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# A Tripodal Ligand Constructed from Mesoionic Carbene Donors

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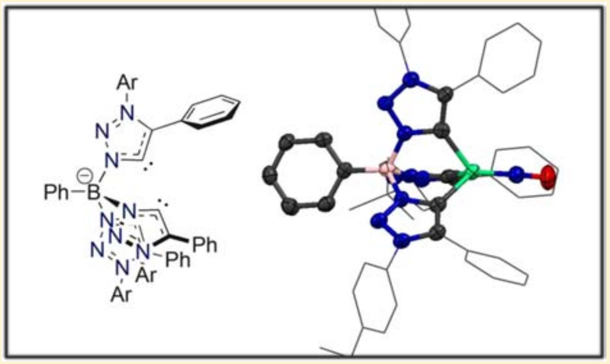
*Supporting Information*

**ABSTRACT:** A tripodal ligand constructed solely from mesoionic carbene donors is reported. The donor strength of this ligand is lower than most imidazol-2-ylidene-based tris(carbene)borate ligands, as measured by IR spectroscopy of $\{NiNO\}^{10}$ and $\{Mn(CO)_3\}^+$ derivatives. The attenuated donor strength is proposed to be due to the collective electron-withdrawing effect of the ligand's aryl substituents.



## INTRODUCTION

Tris(carbene)borate ligands, first introduced by Fehlhammer in the 1990s,[1] provide a facial array of *N*-heterocyclic carbene donors in the same topology as the classic tris(pyrazolyl)borate ligands. Bulky tris(carbene)borate ligands, which create low coordination environments,[2] are strong donors that help stabilize high oxidation states, as exemplified by the isolation of iron(IV)[3] and iron(V)[4] nitride complexes.

Although most tris(carbene)borate ligands are based on imidazol-2-ylidene donors, other stabilized carbenes (Figure 1) also have been incorporated into the ligand framework. Thus, more weakly donating tris(carbene)borates that incorporate 1,2,4-triazol-5-ylidene and benzimidazol-2-ylidene donors have recently been reported.[5] The relative donor strengths of these different families of tris(carbene)borate ligands have been evaluated from $\nu_{NO}$ in four-coordinate $\{NiNO\}^{10}$ derivatives and generally follow the same order established for their monodentate analogues.[5,6]

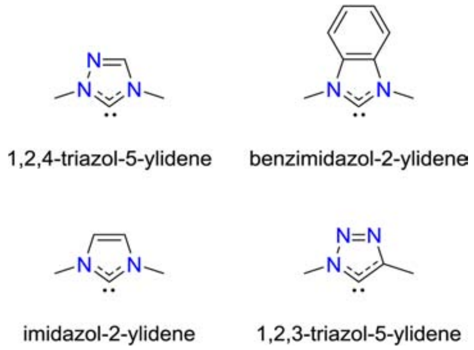


**Figure 1.** Donor groups that have been incorporated into the tris(carbene)borate framework.

On the basis of these results, it might be expected that assembling tris(carbene)borates with more strongly donating *N*-heterocyclic carbenes will provide tripodal ligands with even greater donor strength. Such ligands may better stabilize unusually high oxidation states than existing platforms. Although many strongly donating monodentate carbenes have been reported, 1,2,3-triazol-5-ylidenes are of particular interest due their combination of very high donor strength and ease of synthetic access.[7] These mesoionic carbenes have been found to be stronger donors than imidazol-2-ylidenes by a number of measures, including IR,[7] X-ray photoelectron,[8] and $^{13}C$ NMR spectroscopies.[9]

In this paper, we report the synthesis of a new tris(carbene)borate ligand that incorporates 1,2,3-triazol-5-ylidene donors. Despite expectations, the donor strength of this ligand is lower than anticipated, as evaluated in two different probe metal complexes.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glovebox. Glassware was dried at 150 °C overnight. Diethyl ether, *n*-pentane, tetrahydrofuran (THF), and toluene were purified by the Glass Contour solvent purification system. Deuterated benzene was first dried with $CaH_2$, then over Na/benzophenone, and then the solvent was vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. All

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reagents were purchased from commercial vendors and used as received. The compounds Ni(NO)$(PPh_3)_2$Br and [Mn$(CO)_3$($^t$BuCN)Br$]_2$ were prepared according to literature procedures.[10,15] $^1$H NMR and $^{13}$C NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) at 22 °C. Resonances in the $^1$H NMR spectra are referenced either to residual $CHCl_3$ at $\delta = 7.26$ ppm or $C_6D_5H$ at $\delta = 7.16$ ppm. Resonances in the $^{13}$C NMR spectra are referenced to residual $CHCl_3$ at $\delta = 77$ ppm. Infrared spectra were recorded on a Perkin−Elmer Spectrum One FTIR spectrophotometer. Elemental analysis was performed by Robertson Microlit Laboratories, Madison, NJ.

**Preparation of 1-Azido-4-*tert*-butylbenzene.** This compound was prepared by a slightly modified literature procedure.[11] To a stirred solution of 4-*tert*-butylaniline (15.9 mL, 14.9 g, 0.1 mol) in water (50 mL) at 0 °C was added concentrated HCl (17.5 mL, 0.21 mol). After stirring for 20 min, a solution of $NaNO_2$ (7.2 g, 0.1 mmol) in water (30 mL) was added dropwise to the reaction mixture while maintaining the reaction temperature below 5 °C. After stirring for 10 min, a solution of $NaN_3$ (6.7 g, 0.1 mmol) in water (30 mL) was added dropwise to the reaction mixture while maintaining the reaction temperature below 5 °C. The reaction mixture was stirred below 5 °C for 30 min, followed by stirring at ambient temperature for 3 h. The reaction mixture was extracted with 2 × 100 mL of hexanes. The combined organic layers were dried over anhydrous $NaSO_4$, purified by passing through a short plug of silica gel to afford an orange yellow liquid (16.2 g, 92%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, $J = 7.2$, 2H, ArH), 6.96 (d, $J = 7.2$, 2H, ArH), 1.32 (s, 9H, $C(CH_3)_3$).

**Preparation of 1-(4-*tert*-Butylphenyl)-5-phenyl-1*H*-1,2,3-triazole.** The synthetic method was adapted from a literature procedure.[11] A 250 mL round-bottom flask was charged with 1-azido-4-*tert*-butylbenzene (5.0 g, 28 mmol) and phenylacetylene (2.9 g, 3.1 mL, 28 mmol) in DMSO (50 mL), which was then purged with $N_2$ for 10 min. A solution of tetramethylammonium hydroxide (0.5 g, 5.5 mmol) in water (1.5 mL) was added, and the reaction mixture immediately turned to dark orange. After the reaction was stirred at ambient temperature for 18 h, the resulting solution was poured into water (1 L) followed by stirring for 2 h. The crude off-white compound was filtered, washed with water, and dried in vacuo. The desired product was recrystallized from concentrated diethyl ether (5.6 g, 88%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.85$ (s, 1H, ArH), 7.44−7.27 (m, 9H, ArH), 1.34 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 153$, 138, 135, 133, 130, 130, 130, 129, 128, 127, 126, 124, 35, 32. Anal. Calcd for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 78.13; H, 6.84; N, 15.32.

**Preparation of $1^{2+}(OTf)_2$.** The synthetic method was adapted from a literature procedure.[2b] 1-(4-*tert*-Butylphenyl)-5-phenyl-1*H*-1,2,3-triazole (3.5 g, 15 mmol) was added to a stirred solution of $PhBCl_2$ (0.79 g, 5 mmol) in toluene (10 mL). After 5 min, TMSOTf (2.3 g, 10 mmol) was added, and the reaction mixture was heated to 120 °C for 1 day. After the solution cooled to room temperature, the supernatant was decanted, diethyl ether (100 mL) was added, and the solvent was heated to reflux. The colorless solid was collected by filtration, washed with cold diethyl ether (30 mL), and dried in vacuo (4.7 g, 77%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 8.95$ (s, 3H, ArH), 7.52−7.38 (m, 32H, ArH), 1.31 (s, 27H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 155$, 143, 135, 133, 132, 131, 130, 129, 129, 128, 127, 126, 125, 123, 35, 31. Anal. Calcd for $C_{62}H_{62}BF_6N_9O_6S_2$: C, 61.13; H, 5.13; N, 10.35. Found: C, 60.74; H, 5.29; N, 10.28.

**Preparation of 2.** Under a $N_2$ atmosphere, a solution of LDA (33 mg, 0.3 mmol) in THF (2 mL) was added to a stirred slurry of $1^{2+}(OTf)_2$ (122 mg, 0.1 mmol) in THF (3 mL). The reaction was stirred at ambient temperature for 2 h. The $^1$H NMR spectrum of the crude reaction product is consistent with PhB(1-(4-$^t$Bu$C_6H_4$)-5-$C_6H_5C_2N_3)_3$Li. $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 8.61$ (d, $J = 9.2$, 2H, ArH), 7.54 7.48 (m, 3H, ArH), 6.93 6.84 (m, 27H, ArH), 1.06 (s, 27H, $C(CH_3)_3$). At this point, $Ni(PPh_3)_2$(NO)Br (69 mg, 0.1 mmol) in THF (2 mL) was added, and the resulting solution was stirred for 3 h at ambient temperature. The volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered through Celite. The filtrate was dried in vacuo to yield a red-orange solid (63 mg, 63%). Crystals suitable for X-ray diffraction were grown from slow diffusion of *n*-pentane to a diethyl ether solution of the complex at −30 °C. $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 9.26$ (d, $J = 7.2$, 2H, ArH), 7.93 (d, $J = 7.6$, 2H, ArH), 7.61 (t, $J = 7.6$, 1H, ArH), 7.13−6.82 (m, 27H, ArH), 0.98 (s, 27H, $C(CH_3)_3$). IR: (THF) $\nu_{NO} = 1709$ cm$^{-1}$. Anal. Calcd for $C_{60}H_{59}BN_{10}NiO\cdot 4C_4H_{10}O$: C, 70.10; H, 7.66; B, 0.83; N, 10.76. Found: C, 69.86; H, 7.17; N, 11.09.

**Preparation of 3.** Under a $N_2$ atmosphere, a solution of LDA (33 mg, 0.3 mmol) in THF (2 mL) was added to a stirred slurry of $1^{2+}(OTf)_2$ (122 mg, 0.1 mmol) in THF (3 mL). After the reaction was stirred at ambient temperature for 2 h, a solution of [Mn$(CO)_3$($^t$BuCN)Br$]_2$ (31 mg, 0.05 mmol) in THF (2 mL) was added to the reaction mixture. The resulting solution was stirred for 3 h at ambient temperature, the volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered through Celite. The filtrate was concentrated to approximately 2 mL and precipitated with *n*-pentane (5 mL) to give a yellow solid (87 mg, 82%). $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 9.51$ (d, $J = 7.6$, 2H, ArH), 7.76−7.68 (m, 8H, ArH), 7.49 (t, $J = 6.8$, 1H, ArH), 7.06−6.96 (m, 9H, ArH), 6.83 (d, $J = 8.4$, 6H, ArH), 6.72 (d, $J = 8.4$, 6H, ArH), 0.89 (s, 27H, $C(CH_3)_3$). IR: (THF) $\nu_{CO} = 1987$, 1892 cm$^{-1}$. Anal. Calcd for $C_{63}H_{59}BMnN_9O_3\cdot 4H_2O$: C, 67.08; H, 5.99; N, 11.18. Found: C, 66.92; H, 6.31; N, 11.27.

**Preparation of PhB(MesIm)$_3$Mn(CO)$_3$.** Under a $N_2$ atmosphere a solution of LDA (33 mg, 0.3 mmol) in $Et_2O$ (2 mL) was added to a stirred slurry of PhB(MesImH)$_3$(OTf)$_2$ (95 mg, 0.1 mmol) in $Et_2O$ (3 mL) at −78 °C. The reaction was stirred for 1 h at −78 °C. After the reaction was allowed to warm up to ambient temperature, [Mn$(CO)_3$($^t$BuCN)Br$]_2$ (31 mg, 0.05 mmol) in $Et_2O$ (2 mL) was added, and the resulting solution was stirred for 3 h. The volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered through Celite. The filtrate was dried in vacuo to yield an orange solid (62 mg, 79%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at −30 °C (Figure S1, Supporting Information). $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 8.20$ (d, $J = 7.6$, 2H, ArH), 7.46 7.41 (m, 3H, ArH), 7.25 (s, 3H, ArH), 6.84 (s, 6H, ArH), 6.20 (s, 3H, ArH), 2.10 (s, 18H, $ArCH_3$), 2.01 (s, 9H, $ArCH_3$). IR: (THF) $\nu_{CO} = 1996$, 1900 cm$^{-1}$.

**Single-Crystal X-ray Diffraction.** Crystals were mounted on a MiTeGen support 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 Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo K$\alpha$ fine-focus tube ($\lambda = 0.71073$ Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS). Structure solution and refinement was achieved using the Bruker SHELXTL software package.

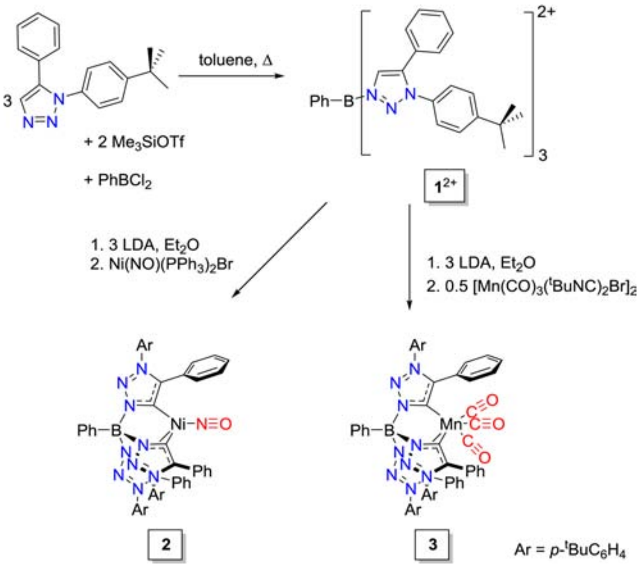
## ■ RESULTS AND DISCUSSION

The 1,2,3-triazol-5-ylidene-based tris(carbene)borate ligand was prepared by a similar synthetic route to that used for the imidazol-2-ylidene analogues. Specifically, 1-(4-*tert*-butylphenyl)-5-phenyl-1*H*-1,2,3-triazole (prepared from the [2 + 3] cycloaddition of 1-azido-4-*tert*-butylbenzene and phenylacetylene)[11] was heated in the presence of $Me_3SiOTf$ and $PhBCl_2$, resulting in precipitation of the dication $1^{2+}OTf_2$. The compound was characterized by $^1$H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. A notable feature of the $^1$H NMR spectrum is the very downfield shifted resonance attributed to the triazolium protons, at $\delta$ 8.95 ppm.

Deprotonation of $1^{2+}OTf_2$ is achieved by reaction with 3 equiv of LDA in room temperature $Et_2O$. The $^1$H NMR spectrum of the crude product is consistent with 3-fold deprotonation, most notably by the absence of the resonance attributed to the triazolium protons. The deprotonated ligand was not isolated but instead transferred in situ to the $\{NiNO\}^{10}$

synthon, $Ni(NO)(PPh_3)_2Br$, yielding the red-orange complex **2** (Scheme 1).

**Scheme 1. Synthesis of a 1,2,3-Triazol-5-ylidene-Based Tris(carbene)borate Ligand and Its Metal Complexes**



The structure of complex **2** was determined by single-crystal X-ray diffraction, confirming a 3-fold symmetric structure, with nickel bound to the tripodal tris(carbene)borate and a terminal nitrosyl ligand (Figure 2). The metrical parameters are similar to those observed in related complexes. The Ni−N bond is short (1.642(3) Å) and the Ni−N−O bond angle is linear (177.9(3)°), similar to the case of many other tris(carbene)-borate $\{NiNO\}^{10}$ complexes.[5,6] Furthermore, the Ni−C distances are within the range previously observed for 1,2,4-triazol-5-ylidene-, benzimidazol-2-ylidene-, and imidazol-2-ylidene-based $\{NiNO\}^{10}$ tris(carbene)borate complexes. Aside from three Cu(I) complexes,[12] we are unaware of any other structurally characterized first-row transition metal complexes bearing 1,2,3-triazolyl-5-ylidenes. The bond lengths and angles within the 1,2,3-triazol-5-ylidene donors of complex **2** are the same within error of other structurally characterized 1,2,3-triazol-5-ylidene complexes.[7] Thus, incorporating this mesoionic donor into the tris(carbene)borate framework does not significantly alter its structural characteristics.

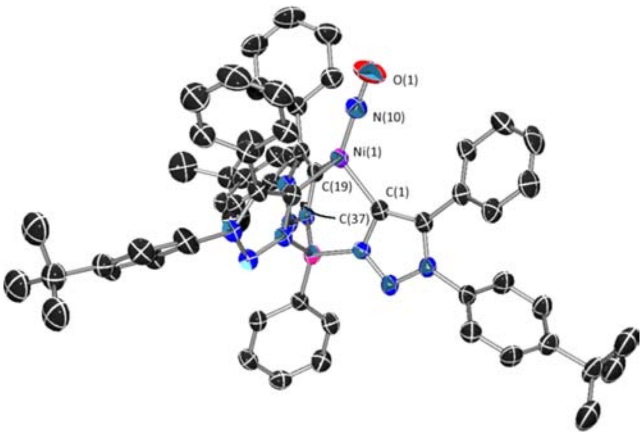


**Figure 2.** X-ray crystal structure of **2**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−N(10) 1.642(3); Ni(1)−C(1) 1.954(4); Ni(1)−C(19) 1.962(4); Ni(1)−C(37) 1.963(4); N(10)−O(1) 1.182(4); C(1)−Ni(1)−C(19) 92.32(15); C(1)−Ni(1)−C(37) 90.59(15); C(19)−Ni(1)−C(37) 89.23(14); Ni(1)−N(10)−O(1) 177.9(3).

The diamagnetic complex was also characterized by $^1H$ NMR and IR spectroscopy. The solution $^1H$ NMR spectrum is consistent with a 3-fold symmetric structure. Most notably, there is a single resonance ($\delta$ 0.98 ppm) that can be assigned to the *p-tert*-butyl groups of the tris(carbene)borate ligand. Interestingly, the resonance attributed to the ortho-protons $B(C_6H_5)$ group is shifted very far downfield ($\delta$ 9.26 ppm), likely due to the close proximity of the electronegative nitrogen atoms of the 1,2,3-triazol-5-ylidene ring.[13] The nitrosyl ligand is characterized by a strong absorption band in the IR spectrum ($\nu_{NO}$ = 1709 $cm^{-1}$).

Similarly to the synthesis of **2**, reaction of the in situ prepared tris(carbene)borate ligand with the $\{Mn(CO)_3\}^+$ synthon $[Mn(CO)_3(^tBuCN)Br]_2$ provides the yellow complex **3** in high yield (Scheme 1). The molecular structure has been determined by single-crystal X-ray diffraction, confirming the expected six-coordinate manganese complex bound to the tris(carbene)borate ligand and three carbonyl ligands (Figure 3). Although no manganese(I) carbonyl 1,2,3-triazol-5-ylidene complexes have been reported, the Mn−C(carbene) bond lengths in **3** are similar to those observed in structurally characterized imidazol-2-ylidene $\{Mn(CO)_3\}^+$ complexes.[14]

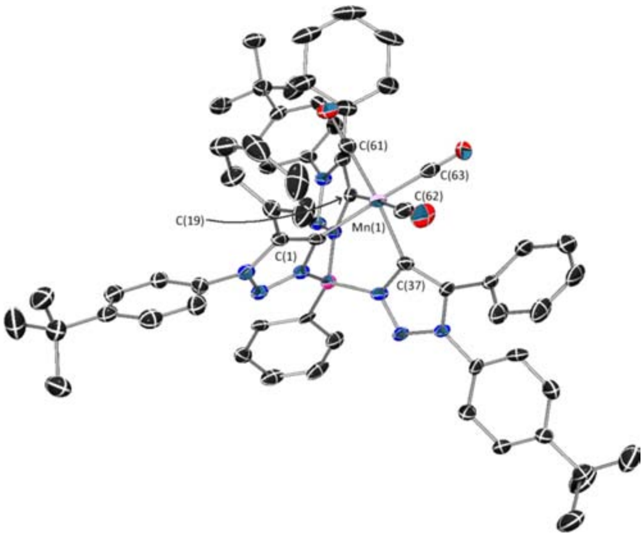
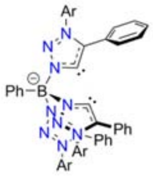
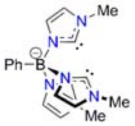


**Figure 3.** X-ray crystal structure of **3**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−C(1) 2.040(4); Mn(1)−C(19) 2.029(4); Mn(1)−C(37) 2.037(4); Mn(1)−C(61) 1.822(4); Mn(1)−C(62) 1.796(4); Mn(1)−C(63) 1.785(4); C(1)−Mn(1)−C(19) 83.63(14); C(1)−Mn(1)−C(37) 84.83(14); C(19)−Mn(1)−C(37) 87.21(14); C(1)−Mn(1)−C(63) 173.03(17); C(19)−Mn(1)−C(62) 175.96(15); C(37)−Mn(1)−C(61) 174.96(15).

The diamagnetic complex has also been spectroscopically characterized. As with complex **2**, a notable feature in the $^1H$ NMR spectrum is the highly shifted resonance attributed to the ortho-protons of the phenyl group bound to boron, which are observed at $\delta$ 9.51 ppm.[14] As expected for a complex having $C_{3v}$ symmetry, the carbonyl ligands are observed as two bands ($\nu_{CO}$ = 1987, 1892 $cm^{-1}$) in the IR spectrum.

Comparison of the frequencies for $\nu_{NO}$ in **2** and $\nu_{CO}$ in **3** with their imidazol-2-ylidene-based tris(carbene)borate analogues leads to an interesting observation (Table 1).[6,15] Both $\nu_{NO}$ and $\nu_{CO}$ are observed at lower frequencies for these complexes than analogues of an aryl-substituted tris(imidazol-2-ylidene)borate, but at higher frequency than analogues of an alkyl-substituted tris(imidazol-2-ylidene)borate. Moreover, $\nu_{NO}$ in **2** is found at a higher frequency than all other alkyl-substituted tris(imidazol-2-ylidene)borate $\{NiNO\}^{10}$ complexes.[6] Although monodentate 1,2,3-triazol-5-ylidene ligands are generally stronger donors than imidazol-2-ylidenes, replacing alkyl substituents by aryl groups in monodentate 1,2,3-triazol-5-ylidenes has been found to their attenuate donor strength,[16] albeit not to the same extent as observed in the case of this tripodal derivative. It is likely that the significantly reduced donor strength of this tris(carbene)borate ligand is due to the combined electron-withdrawing effect of the multiple aryl groups on the periphery of the tripodal ligand.

**Table 1. Stretching Frequencies in Selected $\{NiNO\}^{10}$ and $\{MnCO_3\}^+$ Complexes[a]**

| Ligand[b] | $\nu_{NO}$ in $\{NiNO\}^{10}$ | $\nu_{CO}$ in $\{Mn(CO_3)\}^+$ |
|---|---|---|
|  | 1709 | 1987, 1892 |
|  | 1697[c] | 1986, 1887[d] |
|  | 1724[c] | 1996, 1900[e] |

[a] Infrared spectra measured in THF solution, stretching frequencies listed in cm$^{-1}$. [b] Ar = $p$-$^{t}$BuC$_6$H$_4$. [c] See ref 6. [d] Previously measured in MeCN where $\nu_{CO}$ = 1990, 1889 cm$^{-1}$; see ref 16. [e] This complex has also been structurally characterized, see the Supporting Information for details.

## ■ CONCLUSION

In summary, we have prepared a tripodal ligand based on mesoionic 1,2,3-triazol-5-ylidene donors and shown that it coordinates to mid and late first-row transition metals. The donor strength of this ligand is lower than expected, which we have attributed to the collective effect of the multiple electron-withdrawing aryl substituents on the *N*-heterocyclic carbenes. This result highlights an important subtlety in the design of multidentate ligands incorporating multiple strong donors.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data in CIF format, ORTEP of PhB(MesIm)$_3$Mn(CO)$_3$, and data showing the correlation between BPh *o*-H with the average distance of the protons from the N2 of the 1,2,3-triazol-5-ylidene group. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interests.

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