Halo, Alkyl, Aryl, and *Bis*(imido) Complexes of Niobium Supported by the β-Diketiminato Ligand

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Computational Methods.

DFT calculations were performed with the ORCA program package.[1] The geometry optimization of BDI'Nb(NMe)$_2$ (**11a**) and the single point calculations of the BDI'$^-$ and Nb(NMe)$_2^+$ were performed at the BP86 level of DFT.[2,3] The all-electron Gaussian basis sets were those developed by the Ahlrichs group.[4,5] Triple-ζ quality basis sets TZVP with one set of polarization functions on the metal and on the atoms directly coordinated to the metal center were used.[5] For the carbon and hydrogen atoms, slightly smaller polarized split-valence SV(P) basis sets were used, that were of double-ζ quality in the valence region and contained a polarizing set of d-functions on the non-hydrogen atoms.[4] Auxiliary basis sets used to expand the electron density in the resolution-of-the-identity (RI) approach were chosen to match the orbital basis.[6-8] The SCF calculations were tightly converged (1×10^{-7} E_h in energy, 1×10^{-6} E_h in the density change and 1×10^{-6} in maximum element of the DIIS error vector). The geometry optimization calculation was carried out in redundant internal coordinates without imposing symmetry constraints. The geometry was considered converged after the energy change was less than 5×10^{-6} E_h, the gradient norm and maximum gradient elements were smaller than 1×10^{-4} E_h Bohr^{-1} and 3×10^{-4} E_h Bohr^{-1}, respectively, and the root-mean square and maximum displacements of all atoms were smaller than 2×10^{-3} Bohr and 4×10^{-3} Bohr, respectively. The coordinates for the BDI$^-$ and Nb(NMe)$_2^+$ molecular fragments were taken from the geometry optimized coordinates of **11a**. Canonical orbitals were generated with the program Molekel.[9]

Complete input file for BDI'Nb(NMe)$_2$ (11a).

```
! RKS BP86 RI SlowConv TightSCF SV(P) SV/J PAL6 OPT UCO NORMALPRINT

%basis NewGTO 41 "TZVP" end
       NewGTO 7 "TZVP" end
       NewAuxGTO 41 "TZV/J" end
       NewAuxGTO 7 "TZV/J"  end
       end

%scf directresetfreq 20
     diismaxeq 20
     MaxIter 700
     end

%geom MaxIter 300
       end

*xyz 0 1
 Nb     0.489005    -0.264693     0.269009
 N     -1.103212    -0.087043    -0.618280
 C     -2.028618    -0.046992    -1.711255
 H     -1.563006    -0.337901    -2.685985
 H     -2.459709     0.977568    -1.837957
 H     -2.891267    -0.738500    -1.534997
 N      1.861421    -0.543682    -0.904993
 C      2.383088    -0.708216    -2.231945
 H      2.756817    -1.751036    -2.384928
 H      1.620631    -0.502337    -3.023811
 H      3.246589    -0.019023    -2.405448
 N      0.901842     1.365663     1.656322
 N      0.428153    -1.789437     1.828281
 C      1.467135     2.603796     1.198161
 C      2.878317     2.774598     1.237749
 C      3.419771     3.979136     0.749356
 H      4.514306     4.123689     0.777672
 C      2.593687     4.986197     0.224081
 H      3.036016     5.921839    -0.157607
 C      1.205712     4.794655     0.177943
 H      0.554282     5.581092    -0.241006
 C      0.615634     3.606268     0.659735
 C      3.768386     1.672758     1.762506
 H      3.597436     0.729295     1.194289
 H      4.841524     1.944579     1.667574
 H      3.568072     1.443488     2.833736
 C     -0.882006     3.409795     0.617001
 H     -1.154900     2.459894     0.099791
 H     -1.322791     3.338744     1.638832
```

H	-1.379860	4.252693	0.092499
C	0.596447	2.384222	3.888566
H	0.385644	3.345382	3.376705
H	1.619847	2.465141	4.323242
H	-0.113967	2.260574	4.732937
C	0.518785	1.198219	2.937939
C	0.102166	-0.034130	3.515814
H	-0.220753	0.070941	4.562635
C	0.142198	-1.390752	3.079565
C	-0.097375	-2.430747	4.164554
H	-0.352297	-3.425104	3.746949
H	-0.911879	-2.103254	4.845918
H	0.819600	-2.553072	4.786695
C	0.567515	-3.174775	1.474938
C	1.863448	-3.756693	1.468214
C	1.991380	-5.099305	1.060777
H	2.993932	-5.561267	1.051426
C	0.871932	-5.847411	0.664620
H	0.992686	-6.895762	0.344575
C	-0.399657	-5.254842	0.671938
H	-1.281664	-5.838532	0.356503
C	-0.579212	-3.915582	1.074965
C	3.073770	-2.941287	1.858311
H	3.198847	-2.074831	1.168186
H	3.997359	-3.557095	1.819783
H	2.982253	-2.521915	2.885604
C	-1.953032	-3.285435	1.086164
H	-1.965646	-2.330204	0.512039
H	-2.708062	-3.974387	0.651682
H	-2.281530	-3.030830	2.119901

*

Input files for single point calculations on $Nb(NMe)_2^+$ and BDI'$^-$. Coordinates taken from the geometry optimized coordinates of **11a**.

```
# Nb(NMe)2 cation
! RKS BP86 RI SlowConv TightSCF SV(P) SV/J PAL4 NORMALPRINT

%basis NewGTO 41 "TZVP" end
       NewGTO 7 "TZVP" end
       NewAuxGTO 41 "TZV/J" end
       NewAuxGTO 7 "TZV/J"  end
       end

%scf directresetfreq 20
     diismaxeq 20
     MaxIter 700
     end

*xyz 1 1
.
.
.
*

# BDI prime anion
! RKS BP86 RI SlowConv TightSCF SV(P) SV/J PAL2 NORMALPRINT

%scf directresetfreq 20
     diismaxeq 20
     MaxIter 700
     end

*xyz -1 1
.
.
.
*
```

Final Energies.

(BDI')Nb(NMe)$_2$: -4869.641358579 E_h

$Nb(NMe)_2^+$: -3945.087586565 E_h

BDI'$^-$: -924.107113964 E_h

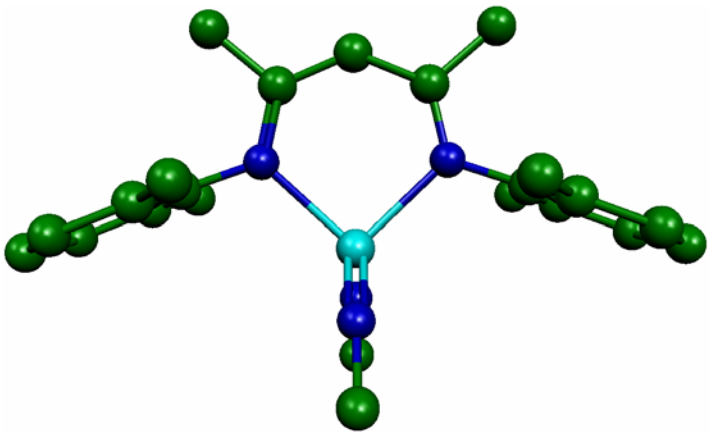
Coordinates for optimized geometry of 11a.

Atom	x	y	z
Nb	0.787812	-0.309895	0.309422
N	-0.662966	-0.141829	-0.791722
C	-1.384889	-0.093469	-2.028725
H	-0.745065	-0.330342	-2.914598
H	-1.825432	0.920761	-2.195865
H	-2.235899	-0.819692	-2.025289
N	2.310199	-0.597081	-0.661931
C	3.048534	-0.767267	-1.879560
H	3.482041	-1.796012	-1.943191
H	2.421400	-0.610578	-2.792116
H	3.903602	-0.048361	-1.931559
N	0.979321	1.349002	1.718113
N	0.495856	-1.800375	1.878506
C	1.320277	2.644577	1.198116
C	2.691719	3.003813	1.077586
C	3.005562	4.257826	0.516275
H	4.065986	4.547369	0.416795
C	1.997154	5.131560	0.081469
H	2.263624	6.108081	-0.355601
C	0.650319	4.756350	0.197617
H	-0.143417	5.438544	-0.151529
C	0.284410	3.513119	0.753014
C	3.778803	2.051373	1.517304
H	3.705689	1.087241	0.962537
H	4.785135	2.486745	1.338756
H	3.703244	1.798828	2.598860
C	-1.166614	3.105913	0.860950
H	-1.346118	2.129139	0.354279
H	-1.485814	2.970310	1.919040
H	-1.829560	3.870497	0.403011
C	0.844269	2.367605	3.949811
H	0.155637	3.176425	3.621983
H	1.868301	2.800911	3.923947
H	0.602986	2.100531	4.998359
C	0.750841	1.159733	3.031344

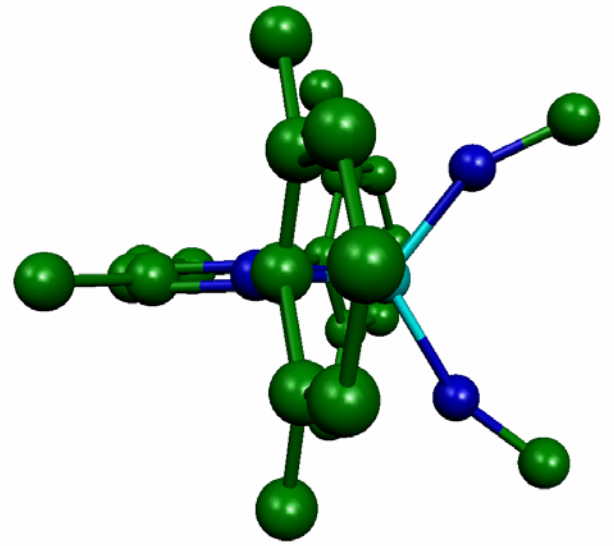
C	0.447922	-0.087378	3.647192
H	0.281278	-0.006611	4.730763
C	0.354961	-1.422375	3.163059
C	0.097243	-2.506135	4.197756
H	-0.814442	-3.091707	3.947825
H	-0.024559	-2.078488	5.213034
H	0.937248	-3.235985	4.222341
C	0.419596	-3.182536	1.492138
C	1.615804	-3.950009	1.424637
C	1.526690	-5.288103	0.991006
H	2.448506	-5.891988	0.933450
C	0.294182	-5.853059	0.628625
H	0.244969	-6.900163	0.287234
C	-0.874082	-5.078537	0.692090
H	-1.842754	-5.518094	0.398808
C	-0.837999	-3.735772	1.120947
C	2.947858	-3.332842	1.781731
H	3.161286	-2.452914	1.130493
H	3.771885	-4.068815	1.664203
H	2.970318	-2.960582	2.830743
C	-2.096523	-2.900586	1.169781
H	-1.985757	-1.974134	0.559772
H	-2.968565	-3.474588	0.790405
H	-2.336820	-2.565797	2.204029

Geometry optimized structure of 11a.

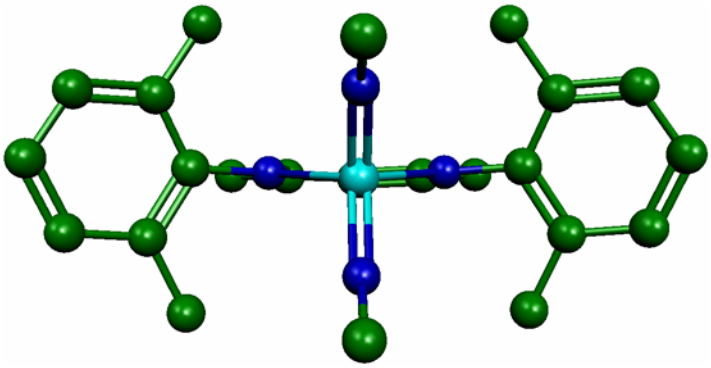
x-axis view



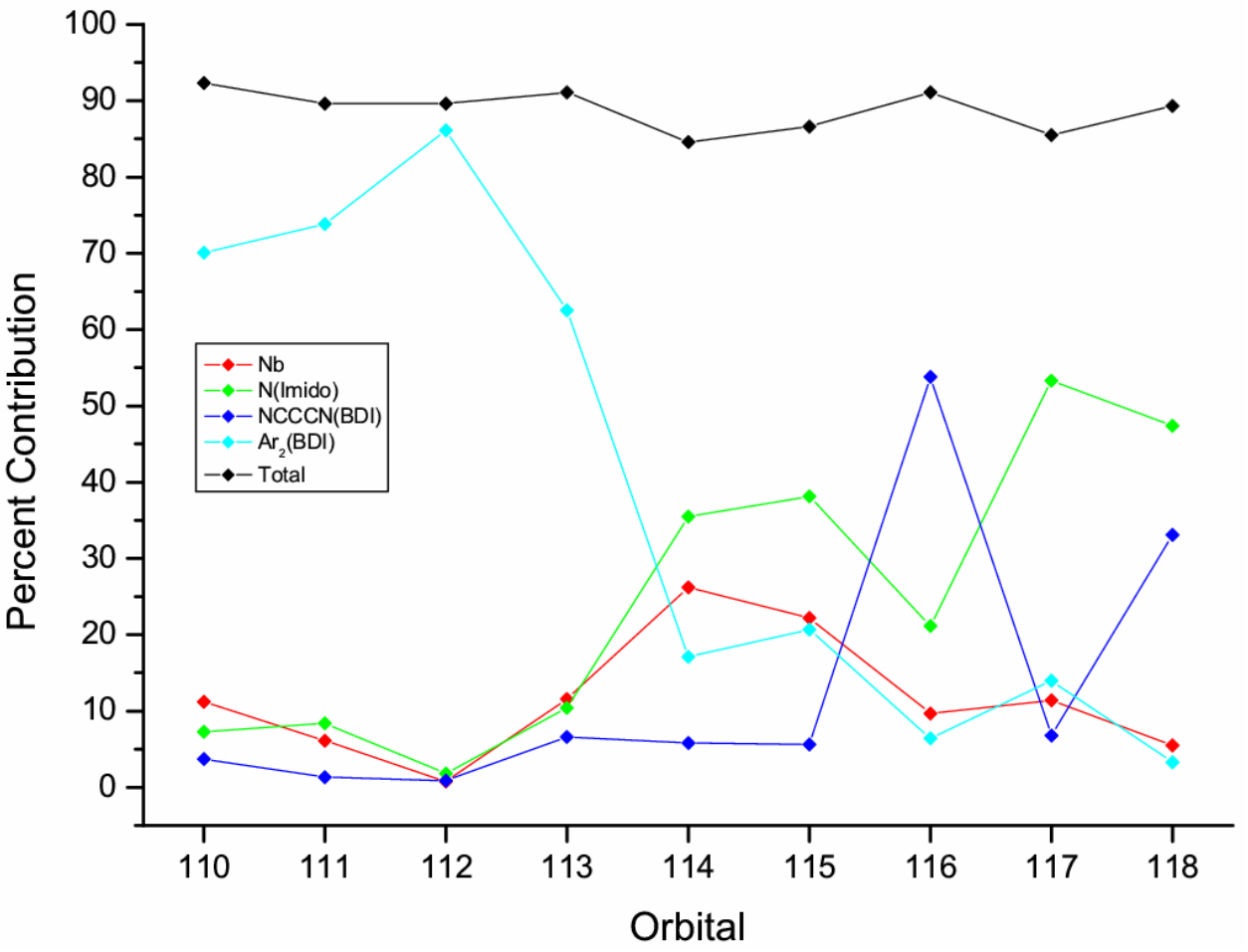
y-axis view



z-axis view

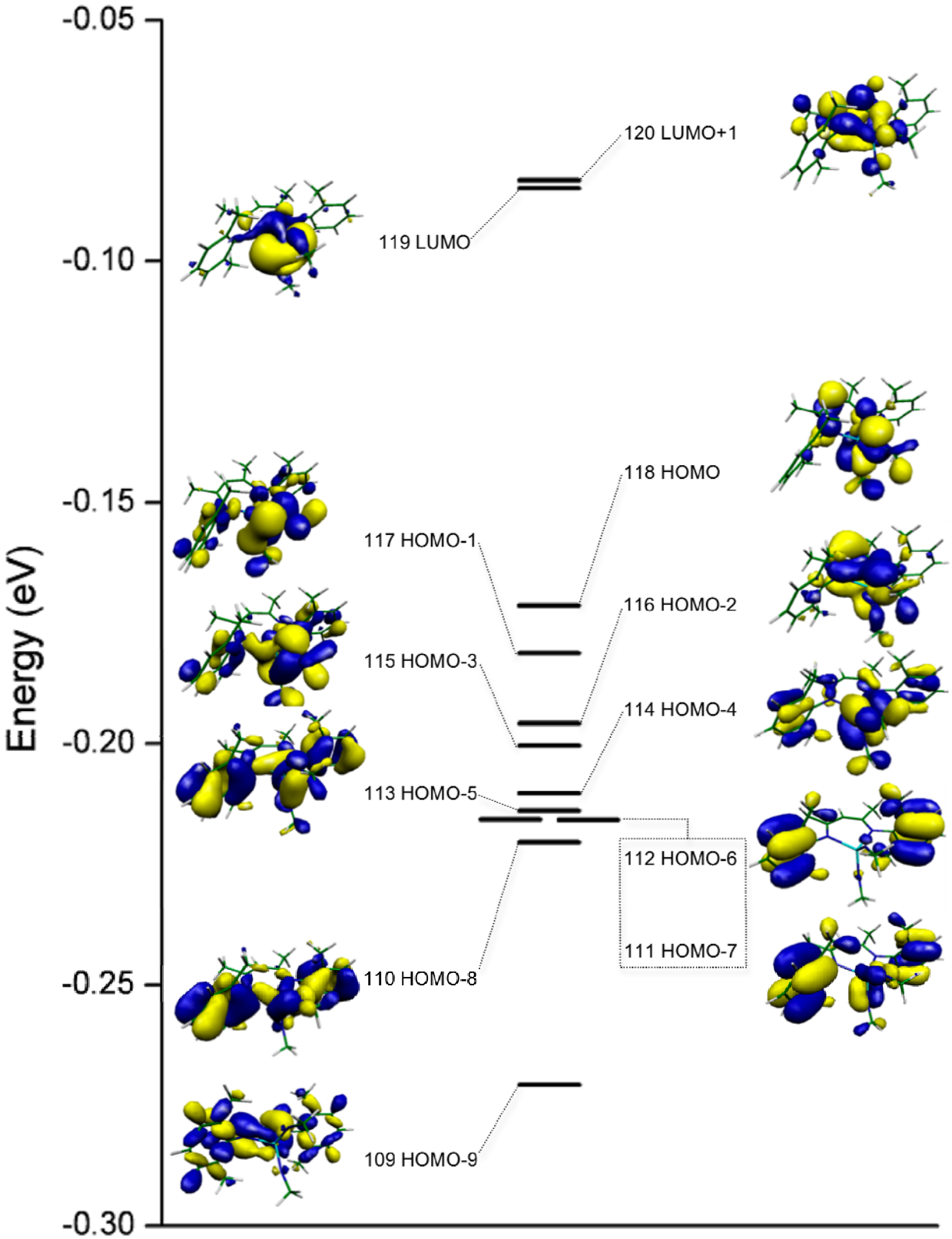


Relative contributions of various molecular fragments to selected orbitals of 11a.



Orbital	Energy (eV)	Occ.	Nb (%)	N(imido) (%)	NCCCN(BDI) (%)	Ar_2(BDI) (%)	Total (%)
120	-0.0832	0	5.4	9.6	71.9	3.3	90.2
119	-0.0849	0	72.5	11.8	6.6	4.8	95.7
118	-0.1714	2	5.5	47.4	33.1	3.3	89.3
117	-0.1813	2	11.4	53.3	6.8	14.0	85.5
116	-0.1958	2	9.7	21.2	53.8	6.4	91.1
115	-0.2004	2	22.2	38.1	5.6	20.7	86.6
114	-0.2103	2	26.2	35.5	5.8	17.1	84.6
113	-0.2139	2	11.6	10.4	6.6	62.5	91.1
112	-0.2157	2	0.8	1.8	0.9	86.1	89.6
111	-0.2158	2	6.1	8.4	1.3	73.8	89.6
110	-0.2204	2	11.2	7.3	3.7	70.1	92.3
109	-0.2708	2	4.9	1.0	54.2	21.9	82.0

Molecular orbital scheme for orbitals 109-120 of 11a.



References for Supporting Information.

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