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Supporting Information for

# Computational Evaluation of Tris(carbene)borate Donor Properties in {NiNO}<sup>10</sup> Complexes.

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Compound	Ni-N (Å)	N-O (Å)	Ni-N-O (°)
1	1.639	1.197	158.09
2	1.635	1.198	167.71
3	1.635	1.196	165.11
4	1.635	1.194	165.53
5	1.639	1.191	165.67
6	1.636	1.191	165.82
7	1.637	1.194	169.75
8	1.636	1.190	168.40
9	1.635	1.190	164.44
10	1.635	1.188	164.55
11	1.633	1.192	170.56
12	1.633	1.191	165.24
13	1.644	1.186	179.55
14	1.634	1.189	168.63
15	1.631	1.191	167.50
16	1.631	1.190	166.70
17	1.635	1.188	168.79
18	1.635	1.188	163.92
19	1.635	1.187	168.95
20	1.635	1.185	168.56
21	1.637	1.187	179.56
22	1.636	1.185	169.94
23	1.633	1.181	176.29
24	1.634	1.183	169.00
25	1.633	1.178	177.80
26	1.633	1.179	172.98

 Table S1. Selected metrical parameters for the optimized {NiNO}<sup>10</sup> complexes.

<sup>a</sup> Compound numbering as in Table 1 of the main text.

#### Solvent Effect

Cmpd.	Exp	Gas	THF	Toluene	Diethylether	Water
7	-	1716	1673	1690	1682	1660
22	1714	1760	1699	1737	1723	1711
16	1703	1735	1699	1716	1706	1688
26	1762	1796	1765	1778	1771	1753

**Table S2**. N=O stretching frequencies (cm<sup>-1</sup>) in different solvents

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Cmpd.	Exp	Calc. THF	Calc.
_	-		Toluene
1	-	1622	1655
7	-	1673	1690
22	1714	1699	1737
16	1703	1699	1716
19	-	1708	1729
26	1762	1765	1778

**Table S3.** N≡O stretching frequencies (cm<sup>-1</sup>) in THF and Toluene

Table S2 illustrates solvent effect on the calculated N=O stretching frequencies for four selected compounds. Within the PCM framework the difference is mainly caused by the different dielectric constants  $\varepsilon$ . The calculated frequencies are lower in a more polar environment, e.g., comparing the numbers for a more polar solvent THF ( $\varepsilon = 7.4$ ) and those for less polar toluene ( $\varepsilon = 2.4$ ). This comparison is for qualitative purpose and neglects the realistic experimental situation (e.g., water is not a suitable solvent for this type of compound). On the other hand, the correlation between the N=O stretching frequency and the ligand in the compound does not change if a different solvent is used. This is more clearly seen in Table S3 where two compounds with the lowest/highest N=O

frequency are included. We note that the frequencies calculated with THF solvent are closer to the experimental results (which were obtained in THF).

# Different functionals and basis set in DFT calculations

**Table S4.** N≡O stretching frequencies compared under different Basis Sets and Methods in Gas phase

6-31G*					
	B3LYP	O3LYP	B3P86	B3PW91	X3LYP
7	1618	1726	1748	1749	1790
22	1760	1778	1789	1790	1840
16	1735	1758	1764	1767	1813
26	1797	1811	1821	1823	1877
SDD					
7	1619	1622	1654	1652	1629
22	1676	1680	1712	1709	1685
16	1660	1664	1696	1692	1669
26	1705	1711	1742	1740	1713
6-311G*					
7	1702	1789	1809	1742	1768
22	1758	1837	1863	1792	1828
16	1725	1818	1827	1761	1793
26	1798	1878	1898	1827	1869

Table S4 shows the N=O stretching frequencies for four compounds employing different functionals and basis sets in the DFT calculation. The B3LYP/6-31G\* level of theory is used as a gauge. A smaller SDD basis set performs worse. The larger 6-311G\* basis set gives comparable results but with significantly increased computational cost.

### Correlation between NO charge and N≡O frequency



Figure S1: Plot of the charge on NO versus N≡O stretching frequency

Natural population analysis was used to evaluate the charge on NO moiety. As shown in Figure S1, the commonly used correlation between the electron donating power of the ligand and the N $\equiv$ O stretching frequency is confirmed by our electronic structure calculations. Here the partial charge on the NO moiety, reflecting the electron donating power of the three ligands, is plotted versus the N $\equiv$ O stretching frequency. The trend is clear and consistent with the previously established qualitative relation.

## Correlation between N=O bond length and N=O frequency



**Figure S2:** N=O bond length versus N=O stretching frequency

X-Ray crystallography measurements are often used to obtain the N $\equiv$ O bond length as an indicator of the ligand donating strength. As shown in Figure S2, the calculated N $\equiv$ O bond length displayed expected correlation with the N $\equiv$ O stretching frequency.

Table S5. Ground state total free energies for different spin states of the hypothetical	l
Ni(IV)N complexes. Gas phase relative energies in kcal/mol, lowest energy spin state	;
shown in red.	

Nitrosyl precursor <sup>a</sup>	<i>S</i> = 0	<i>S</i> = 1	<i>S</i> = 2
1	3.40	0.00	13.51
2	0.00	5.01	15.12
3	0.00	3.45	12.12
4	0.00	2.79	11.82
5	0.00	0.11	10.11
6	0.00	0.03	10.48
7	5.09	0.00	13.35
8	1.46	0.00	10.66
9	0.00	0.75	8.75
10	0.18	0.00	7.80
11	0.00	0.15	8.87
12	0.76	0.00	7.86
13	4.25	0.00	15.57
14	0.00	0.71	10.52
15	4.56	0.00	7.26
16	5.52	0.00	7.15
17	7.52	0.00	7.54
18	2.65	0.00	8.87
19	1.49	0.00	8.70
20	2.63	0.00	9.20
21	7.76	0.00	16.28
22	3.06	0.00	10.22
23	5.31	0.00	11.03
24	2.81	0.00	8.24
25	5.06	0.00	7.26
26	3.59	0.00	8.88

<sup>a</sup> Compound numbering as in Table 1 of the main text.