

A radical mechanism for the addition of bromoalkanes to $[P(\mu\text{-N}Ter)]_2$ and synthesis of a novel P-centered persistent radical

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According to the IUPAC definition biradicals are molecular entities with an even number of electrons with two (possibly delocalized) radical centres which act nearly independently of each other.^[1] They may show a radical reactivity but can also react in a similar way as closed-shell molecules.^[2] So far, for the biradical $[P(\mu\text{-N}Ter)]_2$, first synthesized in our group in 2011, only concerted reactions and insertions into the N_2P_2 four-membered ring have been observed.^{[3],[4]}

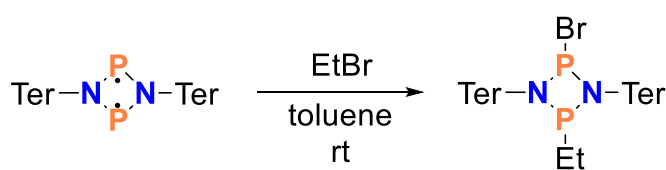


Figure 1: Addition of bromoalkanes to $[P(\mu\text{-N}Ter)]_2$.

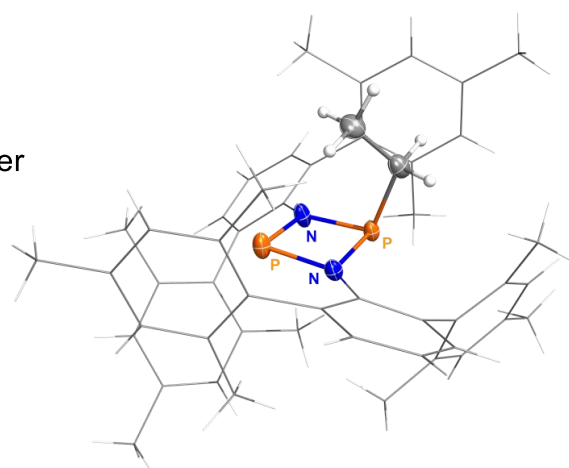


Figure 2: Structure of the novel P-centered persistent radical as determined by single crystal X-ray diffraction.

In this study we present proof for a radical mechanism during the addition of bromoalkanes to $[P(\mu\text{-N}Ter)]_2$ as well as report the synthesis and isolation of a novel persistent phosphorus-centered radical.

This radical was successfully identified as the radical intermediate of the bromoalkane addition to $[P(\mu\text{-N}Ter)]_2$ using EPR-spectroscopy and single crystal X-ray diffraction.

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- [4] A. Hinz, A. Schulz, *Phosphorus, Sulfur Silicon Relat. Elem.* **2016**, *191*, 578–581.