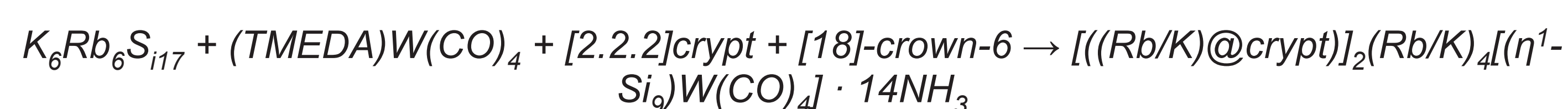


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Homo- or heteroatomic polyanionic clusters of main group metals and semimetals, so called Zintl anions, have been topic of interest ever since their discovery.^[1] Through solid state synthesis of the alkali metal phases and subsequent solution in liquid ammonia, the polyanions can be synthesized and isolated.^[2] A way to modify these polyanions is the functionalization with transition metal complexes. The most recent developments are the reactions with homo- and heteroleptic group six carbonyl complexes and *N*-heterocyclic carbene (NHC) transition metal complexes which show a wide range of resulting clusters.^[3,4] The reactions

with silicon polyanions particularly hold challenges due to their, compared to the other group 14 Zintl clusters, even stronger sensitivity to water and air, and they also can only be handled in liquid ammonia. Because of these problems in the synthesis there are only a few functionalized clusters known, but these show very interesting structure motives. Through the reaction of $K_6Rb_6Si_{17}$ with $(tmeda)W(CO)_4$ (*tmeda* = *N,N,N',N'*-Tetramethylethylenediamin) the first silicide carbonylate complex could be synthesized. The complex $[(Rb/K)@crypt)_2(Rb/K)_4(\eta^1-Si_9)W(CO)_4] \cdot 14NH_3$ was analyzed by single crystal X-ray diffractometry.

Synthesis of $[(Rb/K)@crypt)_2(Rb/K)_4(\eta^1-Si_9)W(CO)_4] \cdot 14NH_3$

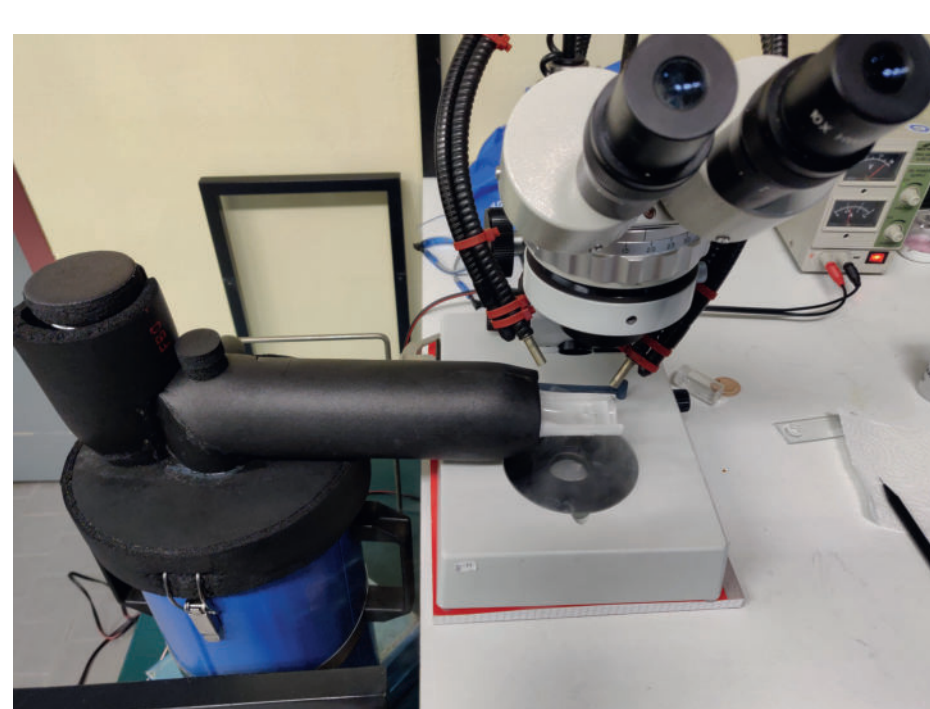
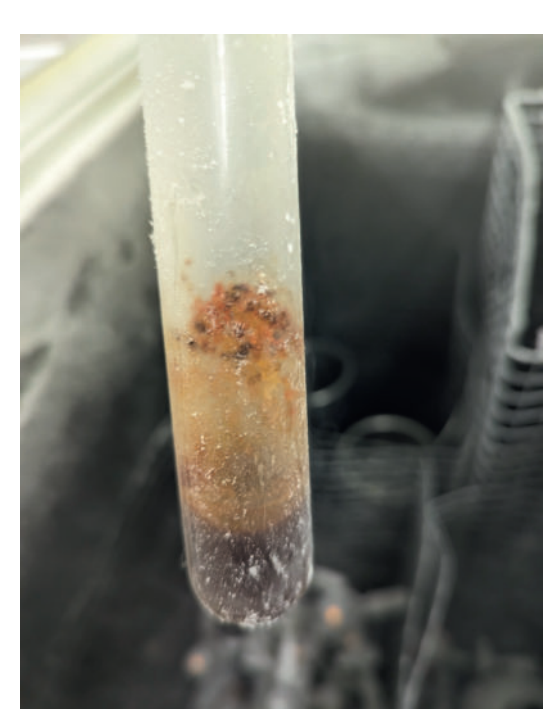
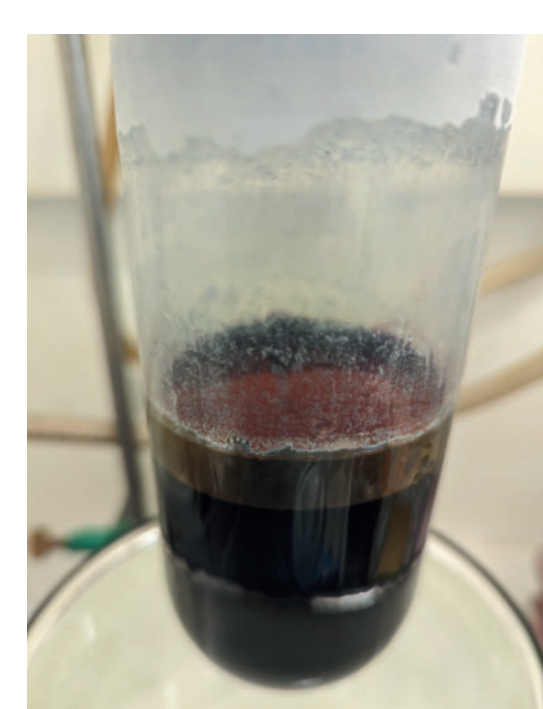


Dried liquid ammonia

Stored for three months at $-70^\circ C$

Picking under cold nitrogen stream

X-ray diffraction

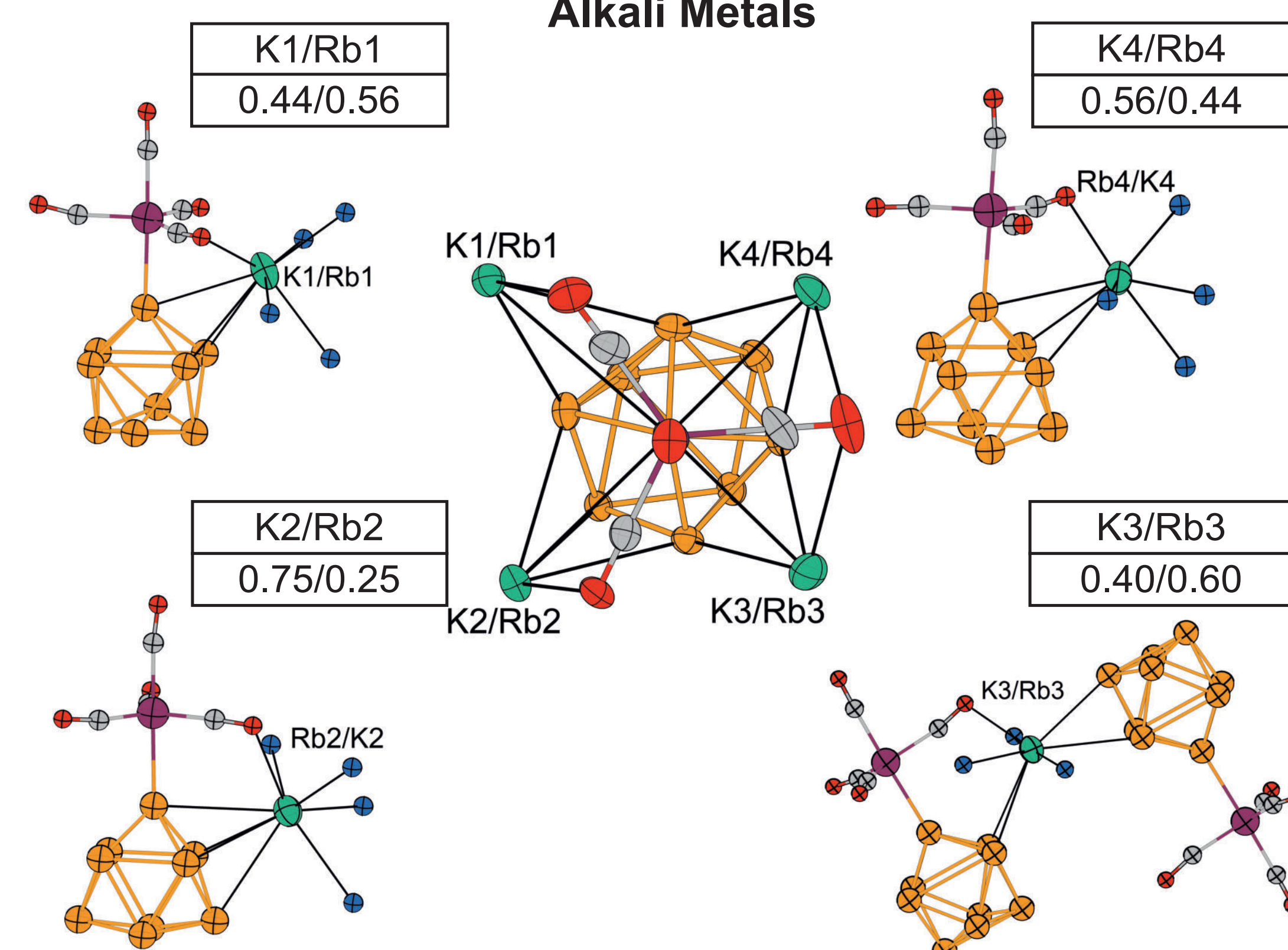


Condensed on reaction mixture

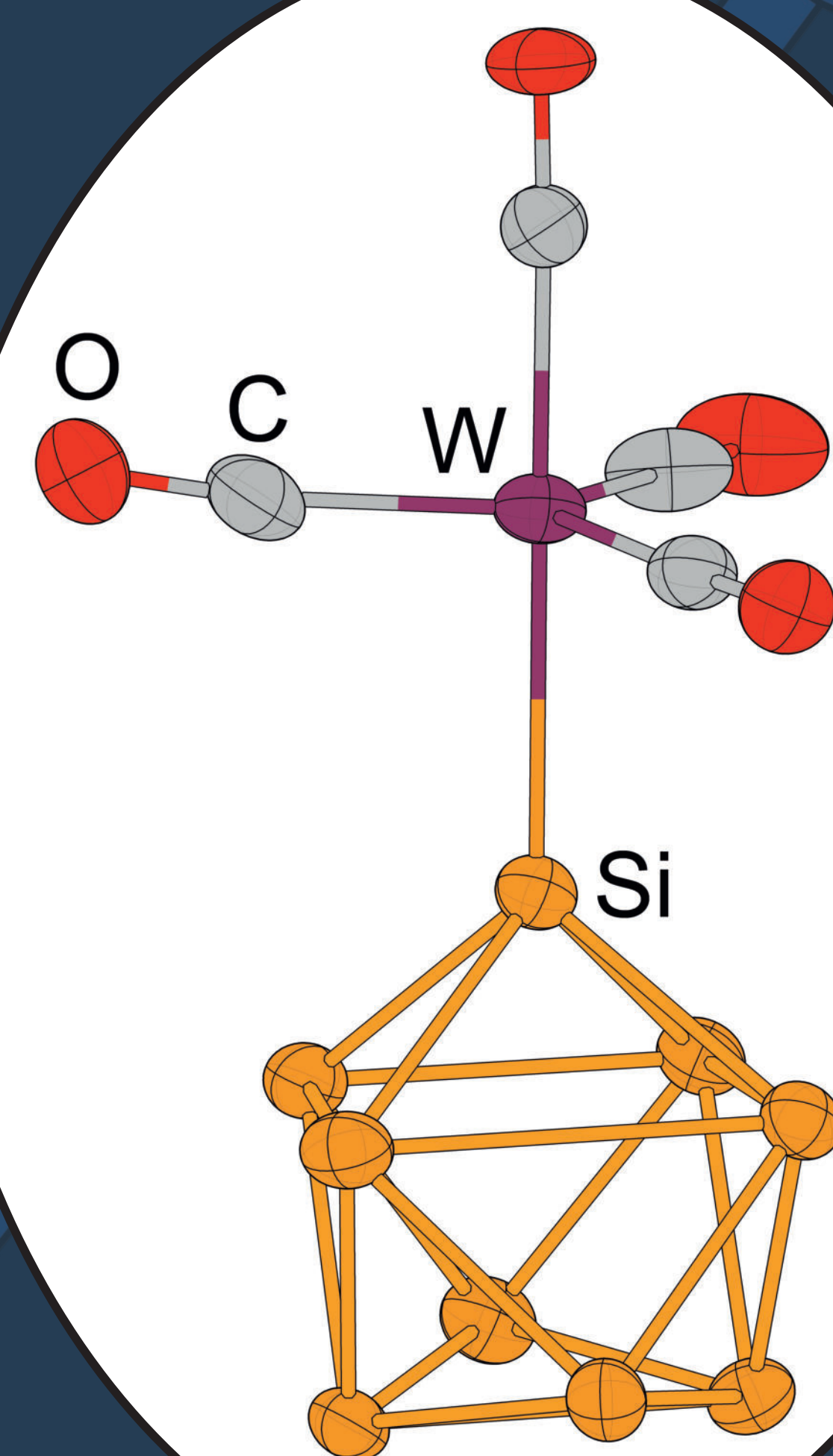
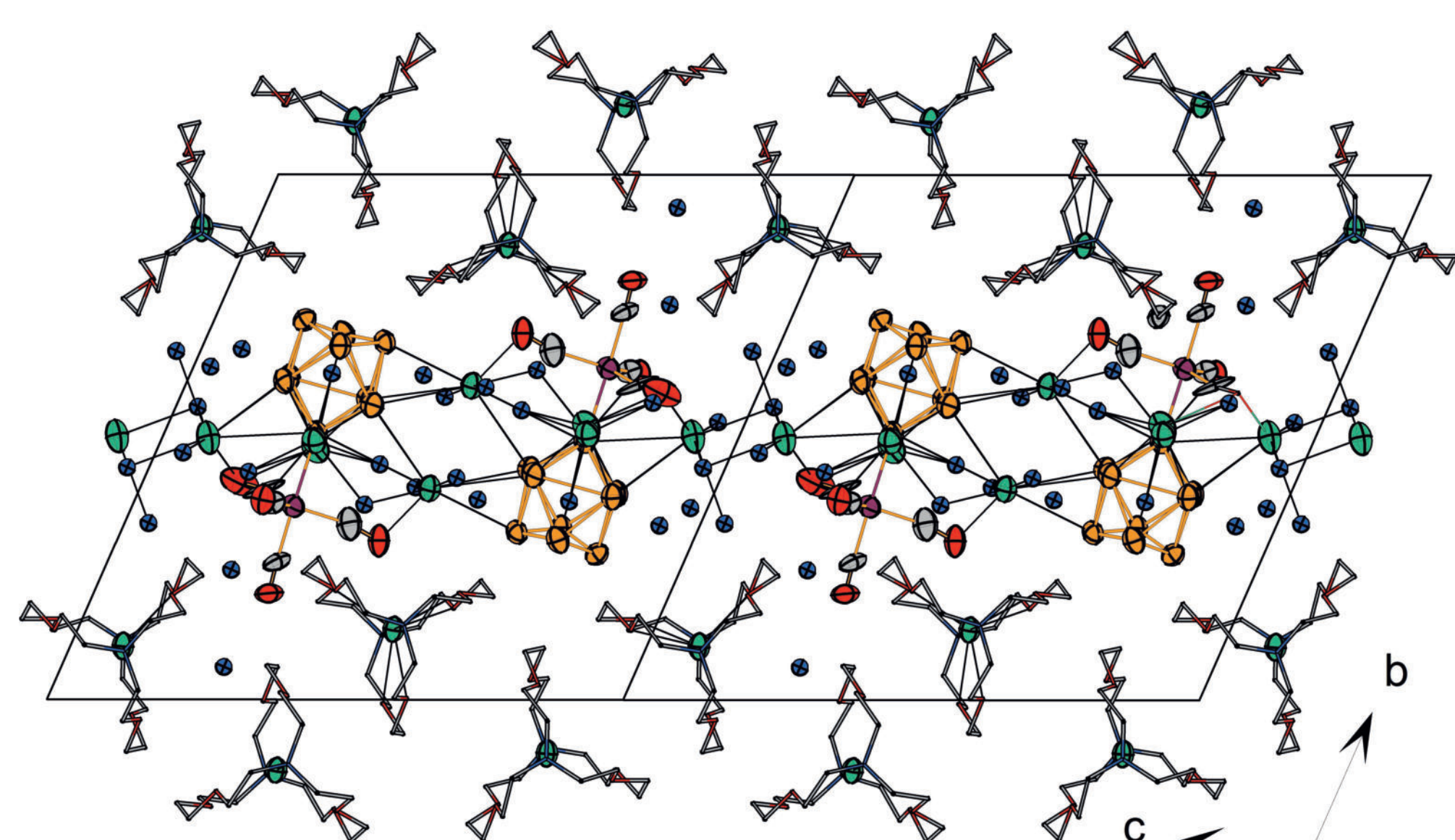
Opened for crystal picking

Fast transport in liquid nitrogen

The Coordination of $[(\eta^1-Si_9)W(CO)_4]^{6-}$ by the Alkali Metals

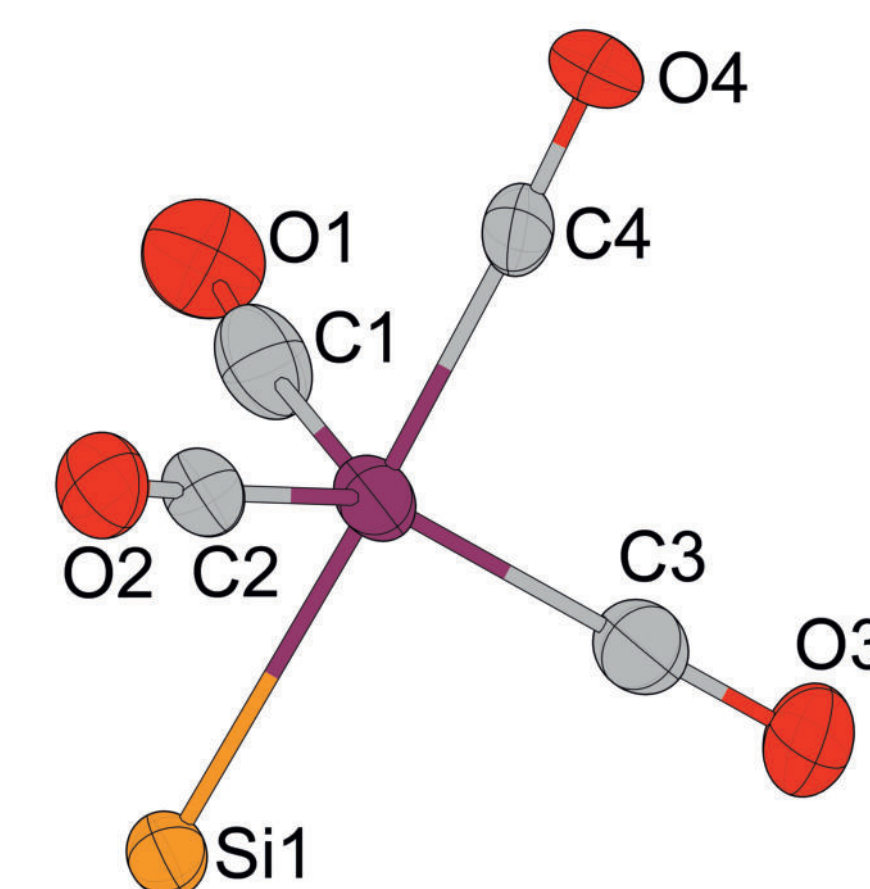


Crystal Structure of $[(Rb/K)@crypt)_2(Rb/K)_4(\eta^1-Si_9)W(CO)_4] \cdot 14NH_3$



Structure of the Heteroleptic Carbonylate

The major focus of the structure is set on the anion. The anion can be viewed from two different perspectives: A Si_9^{4-} cluster with a distorted D_{3h} symmetry which is functionalized with a $(TMEDA)W(CO)_4$ metal carbonylate or a heteroleptic carbonylate that itself has two possible structures which are energetically close: Trigonal bipyramidal and square pyramidal. The presented carbonylate can be assigned to the trigonal bipyramidal structure since the equatorial CO groups (1-3) are separated by a 120° bond angle. The Si1-W1-C4 angle is close to 180° and the angle between the equatorial and axial CO groups is also close to 90° .

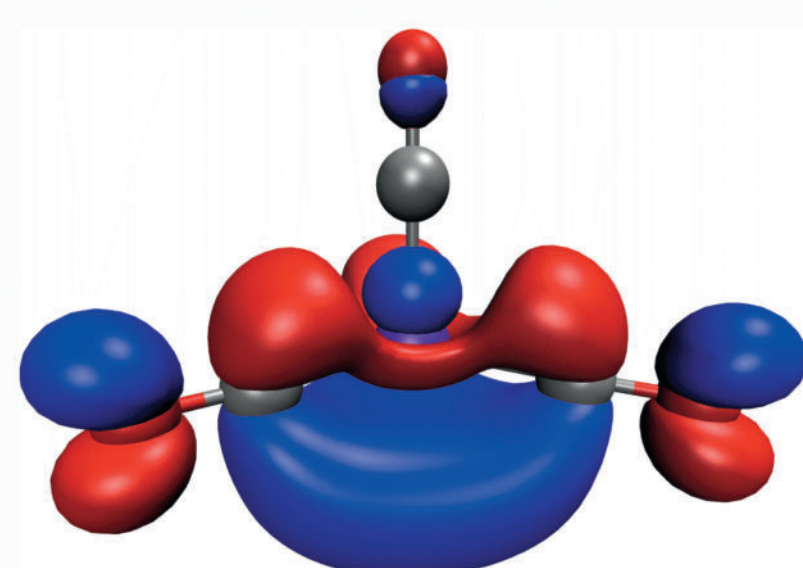
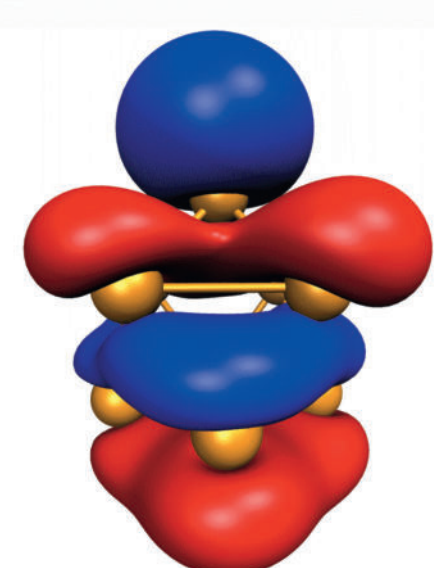


Quantum Chemical Calculations

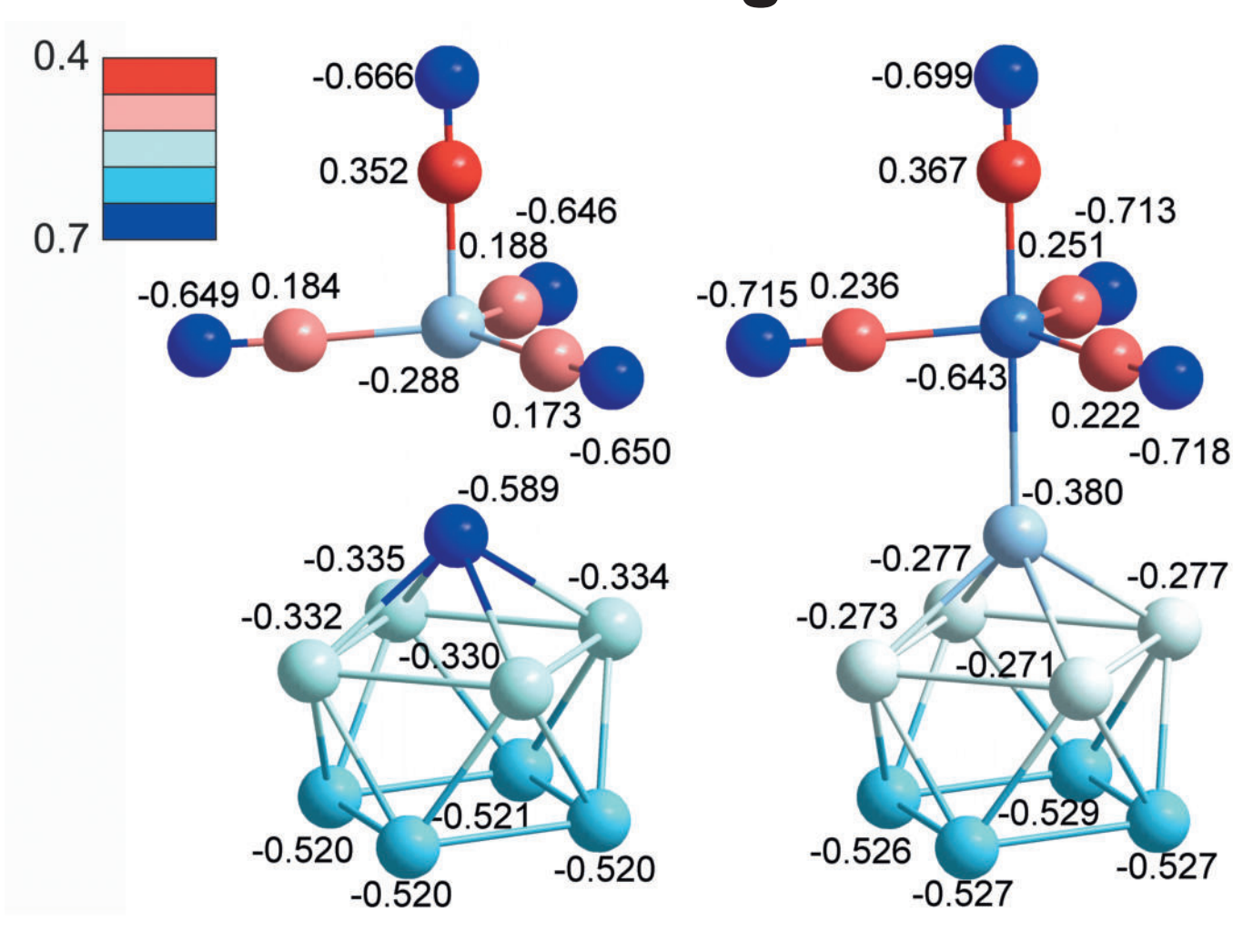
The complex anion $[Si_9W(CO)_4]^{6-}$ is structurally related to the tungsten pentacarbonylate $[W(CO)_5]^{2-}$, which from the point of view of organometallics can be described as an 18-valence electron cluster.^[5] The configuration is achieved by five CO ligands, six electrons from the metal center and two negative charges. One of the CO ligands here is replaced by a $[Si_9]^{4-}$ cluster as ligand. Sevov *et al.* stated that the $[Ge_{10}]^{2-}$ in the structure $[Ge_{10}Mn(CO)_4]^{3-}$ acts as a two-electron ligand via the coordination of a lone pair.^[6] The corresponding molecular orbitals HOMO-3 ($[Si_9]^{4-}$) and LUMO ($[W(CO)_4]^{2-}$) support the description of $[Si_9]^{4-}$ as a two-electron donor ligand.

HOMO-3

LUMO

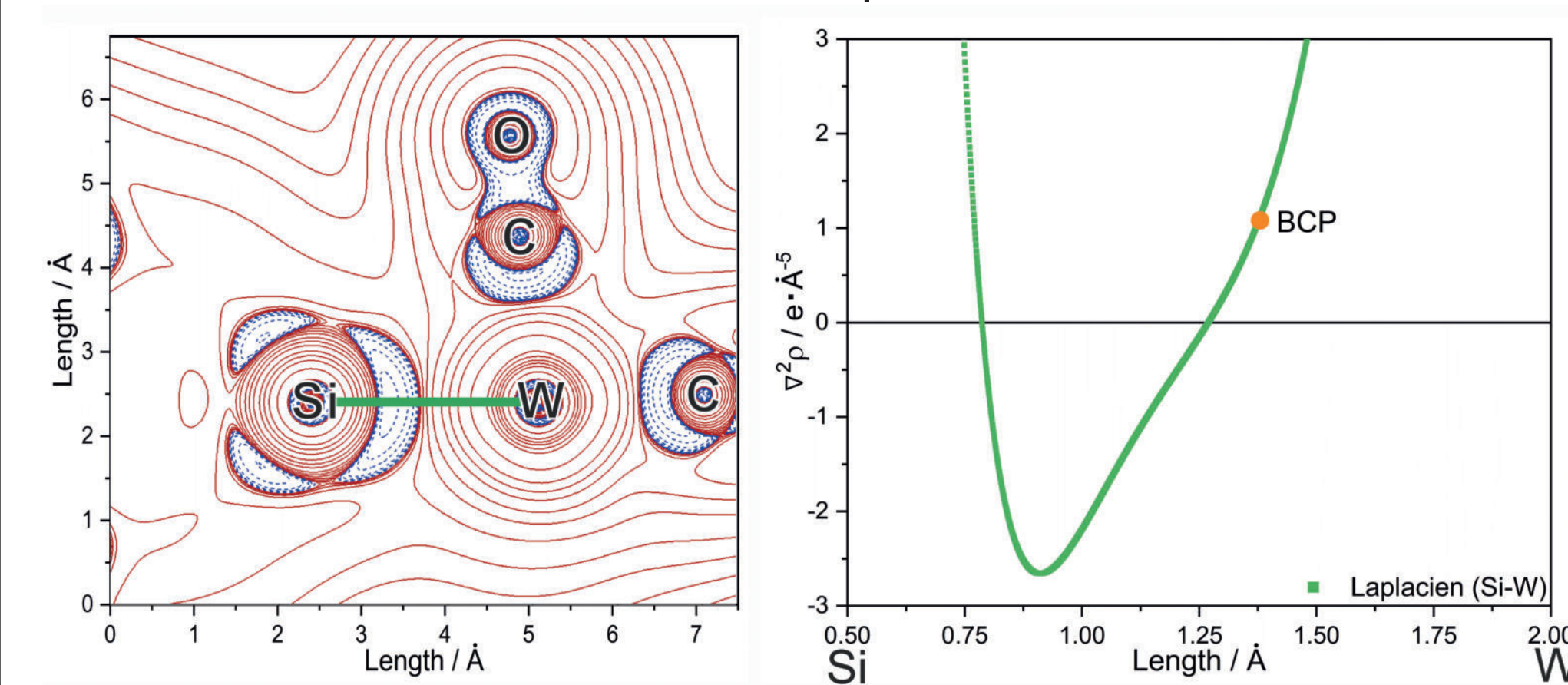


NPA Charges



Laplacian

Viewing the Laplacian of the electron density on the Si-W-(CO) plane and along the Si-W bond axis, it is strongly indicated that the Si lone pair is donating electrons to the W. Further evaluation of the bonding situation with a QTAIM analysis of the bond critical point (BCP) resulted in a positive ρ , $\nabla^2\rho$ and a negative virial potential energy density at the BCP. This can be, according to the criteria of *Bianchi et al.*, interpreted as a dative bond.^[7]



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