Supporting Information for

# Tris(carbene)borate ligands featuring imidazole-2-ylidene, benzimidazol-2-ylidene and 1,3,4-triazol-2-ylidene donors. Evaluation of donor properties in four-coordinate $\{NiNO\}^{10}$ complexes.

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**Results of solid angle calculations**

**Table S1.** Full results of solid angle calculations.

| Ligand | Full ligand | | Truncated ligand[a] | |
|---|---|---|---|---|
| | Solid angle[b] (% sphere) | Cone angle[c] (°) | Solid angle[b] (% sphere) | Cone angle[c] (°) |
| $HB(MeBz)_3^-$ | 37.09 | 150.07 | 37.10 | 150.09 |
| | 36.97 | 149.61 | 36.90 | 149.61 |
| | 36.58 | 148.87 | 37.02 | 149.92 |
| | 36.81 | 149.41 | 36.80 | 149.40 |
| $HB(CH_2CyBz)_3^-$ | 56.26 | 194.38 | 36.90 | 149.62 |
| $PhB(CH_2CyIm)_3^-$ | 52.12 | 184.86 | 39.82 | 156.50 |
| | 52.70 | 186.19 | 37.06 | 150.01 |
| | 53.62 | 188.30 | 40.24 | 157.50 |
| $HB(^tBuIm)_3^-$ (Ni)[d] | 53.18 | 187.29 | 53.18 | 187.28 |
| (Fe)[e] | 49.16 | 178.15 | 48.87 | 177.42 |
| $PhB(^tBuIm)_3^-$ [f] | 51.74 | 183.98 | 51.57 | 183.60 |
| $HB(MesTz)_3^-$ | 63.03 | 210.22 | 49.06 | 177.85 |
| $HB(p\text{-}^tBuTz)_3^-$ | 52.40 | 185.50 | 43.71 | 165.55 |
| Tp* | 37.03 | 149.93 | 36.99 | 149.83 |
| | 36.92 | 149.68 | 36.92 | 149.68 |
| $PhB(CH_2PPh_2)_3^-$ (CN 4)[g] | 55.41 | 192.43 | 54.12 | 189.44 |
| (CN 6)[h] | 53.06 | 187.02 | 45.96 | 170.74 |

[a] Ligand was truncated at a radius of 4 Å from the metal center.

[b] Percent sphere coverage angle normalized to a metal-ligand distance of 2.28 Å.

[c] Cone angle that is size equivalent in size to the solid angle, normalized to a metal-ligand distance of 2.28 Å.

[d] Measured in the complex $HB(^tBuIm)_3NiNO$.

[e] Measured in $HB(^tBuIm)_3FeBr$.

[f] Measured in $PhB(^tBuIm)_3FeCl$.

[g] Measured in the four-coordinate complex $PhB(CH_2PPh_2)_3NiNO$.

[h] Measured in the six-coordinate complex $PhB(CH_2PPh_2)_3Fe(\kappa^2\text{-}OAc)(N_2H_4)$.

**Table S2.** Comparison of selected metrical data in selected four-coordinate $\{NiNO\}^{10}$ complexes.

| **Complex** | **Ni-N (Å)** | **N-O (Å)** | **Ni-N-O** |
|---|---|---|---|
| $PhB(CyCH_2Im)_3NiNO$ **14** | 1.633(9) - 1.668(1) | 1.174(1) – 1.197(1) | 172.7(1) – 177.8(1) |
| $HB(MeBz)_3NiNO$ **15** | 1.643(2) – 1.646(2) | 1.183(3)-1.191(3) | 169.3(2) – 174.8(2) |
| $HB(p\text{-}^tBuPhTz)_3NiNO$ **17** | 1.640(2) . | 1.163(3) | 176.3(3) |
| Tp*NiNO[a] | 1.619(6); 1.617(6) | 1.158(7); 1.170(7) | 175.3(7); 178.5(6) |
| $PhB(CH_2PPh_2)_3NiNO$[b] | 1.624(3) | 1.183(3) | 176.0(3) |
| $Tm^{p\text{-tol}}NiNO$[c] | 1.665(3) | 1.131(4) | 173.9(4) |

[a] Landry, V.K.; Pang, K.; Quan, S.M.; Parkin, G. *Dalton Trans.* **2007**, 820.

[b] MacBeth, C.A.; Thomas, J.C.; Betley, T.A.; Peters, J.C. *Inorg. Chem.* **2004**, *43*, 4645.

[c] Maffet, L.S.; Gunter, K.L.; Kreisel, K.A.; Yap, G.P.A.; Rabinovich, D. *Polyhedron* **2007**, *26*, 4758.

**Table S3.** Selected characterization data for tris(carbene)borate $\{NiNO\}^{10}$ complexes.

| **Complex** | $\nu_{NO}$ ($cm^{-1}$)[a] | $^{13}C\{^1H\}$[b] | **UV-vis (nm)**[a] | $E_{ox}$ **(V)**[c] | $E_{red}$ **(V)** |
|---|---|---|---|---|---|
| $PhB(CyCH_2Im)_3NiNO$ **14** | 1693 | 201.3 | 441 | -0.22 | d |
| $HB(MeBz)_3NiNO$ **15** | 1714 | 210.7 | 433 | d | -1.43 |
| $HB(CyCH_2Bz)_3NiNO$ **16** | 1711 | 211.7 | 435 | d | -1.93 |
| $HB(p\text{-}^tBuPhTz)_3NiNO$ **17** | 1746 | 199.6 | 467 | 0.38 | -1.78 |
| $HB(MesTz)_3NiNO$ **18** | 1742 | 202.1 | 451 | 0.40 | -1.83 |

[a] Recorded in THF solution.

[b] Measured in $CDCl_3$.

[c] Relative to the ferrocene/ferricinum couple (THF, 0.1 M $NBu_4PF_6$). All waves are irreversible.

[d] No electrochemical event observed.

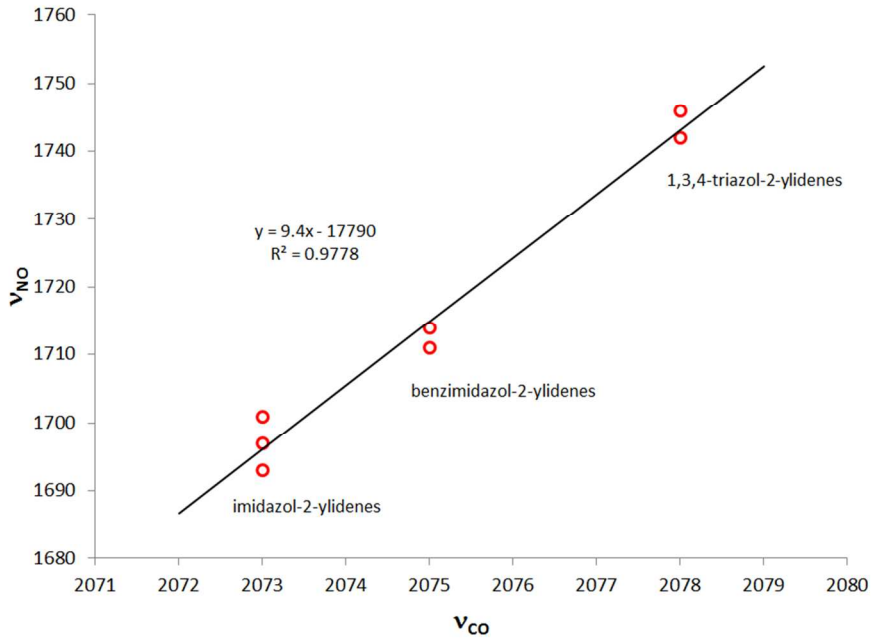


**Fig. S1.** Correlation of $\nu_{CO}$ (symm) for $Rh(CO)_2I(NHC)$ with $\nu_{NO}$ in tris(carbene)borate $\{NiNO\}^{10}$ complexes. Including $PhB(MesIm)_3NiNO$ gives $R^2 = 0.759$. Rh data taken from Herrmann, W.A.; Schütz, J.; Frey, G.D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.

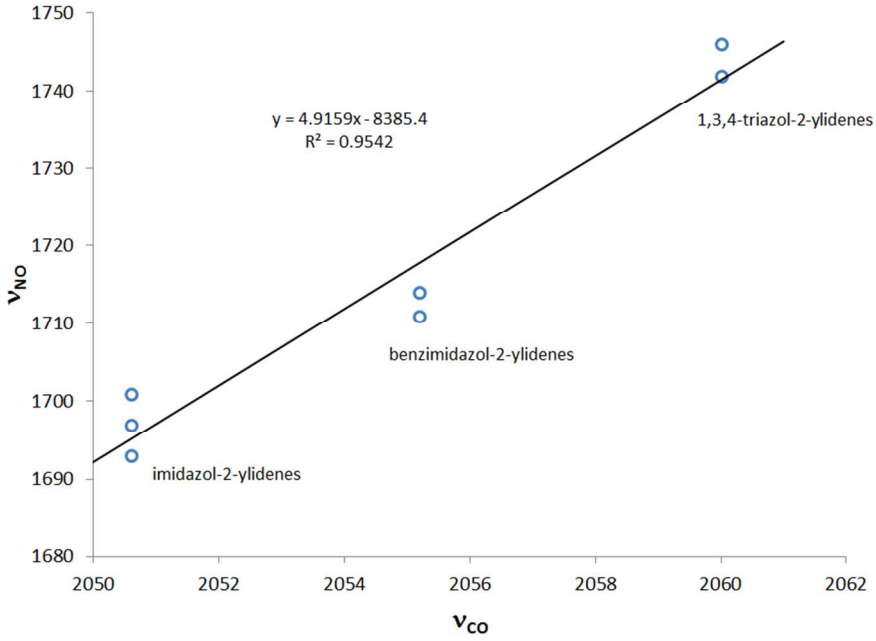


**Fig. S2.** Correlation of $\nu_{NO}$ (symm) for $Ni(CO)_3(NHC)$ with $\nu_{NO}$ in tris(carbene)borate $\{NiNO\}^{10}$ complexes. Including $PhB(MesIm)_3NiNO$ gives $R^2 = 0.725$. Ni data taken from Gusev, D.G. *Organometallics* **2009**, *28*, 6458.

**Details on X-ray structure determinations**

**$PhB(MeCyImH)_3OTf_2$ 6**

Crystals suitable for X-ray structural determination were grown from pentane diffusion into dichloromethane at -25 °C. A colorless needle of $C_{38}H_{53}BF_6N_6O_6S_2$, approximate dimensions 0.30 mm x 0.02 mm x 0.02 mm, was coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Kα sealed-tube (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 88114 reflections to a maximum 2θ angle of 56.75°, of which 22058 were independent. The final cell constants of a = 16.276 Å, b = 17.5825 Å, c = 18.0911 Å, α = 76.2443°, β = 90.0173°, γ = 62.4445°, volume = 4421.753 $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7040 and 0.7457.

**$PhB(MeCyIm)_3NiNO$ 14**

Crystals suitable for X-ray structural determination were grown from pentane diffusion into diethylether at -35 °C. An orange needle-like specimen of $C_{112}H_{160}B_3N_{21}Ni_3O_4$, approximate dimensions 0.08 mm x 0.16 mm x 0.40 mm, was coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy for the X-ray crystallographic analysis. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Ka sealed tube (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 111284 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 22708 were independent (average redundancy 4.901, completeness = 100.0%, $R_{int}$ = 48.76%, $R_{sig}$ = 43.13%) and 6775 (29.84%) were greater than $2\sigma(F^2)$. The final cell constants of a = 26.345(6) Å, b = 37.425(7) Å, c = 11.4322(19) Å, β = 99.762(13)°, volume = 11109.(4) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8076 and 0.9563.

The crystal was poor quality and diffracted weakly. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{112}H_{160}B_3N_{21}Ni_3O_4$. Non-hydrogen atoms were refined anisotropically, with constraints on the anisotropic displacement parameters of C37-C40, C37a-C40a, C45-C50, C46a, C47a C50a, C55-60 and C55a-C60a. Hydrogen atoms were placed in geometrically calculated positions. All H-atms were refined with with $U_{iso} = 1.2U_{equiv}$ of the parent atom ($U_{iso} = 1.5U_{equiv}$ for methyl). Three independent disorders were identified in the structure. These were allowed to refine freely and converged at occupancies of 57/43 for the major and minor positions of the C45-C50 cyclohexyl, 68/32 for the C55-C60 cyclohexyl, and 49/51 for the ether solvent. The final anisotropic full-matrix least-squares refinement on $F^2$ with 1342 variables converged at R1 = 11.26%, for the observed data and wR2 = 38.66% for all data. The goodness-of-fit was 0.958. The largest peak in the final difference electron density synthesis was 0.721 $e^-/Å^3$ and the largest hole was -1.448 $e^-/Å^3$ with an RMS deviation of 0.225 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.240 $g/cm^3$ and F(000), 4440 $e^-$.

**$HB(MeBz)_3NiNO$ 15**

Crystals suitable for X-ray structural determination were grown from pentane diffusion into THF at -35 °C. An orange plate-like specimen of $C_{24}H_{22}BN_7NiO$, approximate dimensions 0.13 mm x 0.18 mm x 0.50 mm, was coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Kα sealed-tube (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 86603 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 24003 were independent (average redundancy 3.608, completeness = 99.9%, $R_{int}$ = 5.49%, $R_{sig}$ = 5.75%) and 16267 (67.77%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.9653(8) Å, b = 17.0466(10) Å, c = 23.6430(13) Å, α = 85.049(3)°, β = 76.475(3)°, γ = 88.960(3)°, volume = 5452.0(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7061 and 0.9113.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 8 for the formula unit, $C_{24}H_{22}BN_7NiO$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 1429 variables converged at R1 = 4.45%, for the

observed data and wR2 = 11.19% for all data. The goodness-of-fit was 1.017. The largest peak in the final difference electron density synthesis was 0.499 $e^-/Å^3$ and the largest hole was -0.388 $e^-/Å^3$ with an RMS deviation of 0.061 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.379 $g/cm^3$ and F(000), 2368 $e^-$.

**$HB(MeCyBz)_3NiNO$ 16**

Crystals suitable for X-ray structural determination were grown from pentane diffusion into THF at -35 °C. An orange block-like specimen of $C_{42}H_{52}BN_7NiO$, approximate dimensions 0.11 mm x 0.17 mm x 0.23 mm, was coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy for the X-ray crystallographic analysis. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Kα sealed tube (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 19853 reflections to a maximum θ angle of 26.02° (0.81 Å resolution), of which 7776 were independent (average redundancy 2.553, completeness = 99.6%, $R_{int}$ = 14.01%, $R_{sig}$ = 20.85%) and 3260 (41.92%) were greater than $2\sigma(F^2)$. The final cell constants of a = 19.241(4) Å, b = 10.847(3) Å, c = 22.885(5) Å, β = 123.991(14)°, volume = 3960.1(16) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8871 and 0.9434.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{42}H_{52}BN_7NiO$. Non-hydrogen atoms were refined anisotropically, with constraints on the anisotropic displacement parameters of C9-C14, C23-C28, C23a-C28a and B1, N1, N3 and N5. The hydrogen atom H1 was found in the diffraction map and was restrained to a B1-H1 distance of 1.04 Å. All other hydrogen atoms were placed in geometrically calculated positions. All H-atms were refined with with $U_{iso}$ = $1.2U_{equiv}$ of the parent atom. One cyclohexyl group was found to be disordered over two positions. These were allowed to refine and converged at equal occupancies for the two positions. The final anisotropic full-matrix least-squares refinement on $F^2$ with 509 variables converged at R1 = 8.76%, for the observed data and wR2 = 25.28% for all data. The goodness-of-fit was 0.970. The largest peak in the final difference electron density synthesis was 1.089 $e^-/Å^3$

and the largest hole was -0.392 $e^-/Å^3$ with an RMS deviation of 0.091 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.242 g/cm$^3$ and F(000), 1576 $e^-$.

**HB(*p*-$^t$BuPhTz)$_3$NiNO 17**

Crystals suitable for X-ray structural determination were grown from pentane diffusion into THF at -35 °C. A red block-like specimen of $C_{48}H_{67}BN_{10}NiO_4$, approximate dimensions 0.16 mm x 0.37 mm x 0.54 mm, was cut from a larger piece, coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Kα sealed-tube (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm after identification of a two-component twin by Cell_now. The integration of the data using a triclinic unit cell yielded a total of 11085 reflections to a maximum θ angle of 27.18° (0.78 Å resolution), of which 11087 were independent (average redundancy 1.000, completeness = 99.4%, $R_{sig}$ = 5.37%) and 8868 (79.99%) were greater than 2σ($F^2$). The final cell constants of a = 13.8678(4) Å, b = 14.1334(4) Å, c = 14.0830(4) Å, α = 107.976(2)°, β = 97.864(2)°, γ = 101.758(2)°, volume = 2510.62(12) Å$^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8027 and 0.9372.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{48}H_{67}BN_{10}NiO_4$. Non-hydrogen atoms were refined anisotropically, with similarity restraints on the anisotropic displacement parameters of disordered C atoms in two THF molecules. The hydrogen atom H1 was found in the diffraction map. All other hydrogen atoms were placed in geometrically calculated positions. All H-atoms were refined with with $U_{iso}$ = 1.2$U_{equiv}$ of the parent atom ($U_{iso}$ = 1.5$U_{equiv}$ for methyl). One entire THF molecule (O4, C45-C48) was found to be disordered over two positions, as were two carbon atoms (C38, C39) in a second THF. The occupancies were allowed to refine and converged at 47/53 for the two atom disorder and 57/43 for the full molecule. The final anisotropic full-matrix least-squares refinement on $F^2$ with 643 variables converged at R1 = 5.38%, for the observed data and wR2 = 14.49% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.631 $e^-/Å^3$ and the largest hole was -0.480 $e^-/Å^3$ with an

RMS deviation of 0.080 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.214 $g/cm^3$ and F(000), 980 $e^-$.

**$HB(MesTz)_3NiNO$ 18**

Crystals suitable for X-ray diffraction were grown from pentane diffusion into THF at -35 °C. A red plate-like specimen of $C_{33}H_{37}BN_{10}NiO$, approximate dimensions 0.22 mm x 0.30 mm x 0.46 mm, was cut from a larger crystal, coated with Paratone oil and mounted on a CryoLoop that had been previously attached to a metallic pin using epoxy for the X-ray crystallographic analysis. The X-ray intensity data were measured on a APEX II CCD system equipped with a graphite monochromator and a Mo Kα sealed-tube (λ = 0.71073 Å).

The total exposure time was 11.93 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 41686 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 8112 were independent (average redundancy 5.139, completeness = 99.8%, $R_{int}$ = 4.37%, $R_{sig}$ = 3.87%) and 6478 (79.86%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7177(17) Å, b = 12.974(3) Å, c = 17.960(4) Å, α = 74.731(4)°, β = 77.159(4)°, γ = 72.128(3)°, volume = 1842.8(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 9978 reflections above 20 σ(I) with 5.085° < 2θ < 53.61°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.865. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7794 and 0.8877.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{33}H_{37}BN_{10}NiO$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{equiv}$ of the parent atom ($U_{iso} = 1.5U_{equiv}$ for methyl groups). The final anisotropic full-matrix least-squares refinement on $F^2$ with 424 variables converged at R1 = 4.02%, for the observed data and wR2 = 10.64% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.562 $e^-/Å^3$ and the largest hole was -0.462 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.188 $g/cm^3$ and F(000), 692 $e^-$. Disordered THF solvent was accounted for using SQUEEZE, which found void spaces of 274 $Å^3$ with 79 $e^-$.