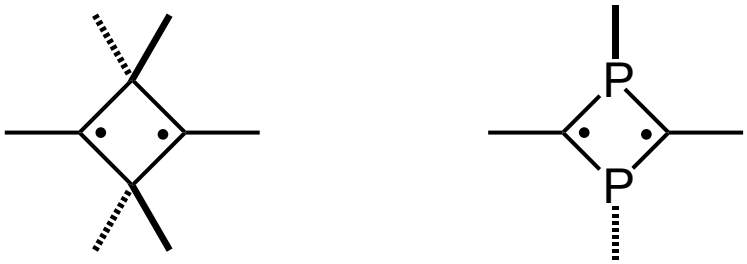
Stable Localized Biradicals



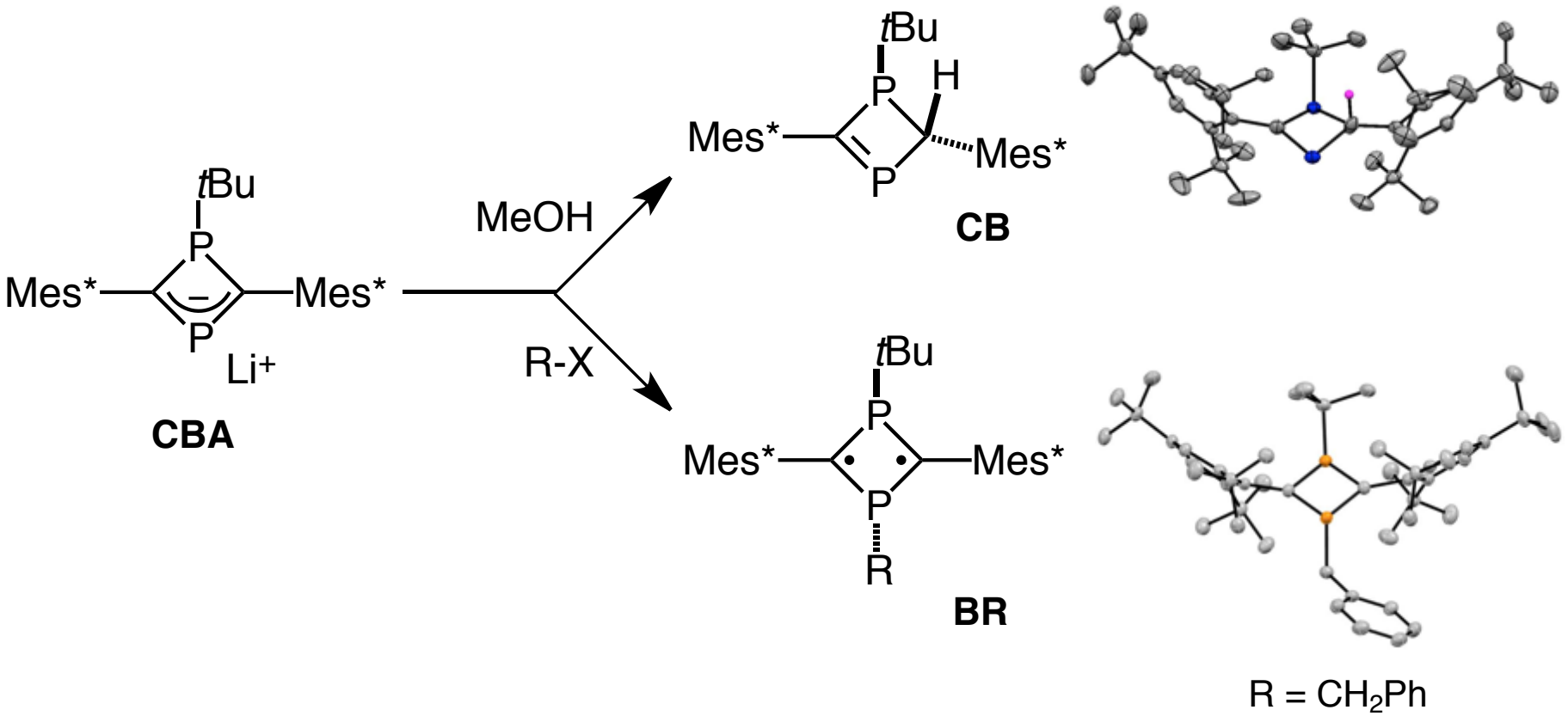
A **B**

Whereas cyclobutane-1,3-diyl **A** is quite reactive even at low temperatures, the heavier congener **B** exhibits considerable thermal stability (Niecke 1995) due to "phosphorus trick" leading to singlet ground state. We found that suitable positioning of the substituents effectively stabilize the exotic open-shell P-heterocycle **B** even in air (*ANIE* 2003). The high stability has promoted further investigations in relation to applications based on electronic functionalities. So far studies on the air-stable **B** have revealed high electron-donating properties as well as considerable stability of the resulting cationic species. The procedures for **B** are suitable to install various substituents on the phosphorus, and the electronic properties of **B** can be widely tuned. Furthermore, the synthetic protocol of the air stable **B** can be appropriable for synthesis of air-tolerant P-heterocyclic monoradicals. Quite recently, we established procedures for exchanging the RP moiety of the biradical system.

S. Ito, *Tetrahedron Lett.* **2018**, *59*, 1–13. *Link*

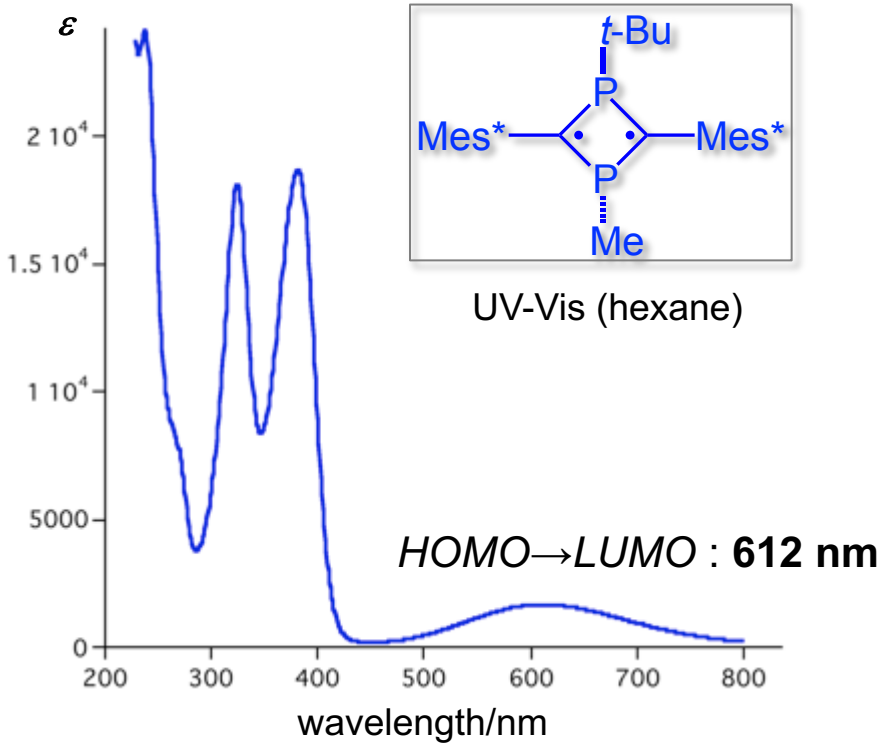
S. Ito, *Chem. Rec.* **2018**, *18*, 445–458. *Link*

Ambident Character of Cyclobutenylanion (CBA)



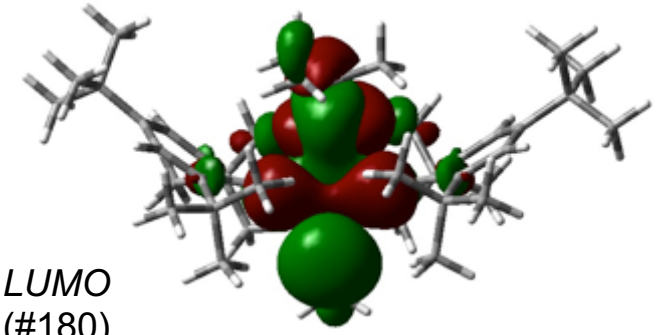
CB: S. Ito, H. Sugiyama, M. Yoshifuji, *Chem. Commun.* **2002**, 1744.
S. Ito, T. T. T. Ngo, K. Mikami, *Chem. Asian J.* **2013**, *8*, 1976.
BR: H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem. Int. Ed.* **2003**, *42*, 3802. (R = Me)
M. Yoshifuji, H. Sugiyama, S. Ito, *J. Organomet. Chem.* **2005**, *690*, 2515. (R = benzyl)

Molecular Orbital: Tunable

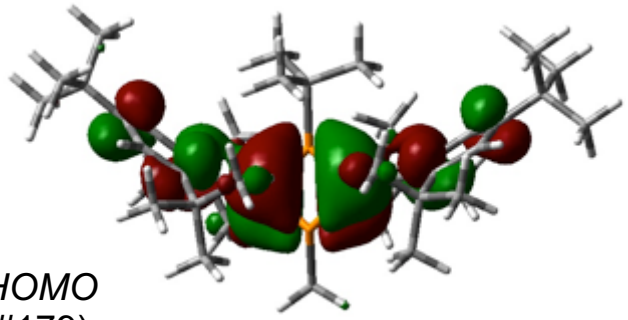


UV-Vis (hexane)

HOMO→LUMO : **612 nm**

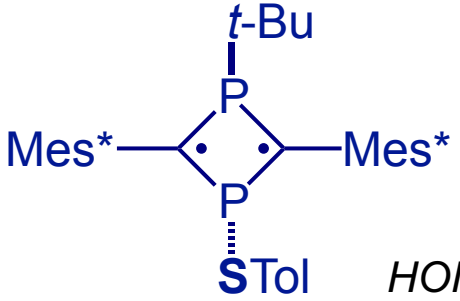


LUMO
(#180)

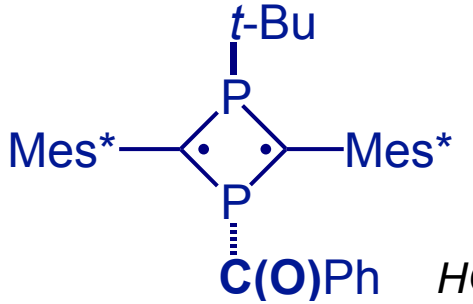


HOMO
(#179)

M06-2X/6-31G(d)



HOMO→LUMO
643 nm

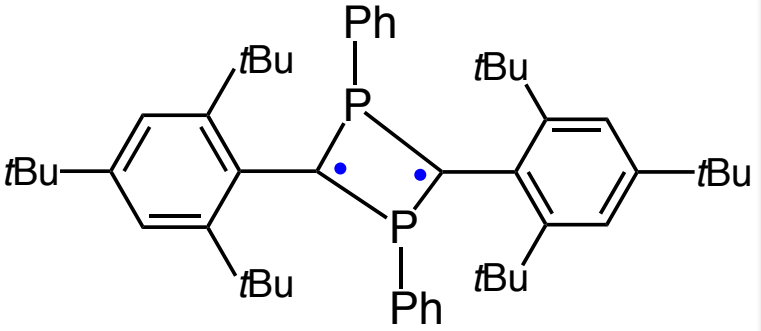


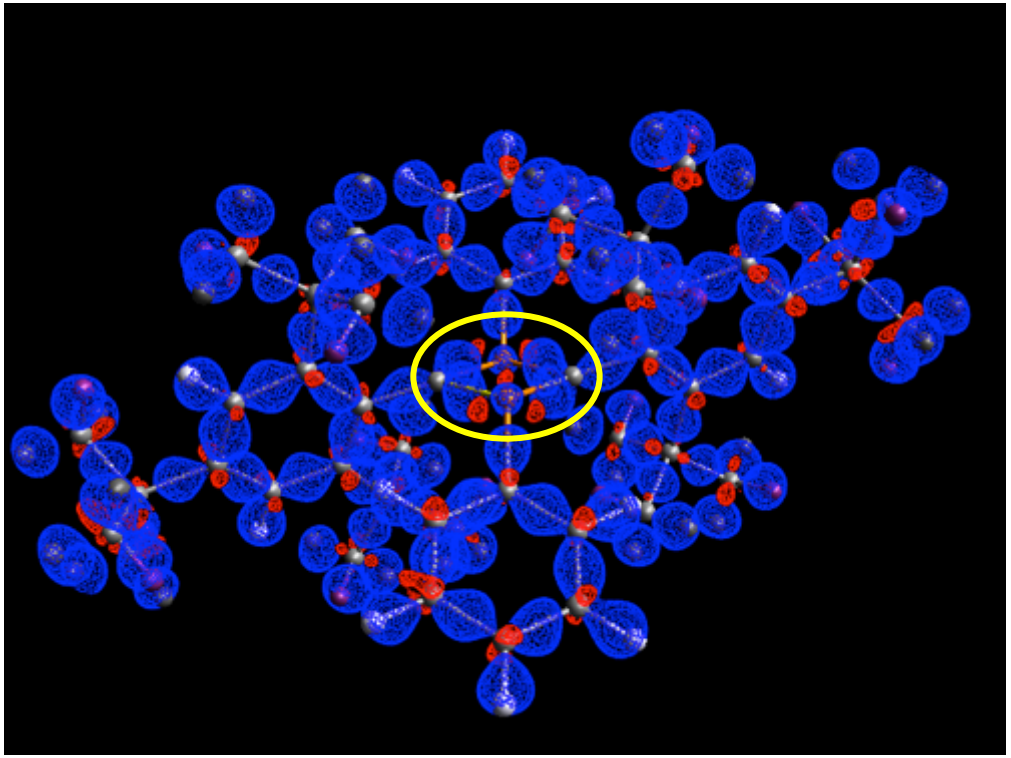
HOMO→LUMO
664 nm

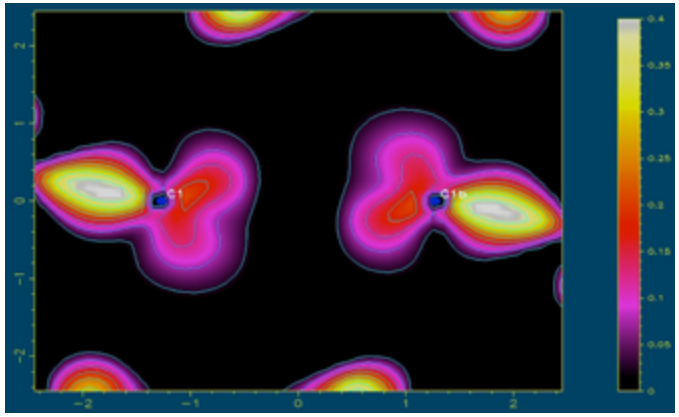
See also: https://pubs.acs.org/doi/10.1021/acs.joc.0c00512

Electron Density Analysis

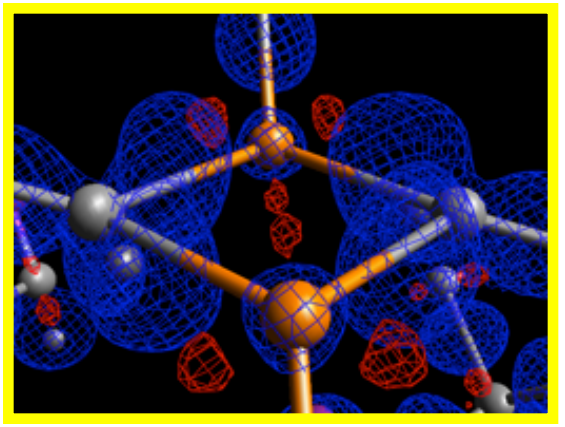
Localized Radicalic Electrons



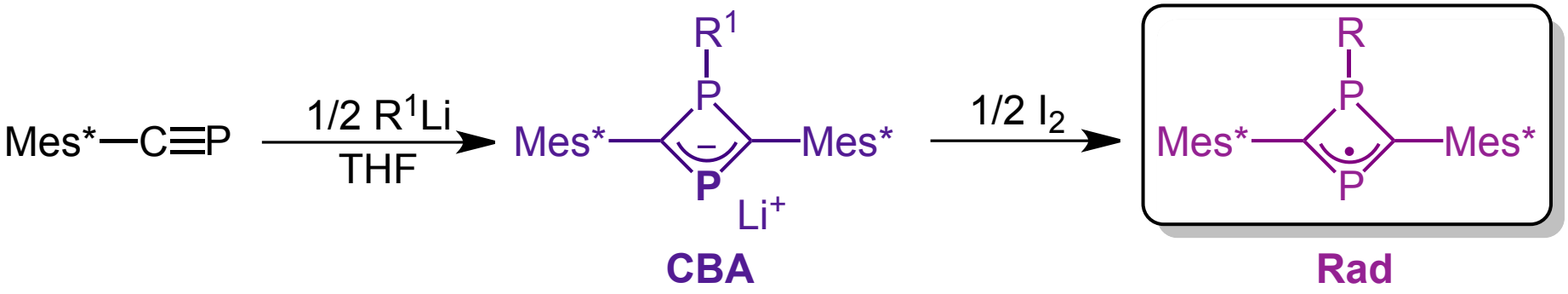


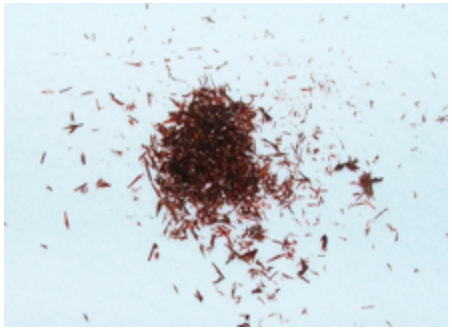


Cross section of the PCPC plane

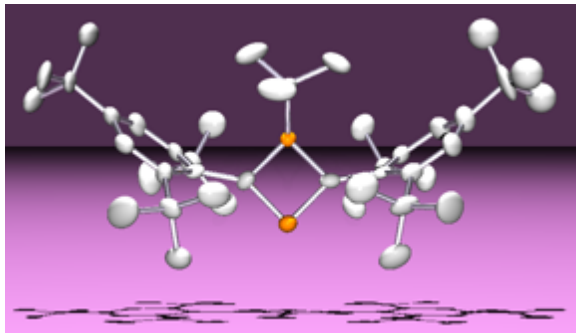


Stable Monoradical (Rad) from Cyclobutenylanion (CBA)

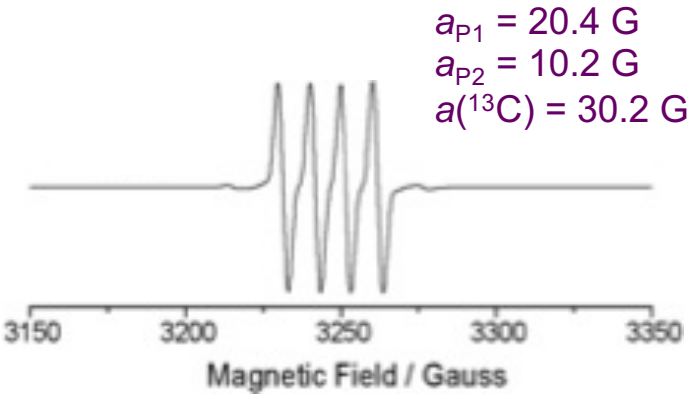




Air-Tolerant Crystals

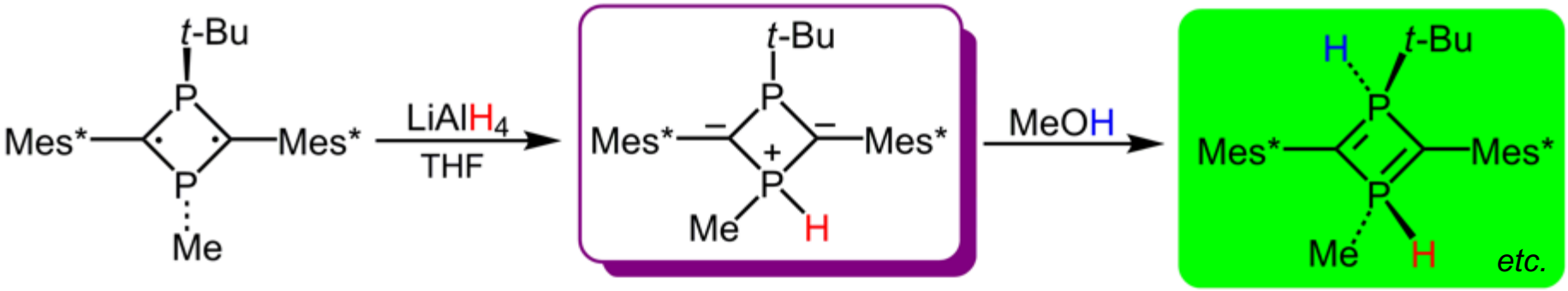


X-ray Characterization



EPR Spectrum

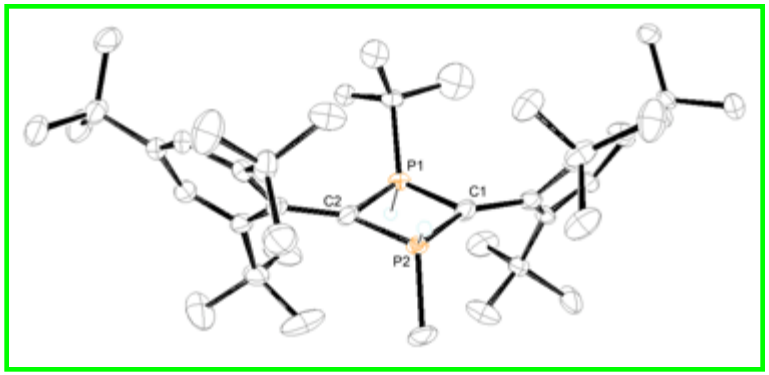
Biradical Bites H_2



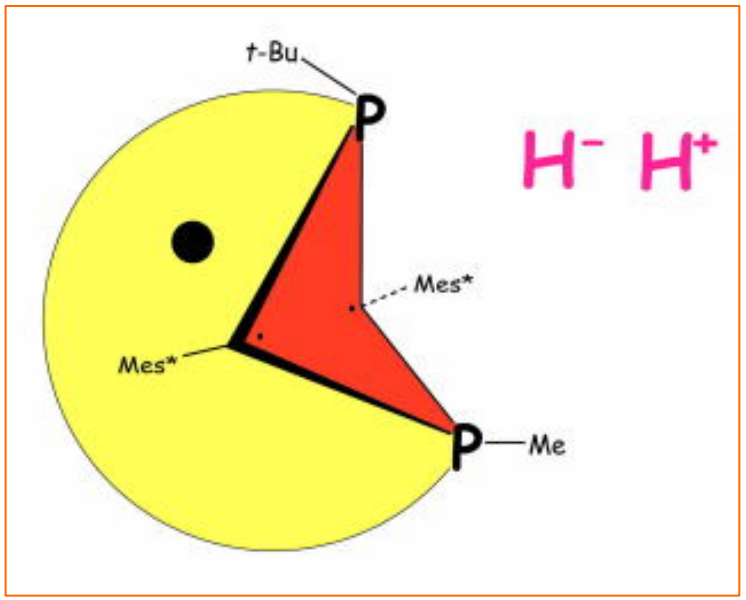
δ_P = –11.3 (MeP), 55.9 (*t*-BuP)
$^2J_{PP}$ = 362.8 Hz

δ_P = –37.1 (MeP), 143.8 (*t*-BuP)
$^2J_{PP}$ = 49.6 Hz
$^1J_{PH}$ = 321.1 Hz, $^2J_{PH}$ = 9.9 Hz

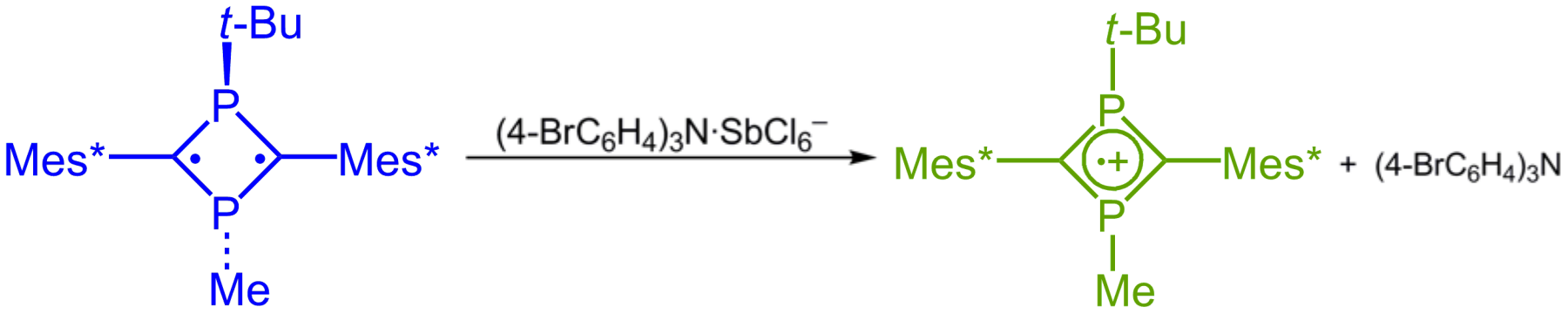
δ_P = 3.3 (MeP), 47.1 (*t*-BuP)
$^2J_{PP}$ = 91.7 Hz



Inorg. Chem. **2009**, *48*, 8063.

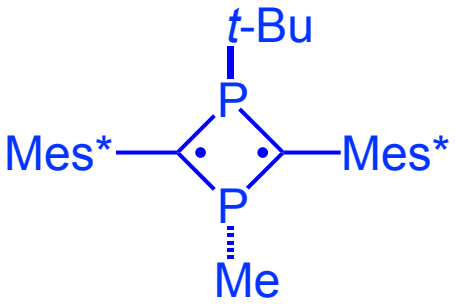


BR for Electronics



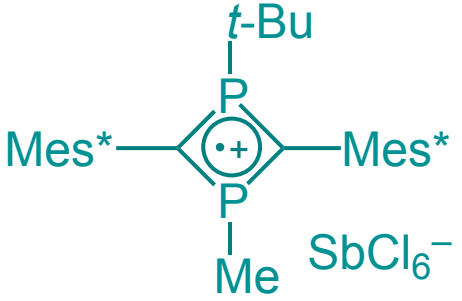
The air-stable phosphorus congener of cyclobutane-1,3-diyl shows highly electron-donating property (= low oxidation potential) and considerable stability of the corresponding radical cation (*Chem. Lett.* 2006). Therefore, the open-shell singlet P-heterocycle would be available as a p-type organic semiconductor. As predicted, several stable derivatives worked as Field-Effect Transistors (FETs) via hole transfer under the relatively low gate (threshold) voltage. The facile generation holes would correspond to the open-shell character.

Biradicals (BR) as Electron-Donors



BAHA (Magic Blue)

CH_2Cl_2



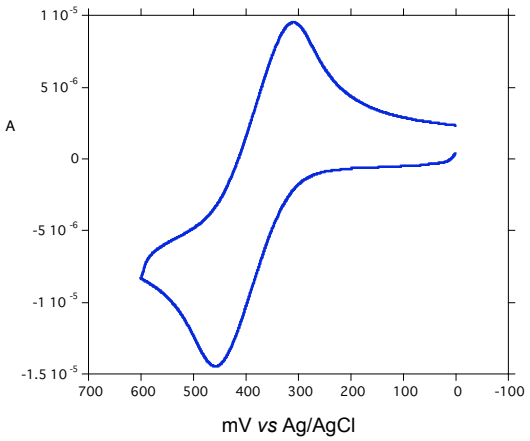
BAHA = $(4\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$

$E_{1/2}^{ox}$ = +0.35 V
vs. Ag/AgCl

a_{P1} = 39.5 G
a_{P2} = 22.3 G
$a(^{13}C)$ = 30 G

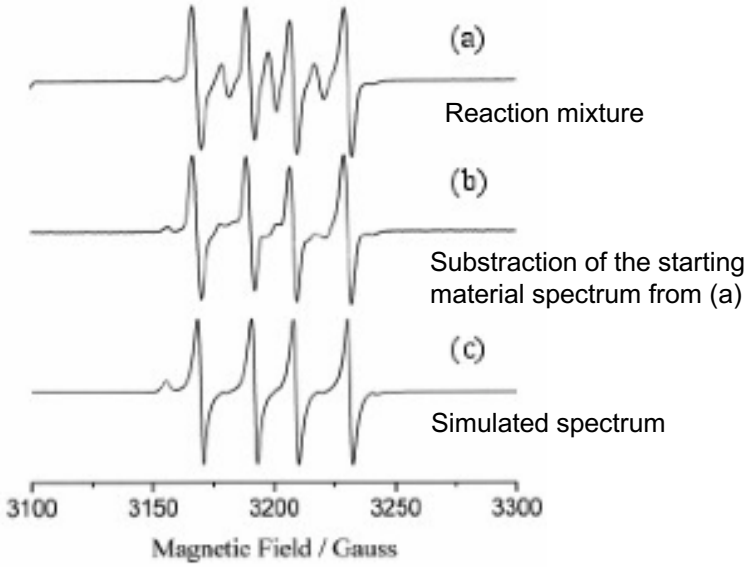
Chem. Lett. **2006**

Cyclic Voltammetry

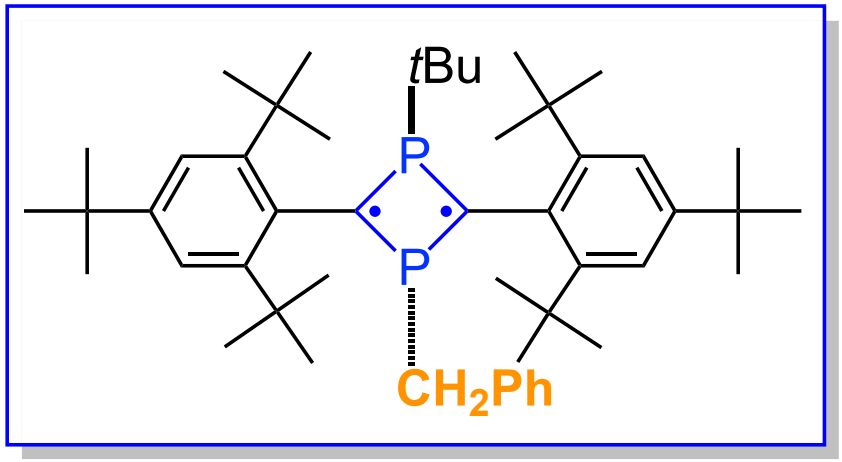


EPR spectrum

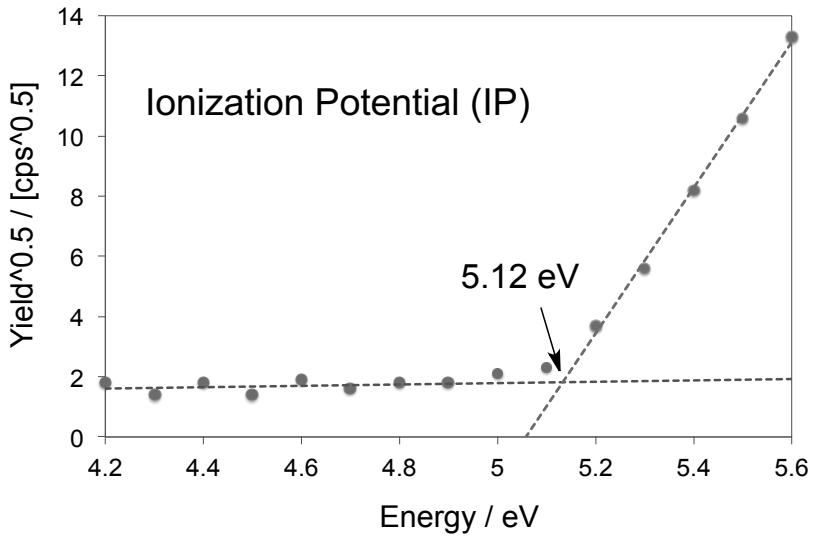
g = 2.0025



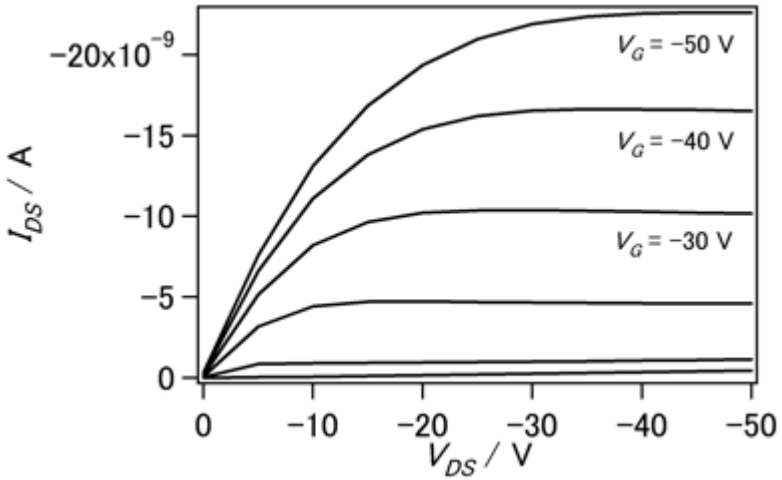
p-Type OFET Property



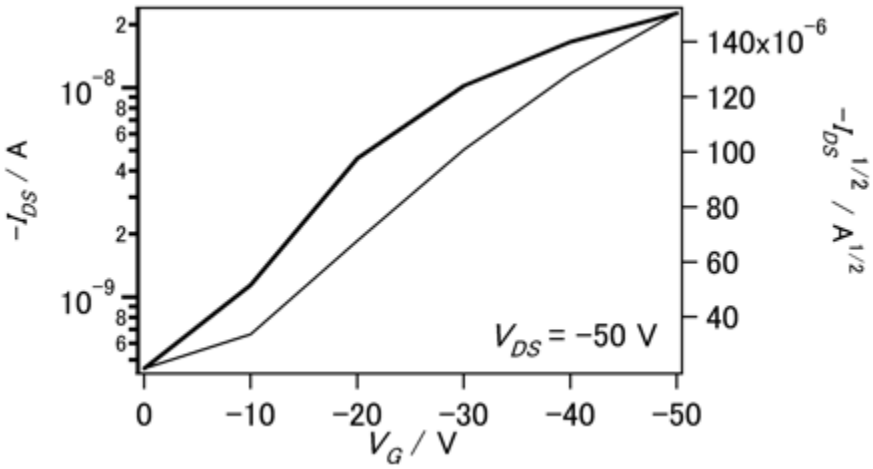
μ = 1.67x10^{-7} cm^{2}V^{-1}s^{-1}
on/off = 70
V_{th} = –0.1 V



Output

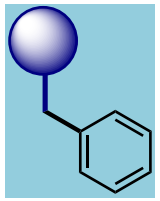


Transfer



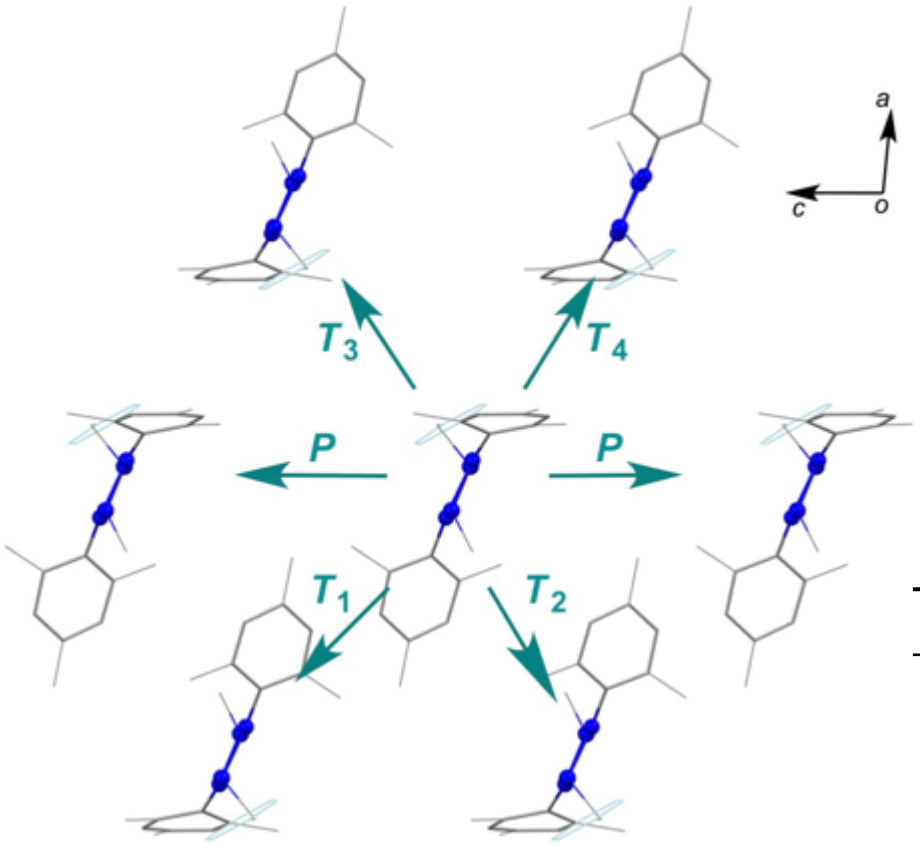
Hole Transfer: Hopping Model

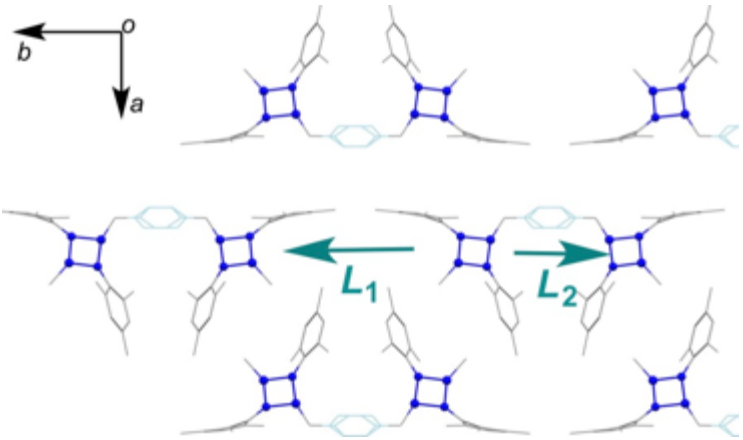
Searching Valuable Hole Coupling Matrix Element



1.67×10^{-7} $cm^2V^{-1}s^{-1}$

JACS 2013





$D_{est} = 3.8 \times 10^{-6}$ cm^2 s^{-1}

$\mu_{est} = 1.5 \times 10^{-4}$ cm^2 V^{-1} s^{-1}

Dimer	V / meV	W / s^{-1}	r / Å
T_1	1.44	24.8×10^8	11.371
T_2	0.69	5.7×10^8	9.552
T_3	1.48	26.2×10^8	10.740
T_4	1.09	14.2×10^8	10.831
P	0.84	8.5×10^8	10.908
L_1	0.41	2.0×10^8	15.209
L_2	0.32	1.2×10^8	10.573