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Phosphavinylidene-Carbenoids [P]=C(Li)X (X = Br, Cl, F): Structure and Dynamics

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Phosphavinylidene-Carbenoids [P]=C(Li)X (X = Br, Cl, F): Structure and Dynamics

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The extraordinary reactivity of carbenoids towards electrophilic as well as nucleophilic reagents awards them for a central importance in organic chemistry. Their unusual bonding situation has been the subject of several theoretical studies¹. Having shown in previous reports² that phosphoranyl carbenoids are significantly stabilized by incorporation of the carbenoid center in delocalized π -systems, we succeeded in isolating the first stable bromo, chloro and fluoro-lithio carbenoids **2a-c.**

$$(Me_3Si)_2C$$

$$Mes^*$$

$$Y$$

$$\frac{nBuLi}{-78^{\circ}C}$$

$$Mes^*$$

$$Mes^*$$

$$Li(thf)_3$$

$$a: X = Br; Y = Br$$

$$b: X = Cl; Y = Cl$$

$$c: X = F; Y = Cl$$

Carbenoids 2a-c were fully characterized including multinuclear NMR-studies and X-ray analyses. They show an increased thermal stability up to -10 °C due to the incorporation into the bis(ylene)phosphorane system. To our best knowledge 2a represents the first stable crystalline lithio-bromo-carbenoid and 2c the first ever fully characterized lithio-fluoro-carbenoid. The isolation of the latter had been considered impossible for a long time due to the very high tendency to extrude LiF to give the corresponding carbene.

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