2,4,6-Triphenylpyridinium: A Bulky, Highly Electron-Withdrawing Substituent Which Enhances Properties of Nickel(II) Ethylene Polymerization Catalysts

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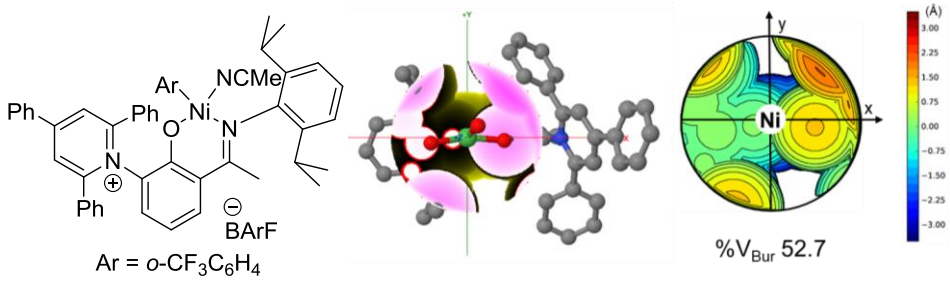
The reactivity of Ni(II) and Pd(II) olefin polymerization catalysts can be enhanced by introduction of electron-withdrawing substituents on the supporting ligands rendering the metal centers more electrophilic. Reported here is a comparison of ethylene polymerization activity of a classical salicyliminato nickel catalyst substituted with the powerful electron-withdrawing 2,4,6-triphenylpyridinium (trippy) group to its' $-CF_3$ analog. The trippy substituent is substantially more electron-withdrawing (σ_{meta} = 0.63) than the trifluoromethyl group (σ_{meta} = 0.43) which results in a ca. 8-fold increase in catalytic turnover frequency. An additional advantage of trippy is its' high steric bulk relative to the trifluoromethyl group. This feature results in a four-fold increase in polymer molecular weight due to enhanced retardation of chain transfer. A significant increase in catalyst lifetime is observed as well.



Salicylketiminato nickel catalyst used in this study, steric map and buried volume ($\%V_{Bur}$).