

OVERCOMING THE STERIC LIMITATIONS OF THE ALKYNE/VINYLDENE REARRANGEMENT

Marcus Korb

The University of Western Australia, School of Molecular Sciences, 35 Stirling Hwy,
6009 Perth, Western Australia, Australia

16 Valence electron half-sandwich complexes of type $[M(dppe)Cp]^+$ ($M = Fe, Ru$) are known for their ability to coordinate and activate functional groups, including nitro (NO_2)¹ and internal alkyne functionalities ($Ar-C\equiv C-Ar'$, **2**).² Those reactive intermediates can be prepared *in situ* from their parent chloride complexes **1** upon halide abstraction (Figure 1). Their reaction with, for example, internal alkynes results in geminal vinylidene complexes of type $[M\{=C=C(Ar)(Ar')\}(dppe)Cp]^+$ (**3**) for which a migration of one of the substituents Ar/Ar' along the unsaturated bond is required.

The kinetics of this process and the impact of either electron donating or withdrawing groups in case of $Ar = Ph$ are well investigated,² and additional donor functionalities,³ such as amines, allow for the synthesis of indole derivatives in a catalytic manner.³ However, those examples are limited to substituents in which steric effects of additional groups are minimized. Furthermore, rearrangement processes at bisalkynes were not investigated until recently by our group.⁴ Herein, the scope of the alkyne/vinylidene rearrangement is extended to sterically hindered alkynes, as well as bisalkynes of various substitution pattern, resulting in homo-bi- and hetero-tetra-metallic organometallic vinylidene complexes. Their properties, solid-state structures and redox properties ($Ar/Ar' = ferrocenyl$) will be discussed. For $M = Fe$, the competition between the vinylidene rearrangement and an iron-mediated nitro/nitroso reduction will be discussed for appropriate bifunctional substrates. Those improvements extend the applicability for catalytic

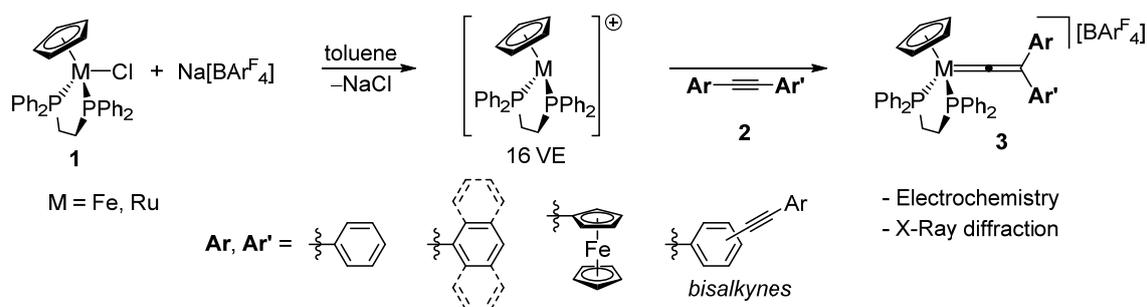


Figure 1. Formation of 16 Valence Electron complexes from half-sandwich chlorides **1** and their activation of internal alkynes **2** into bisarylvinylidene complexes **3**.

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[2] Y. Mutoh, Y. Ikeda, Y. Kimura, Y. Ishii, *Chem. Lett.*, **2009**, *38*, 534–535.

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[4] M. Korb, S. A. Moggach, P. J. Low, *Chem. Commun.* **2021**, *57*, 4251–4254.