identify a series of elusive catalytic intermediates in iron-, cobalt, and copper-mediated cross-coupling reactions (Figure 1).[1,2] Gas-phase experiments on the mass-selected intermediates moreover reveal their microscopic reactivity and permit the direct observation of important elementary steps of the catalytic cycles.[1,2]

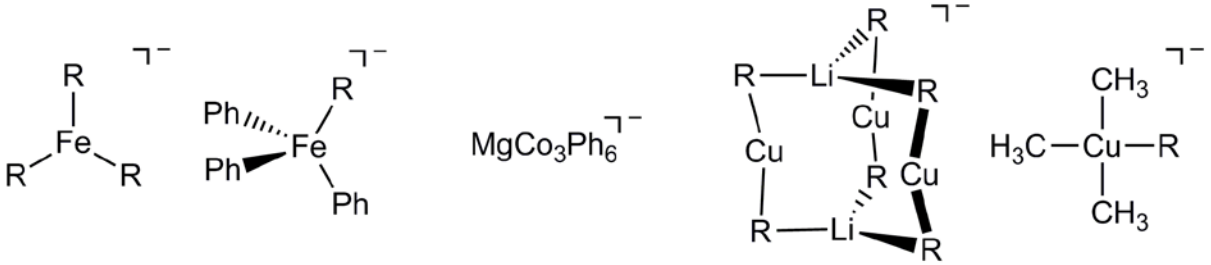

Figure 1. *Selected intermediates of 3d-metal-mediated cross-coupling reactions detected by ESI mass spectrometry.*

1. Putau, A.; Brand, H.; Koszinowski, K. *J. Am. Chem. Soc*. **2012**, *134*, 613-622.
2. Böck, K.; Feil, J. E.; Karaghiosoff, K.; Koszinowski, K. *Chem. Eur. J*. **2015**, *21*, 5548-5560.