IL-01

Neutral *vs* Cationic Electron-Withdrawing Substituents at P Centers: Expected *vs* Unforeseen Effects

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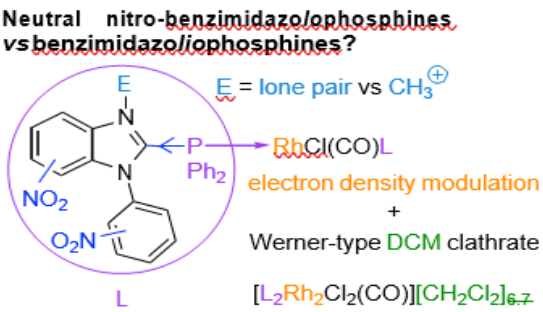
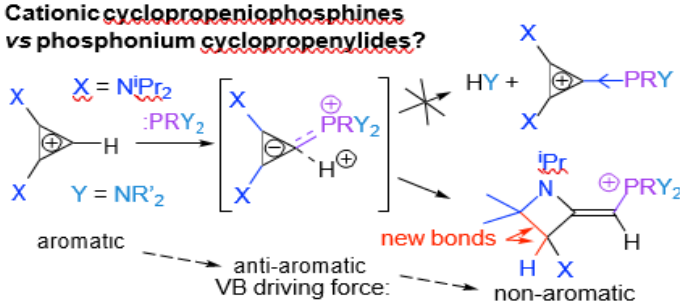
More or less electron-deficient P(III) centers preserving a stable coordination ability while allowing modulation of the electron density at transition metal centers, attracts attention from applied or fundamental viewpoints, regarding the development of specific catalytic processes [1] or analysis of the basic nature of the dative bond [2], respectively.

The case of "extreme" electron-deficiency is achieved by P-conjugation with a cationic substituent, such as an imidazolium or a cyclopropenium fragment, in the so-called α-cationic phosphines (or carbeniophosphanes) [3], where the P atom acquires a phosphenium character with strong π-back-bonding ability [4]. Comparison with neutral isosteres will be addressed through the nitro-benzimidazolophosphine series (Scheme 1) [5], while the search for an access to cyclopropenio-α-aminophosphines, with balanced electron-deficiency, led to the observation of an unprecedented 3→4 ring expansion process (Scheme 2) [6].



Scheme1



Scheme 2

References

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