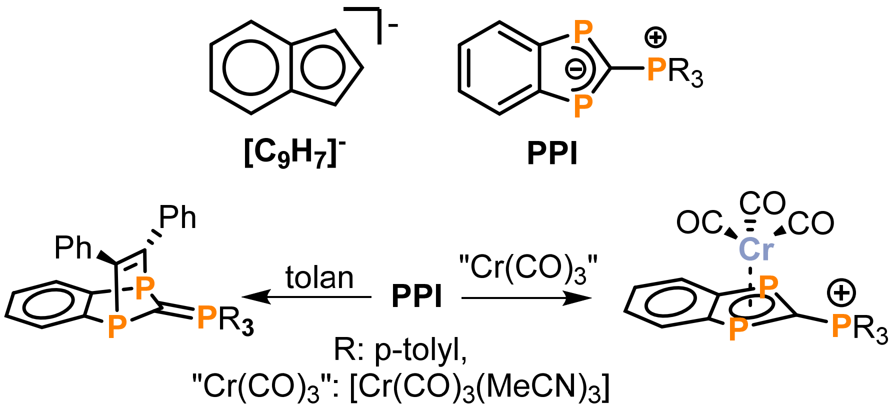
PHOSPHONIUM-SUBSTITUTED DIPHOSPHAINDENYLIDE (PPI): EELECTRONIC STRUCTURE AND LIGAND PROPERTIES

Peter Coburger[a], Clara Schweinzer[b] and Moritz Scharnhölz[b]

[a]Department of Chemistry, Technical University of Munich, Garching, Germany
[b]Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland

The cyclopentadienide anion, $[C_5H_5]^-$, is an ubiquitous ligand in organometallic chemistry with widespread applications in coordination chemistry and catalysis. Complexes of the indenyl anion $[C_9H_7]^-$, the benzannulated derivative of $[C_5H_5]^-$, often show distinctively different properties and reactivities (Scheme 1a).[1] This is attributed to the "indenyl effect" which promotes facile $\eta^5 \rightarrow \eta^3$ hapticity changes.[2] An additional conceivable way to further alter the electronic structure and thus the properties of indenyl complexes is the introduction of endo-cyclic heteroatoms into the five-membered ring of $[C_9H_7]^-$. However, although a number of such formal derivatives exist, their coordination chemistry is largely unexplored.

To close this apparent gap, we here introduce the ylide PPI (Scheme 1). This zwitterionic heterocycle shows a small, but noticeable biradical character as evident from the reaction with diphenyl acetylene (tolan). The even more intriguing ligand properties are discussed on the basis of the complex $[Cr(CO)_3(\eta^5\text{-PPI})]$ (Scheme 1).



Scheme 1. top: indenyl anion and **PPI**; bottom: reactivity of **PPI** towards tolan and chromium tricarbonyl synthons.

---

[1] B. M. Trost, M. C. Ryan, *Angew. Chem. Int. Ed.* **2017**, *56*, 2862–2879.

[2] M. J. Calhorda, C. C. Romão, L. F. Veiros, *Chem. – Eur. J.* **2002**, *8*, 868–875.