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Oxygen Insertion Reactions of Mixed *N*-Heterocyclic Carbene-Oxazolinylborato Zinc Alkyl Complexes

Songchen Xu, William C. Everett, Arkady Ellern, Theresa L. Windus, and Aaron D. Sadow*

We report the synthesis of a new mixed oxazoline-carbene scorpionate ligand, bis(4,4-dimethyl-2-oxazolinyl)(1-mesitylimidazolyl)phenylborate (**[PhB(Ox^{Me2})$_2$Im^{Mes}]$^-$**). Reactions of the protonated form PhB(Ox^{Me2})$_2$(Im^{Mes}H) with dialkylzinc compounds provide four-coordinate zinc alkyl complexes, and X-ray diffraction studies of the {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnR (R = Me, Et) compounds show significant structural distortions involving the R groups shifting away from the carbene donor. The reaction of {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnEt (**3**) and O_2 provides an isolable mononuclear zinc alkylperoxide {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnOOEt (**4**), which has been characterized by single crystal X-ray diffraction and ^{17}O NMR spectroscopy.

Introduction

Reactions of metal-carbon bonds and O_2 are important potential components of new approaches to green oxidative catalysis. Often these reactions can be complicated by unselective product formation from overoxidation rather than formation of metallo-alkylperoxides that might be used as mediators of selective oxidation. This challenge affects organozinc chemistry, and the vigorous reactions of zinc alkyl compounds and oxygen are often difficult to control.[1] For example, reactions of $ZnEt_2$ and O_2 give $Zn(OEt)_2$ or EtZnOEt, while $ZnMe_2$ and O_2 provide MeZnOMe rather than [Zn]OOR.[2-4] Lithium zincates, which can show enhanced reactivity in metalation in comparison to zinc alkyls,[5] also react with O_2 to give bridging alkoxides.[6, 7] Only recently, the interaction of organozinc compounds and oxygen provided isolable and crystallographically characterized zinc alkylperoxide products, and this isolation often required carefully controlled preparative conditions.[3, 8-13] In addition, the products are generally multimetallic species with bridging alkoxide or alkylperoxide groups.

Recently, the synthesis of To^{M}ZnOOR (To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) by reaction of To^{M}ZnR (R = Et, *n*-C_3H_7, *i*-C_3H_7, *t*-Bu) and O_2 was described.[14] In contrast to these alkylzinc compounds, To^{M}ZnMe and To^{M}ZnH are inert to oxygen up to 120 °C and 100 psi of O_2, even in the presence of reacting To^{M}ZnEt/O_2 mixtures. In addition, tris(pyrazolyl)borato zinc alkyls are inert to O_2,[15, 16] while Tp$^{t\text{-}Bu}$MgR (Tp$^{t\text{-}Bu}$ = tris(3-*tert*-butyl)pyrazolylborate) react to give magnesium alkylperoxides.[17, 18] To^{M}MgMe reacts with O_2 to give To^{M}MgOMe species.[19] {HB(3-tBupz)$_2$(5-*t*-Bupz)}AlEt$_2$ (*t*-Bupz = $N_2C_3H_2$*t*-Bu) forms uncharacterized products upon addition of excess O_2.[20] On the basis of the pattern that suggests that To^M enhances the reactivity of Mg and Zn relative to Tp$^{t\text{-}Bu}$, we considered approaches to further enhance the reactivity of {L_2X}ZnMe or {L_2X}ZnH toward reaction with O_2 through modification of the ancillary ligand's electronic properties. However, strategies for this are not entirely straightforward. First, the To^M ligand is currently the only ancillary ligand that has provided monometallic zinc alkylperoxides from zinc alkyls and O_2. Second, in a comparative study, the infrared stretching frequencies of Tp*Re(CO)$_3$ and To^{M}Re(CO)$_3$ suggest To^M is the stronger donor of the two, while the $E_{1/2}$ data indicates that Tp*Re(CO)$_3$ is more easily oxidized than To^{M}Re(CO)$_3$.[21] Furthermore, the electron donating ability of tris(pyrazolyl)borates, at least in comparison to isoelectronic cyclopentadienide, is known to vary across the periodic table.[22]

Some direction comes from the proposed pathway for O_2 insertion into Zn–C bonds. Kinetic evidence supporting a radical chain mechanism in the reaction of To^{M}ZnEt and O_2 suggests that the inertness of To^{M}ZnMe toward O_2 is related to the lack of interaction of To^{M}ZnMe and $^{\bullet}$OOR.[14] We hypothesized that increasing the electron density on the zinc center could further increase the reactivity of zinc methyl and zinc hydride moieties. *N*-Heterocyclic carbenes (NHCs) are strong donors and should increase the electron density on the zinc center.[23-26] Moreover, tris(carbene)borates[27, 28] are sufficiently strong donors to allow access to high oxidation state 3*d* metal complexes,[29] such as a monometallic Fe(V) nitrido,[30] and bis(carbene)borates have been shown to stabilize low coordinate Ni(II) centers[31] and catalytic calcium and strontium centers.[32]. Mixed oxazolinylcarbene-coordinated rhodium complexes catalyze carbonyl hydrosilylation,[33-35] and the combination of oxazolines and *N*-heterocyclic carbenes may offer new possibilities in catalysis. Furthermore, an *N*-heterocyclic carbene zinc dihydride complex was recently isolated and shown to react with carbon dioxide, whereas ZnH_2 is unstable with respect to its elemental components and reportedly inert toward CO_2.[36]

Hence, a modified tridentate monoanionic scorpionate ligand in which one oxazoline ring in To^M was replaced with an *N*-heterocyclic carbene, generated from *N*-substituted imidazolium, was sought to affect the aforementioned reactivity of [Zn]–Me toward oxygen. Typically, *N*-heterocyclic carbenes coordinate to a zinc(II) center as neutral L-type ligands.[23, 24] However, *N*-borylation gives an overall uninegative charge to the bis(oxazolinyl)(carbene)phenylborate, and the reaction of the imidazolium borate and dialkylzinc results in a metalation reaction to give zwitterionic complexes. Recently, a bis(carborane)-substituted NHC provided an interesting dianionic carbene ligand.[37]

The present study describes the synthesis of the first example of a mixed oxazoline-carbene borate ligand, bis(oxazolinyl)(carbene)phenylborate, its metalation chemistry with alkyl zinc reagents to give tetracoordinate $\{L_2X\}ZnR$, and the reactions of $\{L_2X\}ZnR$ and O_2 to give the second example of an ancillary ligand that supports an isolable monomeric zinc alkylperoxide.

Experimental

General synthetic procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, toluene, and pentane were dried and deoxygenated using an IT PureSolv system. Benzene-d_6 was heated to reflux over Na/K alloy and vacuum transferred. Acetonitrile-d_3 was heated to reflux over CaH_2 and vacuum transferred. $[PhB(Ox^{Me2})_2]_n$,[38] and 1-mesitylimidazole[39] were synthesized according to literature procedures. Dimethylzinc solution (2.0 M in toluene) was purchased from Sigma-Aldrich and transferred to flask equipped with resealable Teflon valves for storage inside a glovebox. Diethylzinc was purchased from Strem Chemicals, Inc., and stored inside a glovebox in its original Swagelok cylinder.

^{1}H, $^{13}C\{^{1}H\}$, ^{11}B, and ^{17}O NMR spectra were collected on an Avance II 600 spectrometer. ^{15}N chemical shifts were determined by ^{1}H-^{15}N HMBC experiments on Avance II 600 spectrometer. ^{15}N chemical shifts were originally referenced to an external liquid NH_3 standard and recalculated to the CH_3NO_2 chemical shift scale by adding –381.9 ppm. Infrared spectra were recorded on a Bruker Vertex spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S in Iowa State Chemical Instrumentation Facility.

$PhB(Ox^{Me2})_2(Im^{Mes}H)LiCl$ (1·LiCl). $[PhB(Ox^{Me2})_2(LiCl)]_n$ (1.175 g, 3.598 mmol) was suspended in toluene (15 mL), and 1-mesitylimidazole (0.625 g, 3.36 mmol) was added to give a transparent brown solution. The reaction mixture was stirred at room temperature overnight. The product, as a white precipitate, was observed after 6 h. The resultant suspension was allowed to settle in a centrifuge over 7 min. at 4000 rpm, the top clear brown solution was decanted. The precipitate was washed with toluene (3 × 5 mL) and dried *in vacuo* to afford the product as a white solid (1.144 g, 2.232 mmol, 66.8%). ^{1}H NMR (acetonitrile-d_3, 600 MHz): δ 8.15 (s, 1 H, 2H-$N_2C_3H_3$Mes), 7.31-7.18 (m, 7 H, C_6H_5, 4- and 5H-$N_2C_3H_3$Mes), 7.07 (s, 2 H, *m*-$C_6H_2Me_3$), 3.74 (m, 4 H, $CNCMe_2CH_2O$), 2.33 (s, 3 H, *p*-$C_6H_2Me_3$), 2.01 (s, 6 H, *o*-$C_6H_2Me_3$), 1.33 (s, 6 H, $CNCMe_2CH_2O$), 1.24 (s, 6 H, $CNCMe_2CH_2O$). $^{13}C\{^{1}H\}$ NMR (acetonitrile-d_3, 150 MHz): δ 179.53 (br, $CNCMe_2CH_2O$), 146.96 (br, *ipso*-C_6H_5), 139.95 (2C-$N_2C_3H_3$Mes), 135.85 (*ipso*-$C_6H_2Me_3$), 133.33 (*o*-C_6H_5), 132.79 (*o*-$C_6H_2Me_3$), 130.18 (*m*-$C_6H_2Me_3$), 129.92 (*p*-$C_6H_2Me_3$), 128.49 (*m*-C_6H_5), 127.09 (4,5C-$N_2C_3H_3$Mes), 126.26 (*p*-C_6H_5), 123.12 (4,5C-$N_2C_3H_3$Mes), 78.30 ($CNCMe_2CH_2O$), 68.14 ($CNCMe_2CH_2O$), 28.72 ($CNCMe_2CH_2O$), 28.52 ($CNCMe_2CH_2O$), 21.17 (*p*-$C_6H_2Me_3$), 17.51 (*o*-$C_6H_2Me_3$). ^{11}B NMR (acetonitrile-d_3, 128 MHz): δ –9.2. $^{15}N\{^{1}H\}$ NMR (acetonitrile-d_3, 71 MHz): δ –139 ($CNCMe_2CH_2O$), –180 ($N_2C_3H_3$Mes), –202 ($N_2C_3H_3$Mes). IR (KBr, cm^{-1}): 3164 w, 2962 m, 2927 w, 1658 s (CN), 1546 m, 1461 w, 1135 s, 990 m, 969 m, 767 m. Anal. Calcd for $C_{28}H_{35}BClLiN_4O_2$: C, 65.58; H, 6.88; N, 10.93. Found: C, 67.76; H, 7.04; N, 10.56. Mp, 127-130 °C.

$\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnMe$ (2). $PhB(Ox^{Me2})_2(Im^{Mes}H)LiCl$ (**1**, 0.351 g, 0.684 mmol) was suspended in benzene (10 mL), and a 2.0 M solution of $ZnMe_2$ (0.380 mL, 0.760 mmol) in toluene was added. The white suspension was stirred at room temperature overnight. The suspension was filtered, and the solvent was removed under reduced pressure to afford a white solid, which was triturated with pentane (2 × 10 mL) and dried *in vacuo* (0.336 g, 0.611 mmol, 89.3%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.45 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *o*-C_6H_5), 7.55 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H, *m*-C_6H_5), 7.40 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, *p*-C_6H_5), 6.75 (s, 2 H, *m*-$C_6H_2Me_3$), 6.62 (s, 1 H, $N_2C_3H_2$Mes), 6.06 (s, 1 H, $N_2C_3H_2$Mes), 3.55 (d, $^{2}J_{HH}$ = 7.8 Hz, 2 H, $CNCMe_2CH_2O$), 3.53 (d, $^{2}J_{HH}$ = 7.8 Hz, 2 H, $CNCMe_2CH_2O$), 2.09 (s, 3 H, *p*-$C_6H_2Me_3$), 1.97 (s, 6 H, *o*-$C_6H_2Me_3$), 1.08 (s, 6 H, $CNCMe_2CH_2O$), 1.03 (s, 6 H, $CNCMe_2CH_2O$), –0.52 (s, 3 H, $ZnCH_3$). $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 150 MHz): δ 188.56 (br, $CNCMe_2CH_2O$), 186.02 (br, 2C-$N_2C_3H_2$Mes), 143.39 (*ipso*-C_6H_5), 138.29 (*p*-$C_6H_2Me_3$), 137.40 (*o*-$C_6H_2Me_3$), 137.01 (*o*-C_6H_5), 135.26 (*ipso*-$C_6H_2Me_3$), 129.47 (*m*-$C_6H_2Me_3$), 127.75 (*m*-C_6H_5), 127.23 (*p*-C_6H_5), 124.61 (4,5C-$N_2C_3H_2$Mes), 119.01 (4,5C-$N_2C_3H_2$Mes), 80.46 ($CNCMe_2CH_2O$), 66.14 ($CNCMe_2CH_2O$), 28.40 ($CNCMe_2CH_2O$), 28.31 ($CNCMe_2CH_2O$), 21.36 (*p*-$C_6H_2Me_3$), 18.19 (*o*-$C_6H_2Me_3$), –16.91 ($ZnCH_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ –9.9. $^{15}N\{^{1}H\}$ NMR (benzene-d_6, 71 MHz): δ –148 ($CNCMe_2CH_2O$), –171 (3N-$N_2C_3H_2$Mes), –190 (1N-$N_2C_3H_2$Mes). IR (KBr, cm^{-1}): 3123 w, 3076 w, 2956 s, 2926 m, 2891 m, 2824 w, 1594 s (CN), 1491 m, 1461 m, 1268 s, 1193 m, 1183 m, 1158 s, 1108 w, 1015 w, 951 m, 819 m, 704 m, 669 m, 640 m, 523 w. Anal. Calcd for $C_{29}H_{37}BN_4O_2Zn$: C, 63.55;

H, 6.78; N, 10.19. Found: C, 63.77; H, 6.72; N, 10.77. Mp, 173-176 °C.

{PhB(Ox^{Me2})$_2$Im^{Mes}}ZnEt (3). PhB(Ox^{Me2})$_2$(Im^{Mes}H)LiCl (**1**, 0.740 g, 1.44 mmol) was suspended in benzene (10 mL), and $ZnEt_2$ (0.165 mL, 1.61 mmol) was added. The white suspension was stirred at room temperature overnight. The suspension was filtered, the solvent was removed under reduced pressure, the resulting white solid was triturated with pentane (2 × 10 mL), and dried *in vacuo* (0.754 g, 1.34 mmol, 92.7%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.45 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *o*-C_6H_5), 7.55 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *m*-C_6H_5), 7.40 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, *p*-C_6H_5), 6.79 (s, 2 H, *m*-$C_6H_2Me_3$), 6.61 (s, 1 H, 4,5H-$N_2C_3H_2$Mes), 6.05 (s, 1 H, 4,5H-$N_2C_3H_2$Mes), 3.54 (m, 4 H, CNCMe$_2$C*H$_2$*O), 2.12 (s, 3 H, *p*-$C_6H_2Me_3$), 1.96 (s, 6 H, *o*-$C_6H_2Me_3$), 1.31 (m, 3 H, ZnCH$_2$C*H$_3$*), 1.07 (s, 6 H, CNC*Me$_2$*CH$_2$O), 1.04 (s, 6 H, CNC*Me$_2$*CH$_2$O), 0.44 (m, 2 H, ZnC*H$_2$*CH$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 188.53 (br, *C*NCMe$_2$CH$_2$O), 186.24 (2C-$N_2C_3H_2$Mes), 143.83 (br, *ipso*-C_6H_5), 138.47 (*p*-*C$_6$*H$_2$Me$_3$), 137.75 (*o*-*C$_6$*H$_2$Me$_3$), 136.90 (*o*-C_6H_5), 135.56 (*ipso*-$C_6H_2Me_3$), 129.44 (*m*-$C_6H_2Me_3$), 127.74 (*m*-C_6H_5), 127.20 (*p*-C_6H_5), 124.81 (4,5C-$N_2C_3H_2$Mes), 118.89 (4,5C-$N_2C_3H_2$Mes), 80.34 (CNCMe$_2$*C*H$_2$O), 66.09 (CN*C*Me$_2$CH$_2$O), 28.50 (CNC*Me$_2$*CH$_2$O), 28.28 (CNC*Me$_2$*CH$_2$O), 21.37 (*p*-C$_6$H$_2$*Me$_3$*), 18.06 (*o*-C$_6$H$_2$*Me$_3$*), 14.45 (ZnCH$_2$*C*H$_3$), –1.48 (Zn*C*H$_2$CH$_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ –10.0. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ –148 (CNCMe$_2$CH$_2$O), –170 (3N-$N_2C_3H_2$Mes), –190 (1N-$N_2C_3H_2$Mes). IR (KBr, cm^{-1}): 3132 w, 3008 w, 2971 s, 2927 s, 2885 s, 2852 m, 1592 s (CN), 1492 m, 1464 m, 1398 w, 1366 w, 1269 s, 1193 m, 1183 m, 1157 s, 1109 w, 1010 w, 963 s, 822 w, 744 m, 704 m, 672 m, 641 m. Anal. Calcd for $C_{30}H_{39}BN_4O_2Zn$: C, 63.90; H, 6.97; N, 9.94. Found: C, 64.07; H, 6.81; N, 10.32. Mp, 199-201 °C.

{PhB(Ox^{Me2})$_2$Im^{Mes}}ZnOOEt (4). A benzene solution (15 mL) of {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnEt (**3**, 0.700 g, 1.24 mmol) was degassed with "freeze-pump-thaw" cycles (3×), and then oxygen was added (1 atm). The solution was allowed to stir at room temperature overnight. Evaporation of the mixture to dryness gave a white solid. The crude product was dissolved in a minimal amount of toluene, and the solution was cooled to –30 °C to produce colorless crystals. The crystals were isolated by filtration, washed with pentane (2 × 2 mL) and dried *in vacuo* (0.621 g, 1.04 mmol, 84.0%). ^{1}H NMR (benzene-d_6, 600 MHz): δ 8.4 (2 H, *o*-C_6H_5), 7.5 (m, 2 H, *m*-C_6H_5), 7.4 (m, 1 H, *p*-C_6H_5), 6.7 (s, 2 H, *m*-$C_6H_2Me_3$), 6.6 (s, 1 H, 4,5H-$N_2C_3H_2$Mes), 6.0 (s, 1 H, 4,5H-$N_2C_3H_2$Mes), 3.8 (m, 2 H, ZnOOC*H$_2$*CH$_3$), 3.6 (m, 4 H, CNCMe$_2$C*H$_2$*O), 2.1 (s, 3 H, *p*-$C_6H_2Me_3$), 2.0 (s, 6 H, *o*-$C_6H_2Me_3$), 1.3 (s, 6 H, CNC*Me$_2$*CH$_2$O), 1.2 (s, 6 H, CNC*Me$_2$*CH$_2$O), 1.1 (m, 3 H, ZnOOCH$_2$C*H$_3$*). ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz): δ 188.77 (br, *C*NCMe$_2$CH$_2$O), 181.45 (2C-$N_2C_3H_2$Mes), 142.44 (br, *ipso*-C_6H_5), 138.38 (*p*-*C$_6$*H$_2$Me$_3$), 136.93 (*o*-*C$_6$*H$_2$Me$_3$), 136.84 (*o*-C_6H_5), 135.23 (*ipso*-$C_6H_2Me_3$), 129.44 (*m*-$C_6H_2Me_3$), 127.74 (*m*-C_6H_5), 127.32 (*p*-C_6H_5), 124.99 (4,5C-$N_2C_3H_2$Mes), 119.48 (4,5C-$N_2C_3H_2$Mes), 80.77 (CNCMe$_2$*C*H$_2$O), 71.29 (ZnOO*C*H$_2$CH$_3$), 65.9 (CN*C*Me$_2$CH$_2$O), 28.18 (CNC*Me$_2$*CH$_2$O), 28.04 (CNC*Me$_2$*CH$_2$O), 21.21 (*p*-C$_6$H$_2$*Me$_3$*), 18.00 (*o*-C$_6$H$_2$*Me$_3$*), 14.62 (ZnOOCH$_2$*C*H$_3$). ^{11}B NMR (benzene-d_6, 128 MHz): δ –10.0. ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ –150 (CNCMe$_2$CH$_2$O), –169 ($N_2C_3H_2$Mes), –190 ($N_2C_3H_2$Mes). ^{17}O NMR (benzene-d_6, 81 MHz): δ 328 (Zn*O*OCH$_2$CH$_3$), 165 (ZnO*O*CH$_2$CH$_3$). IR (KBr, cm^{-1}): 3133 w, 2966 s, 2927 m, 2888 m, 1610 s (CN), 1462 m, 1276 w, 1179 m, 1154 s, 1065 m, 968 s, 853 w, 849 w, 734 m, 704 m. Anal. Calcd for $C_{30}H_{39}BN_4O_4Zn$: C, 60.47; H, 6.60; N, 9.40. Found: C, 60.98; H, 6.64; N, 8.92. Mp, 138-141 °C.

X-ray Crystallography. Single-crystal X-ray diffraction experiments for **1-4** were carried out on a Bruker diffractometer with an APEX II CCD detector using graphite monochromated MoKα radiation with a detector distance of 50.6 mm. Full-sphere data collection with exposures of 30 s per frame were made with ω scans in the range 0–180° at φ = 0, 120, and 240°. A semi-empirical absorption correction was based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements[40] using SADABS software.[41] The experiment was optimized to collect data to a resolution of 0.71 Å, however, the datasets have been truncated to obtain the statistically relevant resolution. The positions of metal atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in the full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. All calculations were performed using the BRUKER APEX II software suite.[42]

SQUEEZE was used to treat diffused electron density in solvent accessible voids for structures **1**-**3**.[43] Crystallographic data and structure refinement parameters for **1**-**4** are summarized in Table 1.

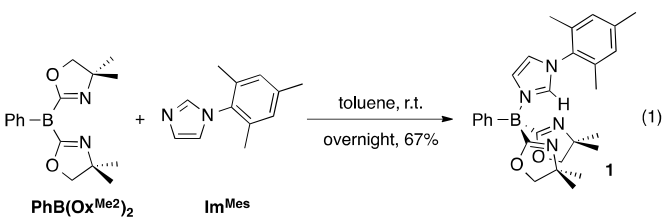
DFT calculations. All calculations were performed with the NWChem computational chemistry software.[44] Density functional theory with the B3LYP functional was used for single point energy calculations, geometry optimization and frequency calculations.[45-47] The 6-311G(d,p) basis set was used for H, C, N, O, and B.[48] The Stuttgart 1997 relativistic small core basis set with effective core potential was used for Zn.[49]

Results and discussion

The compound PhB(Ox^{Me2})$_2$(Im^{Mes}H) (**1**; Im^{Mes}H = 1-mesitylimidazolium; Ox^{Me2} = 4,4-dimethyl-2-oxazoline) is synthesized in 67% yield by the reaction of bis(4,4-dimethyl-2-oxazolinyl)phenylborane (**PhB(Ox^{Me2})$_2$**) and 1-mesitylimidazole (**Im^{Mes}**) in toluene (eqn. (1)).[38, 39] Previously, a related strategy for the synthesis of heteropodal multidentate oxazolinylborate ligands involved addition of sodium cyclopentadienide to PhB(Ox^{Me2})$_2$ to provide the compound Na[PhB(Ox^{Me2})$_2$(C$_5$H$_5$)].[50] It appears that this ligand synthesis approach has some versatility in varying donor groups linked to oxazolines through a borate center.

Table 1. Crystallographic data for compounds 1-4.

	1	**2**	**3**	**4**
Chemical formula	$C_{37}H_{44}BClLiN_4O_4$	$C_{29}H_{37}BN_4O_2Zn$	$C_{32.5}H_{45}BN_4O_2Zn$	$C_{33.5}H_{47}BN_4O_4Zn$
Formula weight	629.96	549.81	599.91	645.93
Crystal system	triclinic	trigonal	trigonal	monoclinic
Unit-cell dimensions	a = 11.152(1) Å b = 12.661(1) Å c = 13.378(1) Å α = 85.243(2)° β = 69.278(1)° γ = 88.683(2)°	$a = b$ = 29.159(2) Å c = 19.403(3) Å α = β = 90°; γ = 120°	$a = b$ = 28.780(3) Å c = 20.259(2) Å α = β = 90°; γ = 120°	a = 9.497(1) Å b = 26.859(3) Å c = 13.405(2) Å α = γ = 90° β = 96.814(2)°
Volume	1760.5(3) $Å^3$	14287(2) $Å^3$	14542(2) $Å^3$	3395.0(7) $Å^3$
Space group	P-1	R-3	R-3	P 1 2_1/n 1
Z	2	18	18	4
Reflections collected	19082	53056	53004	44529
Independent reflections	8984	8974	8740	7785
R_{int}	0.0261	0.0303	0.0356	0.0327
R $I>2\sigma(I)$	R_1 = 0.0424 wR_2 = 0.0963	R_1 = 0.0415 wR_2 = 0.1480	R_1 = 0.0314 wR_2 = 0.0839	R_1 = 0.0448 wR_2 = 0.1329
R_{all}	R_1 = 0.0610 wR_2 = 0.1062	R_1 = 0.0553 wR_2 = 0.1602	R_1 = 0.0432 wR_2 = 0.0878	R_1 = 0.0537 wR_2 = 0.1398



This material is poorly soluble in toluene and benzene, but dissolves readily in acetonitrile. The ^{1}H NMR spectrum of the substance, acquired in acetonitrile-d_3, contained a diagnostic downfield singlet at 8.15 ppm, which was assigned to the 2-H on the imidazolium ring. Signals at 1.24 (6 H) and 1.33 ppm (6 H) were assigned to oxazoline methyl groups and two singlets at 2.01 (6 H) and 2.33 ppm (3 H) were assigned to the mesityl group. For comparison, the ^{1}H NMR chemical shifts of Im^{Mes} appear at 7.06 (2-H), 1.58 (*ortho*-Mes), and 1.97 ppm (*para*-Mes) in acetonitrile-d_3. These signals are distinct from those of **1**, and this provides convinced evidence that the imidazole is coordinated to the boron center even in a donor-solvent such as acetonitrile. Inequivalent oxazoline methyl groups indicate that the C_{2v}-symmetry of $PhB(Ox^{Me2})_2$ is disrupted by coordination of the imidazole to the boron center. The ^{11}B NMR spectrum, also acquired in acetonitrile-d_3, showed one singlet at –9.2 ppm. This result is consistent with a four-coordinate boron center. The $^{13}C\{^1H\}$ NMR spectrum, acquired in acetonitrile-d_3, shows a sharp peak at 139.95 ppm and a broad peak at 179.62 ppm, which were assigned to the 2-C on the imidazolium ring and the 2-Cs on the oxazoline rings, respectively. Interestingly, the ^{15}N NMR chemical shifts for oxazoline and both imidazolium nitrogen atoms were obtained through ^{1}H-^{15}N HMBC experiments. The oxazoline chemical shift (–139 ppm) was easily identified by correlations to its methyl groups; both imidazolium nitrogen atoms correlated with the imidazolium 2-H, 4-H, and 5-H, although only 1-N (–202 ppm) generated crosspeaks with the mesityl group. That signal is similar to ^{15}N NMR values of 1-alkyl substituted imidazolium salts. The ^{15}N NMR chemical shift of the boron-coordinated 3-N (–180 ppm, referenced to nitromethane) is further downfield than the signals from alkyl and aryl-substituted imidazoles,[51] although this signal is similar to that reported for silver-coordinated *N*-heterocyclic carbenes.[52] For comparison, the ^{15}N NMR chemical shifts of Im^{Mes} are –206 and –121 ppm for the 1-N and 3-N, respectively.

Crystals obtained from a concentrated toluene solution cooled to –30 °C were subjected to an X-ray diffraction study, verifying the connectivity of compound **1** as containing an imidazole coordinated to the boron center. A trace amount of benzene facilitates the crystallization and two benzene molecules are included in the unit cell. The molecular structure is shown to be the centrosymmetric dimer (**1**·LiCl)$_2$ (Figure 1); the two oxazolines of **1** are coordinated to a lithium cation, and each half of the dimer are related by a crystallographically imposed inversion center. As a result, the two imidazolium rings are located on opposite faces of the $(LiCl)_2$ parallelogram.

The Li centers are four coordinate, and the N1-Li1-N2 angle of 93.7(1)° and Cl1-Li1-Cl1# angle of 95.12(8)° are much smaller than the N1-Li1-Cl1 or N2-Li1-Cl1 angles that range from 112.8(1)° to 123.3(1)°. As expected based on VSEPR considerations, the Li1-Cl1-Li1# angles are acute (84.88(8)°).

LiCl is carried over in variable amounts from the reaction of 2-$LiOx^{Me2}$ and $PhBCl_2$ for preparation of $[PhB(Ox^{Me2})_2]_n$, although $[PhB(Ox^{Me2})_2]_n$ may be purified from LiCl by repeated extractions with benzene or by column chromatography. The solution phase NMR spectroscopy above describes **1**·LiCl, likely with acetonitrile-d_3 coordinated to the lithium center. The presence of LiCl does not interfere in later

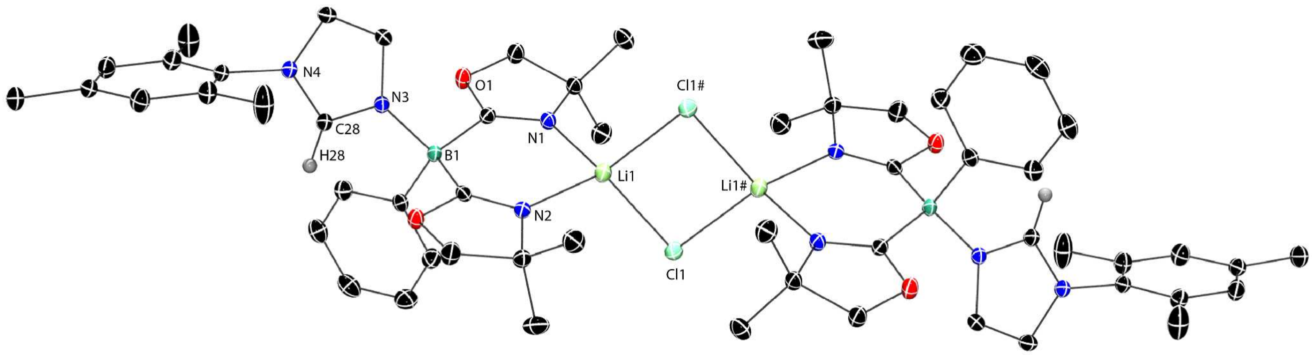
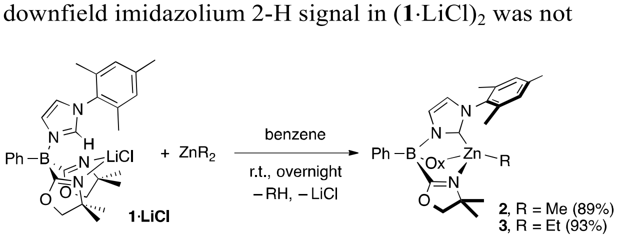


Figure 1. Rendered thermal ellipsoid diagram of (**1**·LiCl)$_2$ with ellipsoids plotted at 35% probability. H28 atoms are illustrated, but all other H atoms and two co-crystallized benzene molecules are not depicted for clarity. Atoms with designator # related to the basic atom with transformation *2-x, 2-y, 2-z*. Selected interatomic distances (Å): Li1-N1, 2.070(3); Li1-N2, 2.079(3); Li1-Cl1, 2.371(2); Li1-Cl1#, 2.439(2). Selected interatomic angles (°): N1-Li1-N2, 93.7(1); Cl1-Li1-Cl1#, 95.12(8); Li1-Cl1-Li1#, 88.88(8); N1-Li1-Cl1, 119.3(1); N1-Li1-Cl1#, 112.8(1); N2-Li1-Cl1, 114.7(1); N2-Li1-Cl1#, 123.3(1), Li1-Cl1-Li1#, 84.88(8).

metalation chemistry with dialkylzinc compounds, and (**1**·LiCl)$_2$ may be used in further reactions described here. Although LiCl sometimes enhances metalation chemistry,[5, 53, 54] typically the LiCl is associated with the base rather than the substrate. In fact, LiCl must be removed from (**1**·LiCl)$_2$ for the successful deprotonation of **1** by more aggressive bases, such as PhCH$_2$K. That work will be described elsewhere. In addition, elemental analysis data for (**1**·LiCl)$_2$ was consistently high for carbon which may reflect slightly variable quantities of LiCl and coordinated donor in **1**.

Compound **1** is readily metalated at the imidazolium 2-H by reaction with dialkylzinc compounds to give {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnR (R = Me (**2**), Et (**3**)) in 89 and 93% yield, respectively (eqn. (2)). The most convenient preparation involves the reaction of (**1**·LiCl)$_2$ as a suspension in benzene with ZnMe$_2$ or ZnEt$_2$. As the reaction proceeds and **2** or **3** is formed, LiCl is eliminated and the cloudy suspension becomes less opaque. Methane or ethane by-products are formed, and these species are detected by ^{1}H NMR spectroscopy in micromolar scale reactions performed in benzene-d_6.

A singlet resonance at –0.52 ppm in the ^{1}H NMR spectrum of **2** in benzene-d_6 was assigned to a zinc methyl group on the basis of its upfield chemical shift and integration (3 H). The downfield imidazolium 2-H signal in (**1**·LiCl)$_2$ was not



(2)

observed in the spectra of **2** or **3**, which suggested that the 2-C on the imidazolium had been metalated in both cases. The oxazoline groups are equivalent, as are the *ortho*-methyl groups on the mesityl ring. These data indicate that the compounds have effective C_s symmetry. For compound **2** for example, two singlets in the alkyl region at 1.03 (6 H) and 1.08 ppm (6 H) assigned to the methyl groups on the oxazoline rings correlated in a ^{1}H-^{15}N HMBC experiment to a ^{15}N NMR signal at –148 ppm (referenced to nitromethane). The zinc methyl ^{1}H NMR resonances also correlated with the oxazoline nitrogen, proving that both oxazolines are coordinated to the zinc center in solution. Three additional crosspeaks in the ^{1}H-^{15}N HMBC experiment showed correlations between the imidazole 1-N (–190 ppm) and the ^{1}H NMR resonances assigned to *meta*-C$_6$H$_2$Me$_3$ (6.75 ppm) and the imidazole 4-H and 5-H (6.68 and 6.08 ppm). Two more crosspeaks between a ^{15}N NMR signal at –171, assigned to the 3-N bonded to the boron center, and the imidazole 4-H and 5-H completed the assignment of the nitrogen centers in **2**. Thus, the ^{15}N NMR chemical shift values for both oxazoline and imidazole groups change from those of (**1**·LiCl)$_2$ upon metalation with zinc. In the ^{13}C{^{1}H} NMR spectrum, a signal at 186.02 ppm was assigned to the zinc-coordinated *N*-heterocyclic carbene. This chemical shift is essentially identical to that reported for HB(Im$^{t\text{-Bu}}$)$_3$MgBr.[28] Similar ^{15}N and ^{13}C NMR data describing the ancillary mixed oxazoline-carbene borate ligand were obtained for compound **3**.

Compounds **2** and **3** are readily crystallized from concentrated benzene solutions at room temperature. Results from single crystal X-ray diffraction studies are presented in Figures 2 and 3. Interestingly, both **2** and **3** are solved in the space group R-3 (trigonal crystal system).

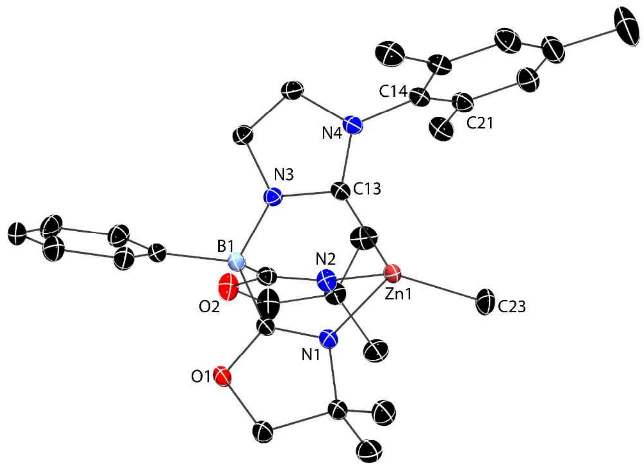


Figure 2. Rendered thermal ellipsoid diagram of {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnMe (**2**) with ellipsoids at 35% probability. H atoms are not depicted for clarity. Selected interatomic distances (Å): Zn1-C13, 2.043(2); Zn1-N1, 2.104(2); Zn1-N2, 2.193(2); Zn1-C23, 1.978(2). Selected interatomic angles (°): B1-Zn1-C23, 166.8(1); C13-Zn1-C23, 138.1(1); N1-Zn1-C23, 116.08(9); N2-Zn1-C23, 120.1(1); N1-Zn1-N2, 88.79(7); C13-Zn1-N1, 92.74(7); C13-Zn1-N2, 88.27(7); C13-N4-C14-C21, 60.1(3).

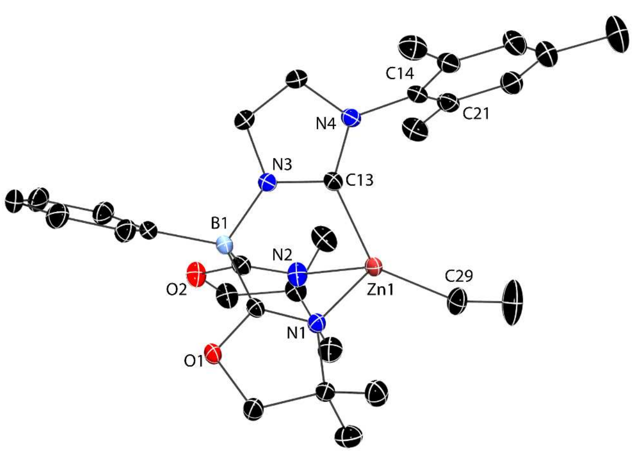


Figure 3. Rendered thermal ellipsoid diagram of {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnEt (**3**) with ellipsoids at 35% probability. H atoms and 0.5 disordered pentane are not depicted for clarity. Selected interatomic distances (Å): Zn1-C13, 2.043(1); Zn1-N1, 2.125(1); Zn1-N2, 2.165(1); Zn1-C29, 1.979(2). Selected interatomic angles (°): B1-Zn1-C29, 164.8(1); C13-Zn1-C29, 140.01(6); N1-Zn1-C29, 118.04(6); N2-Zn1-C29, 115.94(6); N1-Zn1-N2, 88.61(5); C13-Zn1-N1, 92.25(5); C13-Zn1-N2, 88.36(5); C13-N4-C14-C21, 63.5(3).

The distinguishing feature of the molecular structures of both compounds **2** and **3** is a distortion of the zinc alkyl group from the pseudo tetrahedral position where the ligand-zinc-carbon angles would be similar and the boron-zinc-carbon angles would be 180°. Instead, the B1-Zn1-C23 and B1-Zn1-C29 angles in **2** and **3** are 166.8(1) and 164.8(1)°, respectively. The large obtuse carbene-zinc-alkyl angles in **2** and **3** are 138.1(1) and 140.01(6)°, while the nitrogen-zinc-carbon angles range from 116 – 120°. The three angles from the donors on the ancillary ligand are similar in both mixed carbene-oxazolinylborato zinc methyl and ethyl compounds (ranging from 88 – 92°).

The mesitylcarbene donor is much larger than the oxazoline donors, and the steric properties of [PhB(Ox^{Me2})$_2$Im^{Mes}]$^-$ (solid angle, 6.26 steradians, 49.9%) are greater than those of [To^M]$^-$ (solid angle, 5.51 steradians, 43.9%).[55, 56] The steric bulk of the mesitylcarbene donor might be responsible for the distortion. However, a few features argue against sterics as responsible for the unusual geometry. First, there are no unfavorable interligand interactions, as determined by the above solid angle calculations. Second, the zinc-oxazoline and zinc-alkyl distances in **2** and **3** are similar to those in the C_{3v}-symmetric, undistorted To^{M}ZnMe and To^{M}ZnEt.[14, 57] For example, the Zn–C interatomic distances in **2** and **3** are 1.979(2) and 1.978(2) Å, whereas the distances are 1.97 and 1.99 Å in To^{M}ZnMe and To^{M}ZnEt, respectively. The Zn–N interatomic distances in **2** and **3** range from 2.10 – 2.19 Å, whereas the Zn–N distances in To^{M}ZnEt and To^{M}ZnMe range from 2.06 – 2.10 Å. Thus, the coordination environment at zinc appears unremarkable with the exception of the unexpected alkyl ligand position.

Additionally, the mesityl group is twisted with respect to the imidazole ring by approximately 60° in both **2** and **3**. The shortest H···H distance in **2** between a mesityl *ortho*-methyl and the zinc methyl is 2.83 Å (the C···C distance is 3.877 Å) and these are greater than the sum of the van der Waals radii of H and Me groups. In compound **3**, the ethyl ligand is oriented with the methyl group pointing into the open space resulting from the canted mesityl group. It is unreasonable that the mesityl ring would twist to form close contacts to an alkyl group on zinc, and then subsequently push the alkyl group into a distortion.

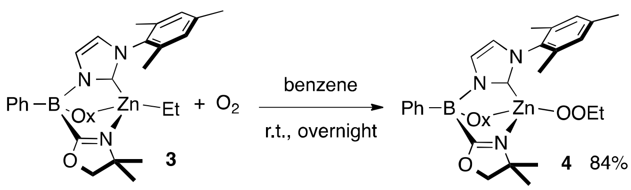
However, an electronic effect for the alkyl group's unusual position would also be surprising in the context of a metal-centered electronic distortion because compounds **2** and **3** are closed-shell, d^{10} complexes and unlikely to be distorted, even though the structural distortion of **2** and **3** is reminiscent of the tetragonal distortion of Cu(II) in spinels.[58] In addition, bending the ligand from a pseudo-tetrahedral position does not lower the overall symmetry of the complex.

To further probe these unusual structural features, the full structure of **2** was computationally optimized. In the gas-phase minimized structure, the methyl distortion is maintained (carbene-zinc-carbon angle, 139.4°), while the imidazole-mesityl torsion angle rotates to 84.3° (in comparison to 60.1° in the structure obtained by X-ray diffraction). From this, we conclude that the canted mesityl group does not relate to the distortion of the zinc's coordination sphere.

To further emphasize this point, the methyl position was straightened with both gas-phase and X-ray mesityl torsion angles of 84.3° and 60.1°. In both cases, the energy of the linear

B-Zn-Me structures are higher by 0.9 and 1.2 kcal/mol, respectively, than structures with the observed B-Zn-Me angle of 167°. This small energy change related to the methyl position suggests that there are subtle electronic effects rather than steric effects in play and, indeed, it is difficult to identify any single electronic feature that is responsible for the distortion from pseudo-C_{3v} symmetry.

Compound **3** and O_2 (1 atm) react at room temperature overnight to give $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnOOEt$ (**4**) (eqn. (3)), which is isolated as a white solid in 84% yield. Other possible products, including zinc ethoxy $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnOEt$ or 2-*O*-imidazolone, were not detected in ^1H NMR spectra of crude reaction mixtures.



(3)

The reaction at the [Zn]-CH_2CH_3 is readily assessed by changes in the ^1H and $^{13}C\{^1H\}$ NMR spectra acquired in benzene-d_6. The ^1H NMR signals for the CH_2CH_3 appeared at 0.44 ppm in **3** and 3.8 ppm in **4**. The $^{13}C\{^1H\}$ NMR signals for the CH_2CH_3 was upfield of tetramethylsilane in the zinc alkyl starting material **3** at –1.48 ppm, and the signal in **4** was downfield in the ether region at 71.29 ppm. The 2-C signal in the $^{13}C\{^1H\}$ NMR spectra of **3** (186.24 ppm) and **4** (181.45 ppm) were barely affected by exposure to oxygen. In addition, **3** was allowed to react with ^{17}O-labelled O_2 to give **4**-$^{17}O_2$. An ^{17}O NMR spectrum acquired in benzene-d_6 contained two broad peaks at 328 and 165 ppm. The downfield resonance was assigned to the oxygen bonded to zinc (O_α), and the upfield resonance was then assigned to ZnO*O*Et (O_β); the difference $\Delta(\delta O)$ is 163 ppm ($\Delta(\delta O) = \delta O_\alpha - \delta O_\beta$). For comparison, the ^{17}O NMR signals for $To^MZnOOEt$ were detected at 319 and 169 ppm and have a smaller difference in chemical shift ($\Delta(\delta O)$ = 150 ppm),[14] while the signals for $Tp^{t\text{-}Bu}MgOOEt$ are even more separated ($\Delta(\delta O) = \delta O_\alpha - \delta O_\beta = 407 - 130 = 277$ ppm).[17,18] Thus, the ^{17}O chemical shifts of **4**-$^{17}O_2$ are upfield for O_α and downfield for O_β with respect to the corresponding shifts in $To^MZnOOEt$.

Compound **4** crystallizes from a concentrated toluene solution at –30 °C. The solution to the single crystal X-ray diffraction study confirmed that O_2 inserted into the Zn–C bond (Figure 4). Most importantly, the formation of a ZnOOEt moiety is confirmed, and the zinc-carbene interaction is intact. The OOEt ligand is disordered over two positions, and the interatomic distances and angles must be cautiously interpreted; however, it is worth noting that the model places O3a and O3b at the same position, and this position gives the same type of distortion observed and described above for compounds **2** and **3**. In addition, the C22-N4-C19-C12 torsion angle (72.3(2)°) that describes the mesityl group position is larger than in **2** and **3**.

As noted above, the alkyl ligands of **2** and **3** are distorted with respect to ideal positions. However, this distortion apparently did not translate into enhanced reactivity for the zinc methyl, at least with respect to the interaction of **2** and oxygen. In fact, compound **2** is stable under O_2 (1-3 atm) up to 60 °C. The inert nature of the zinc methyl in **2** follows the reactivity of To^MZnMe and To^MZnH, which, as noted above, also are inert toward reaction with O_2.

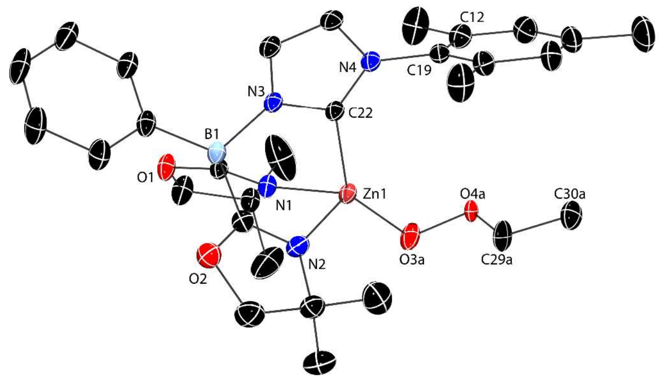


Figure 4. Rendered thermal ellipsoid diagram of $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnOOEt$ (**4**) with ellipsoids plotted at 35% probability. The OOCC heavy atom positions are disordered over two positions, and only O3a, O4a, C29a, C30a atoms of the alkyl peroxide moiety are shown. The two positions for the OOEt group were refined using similarity restraints. However, O3a and O3b positions are identical. H atoms and a disordered toluene solvent molecule are not depicted for clarity.

We were unable to isolate $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnOO$*t*-Bu from the reaction of **3** and *t*-BuOOH. Even though a small amount of ethane was detected by ^1H NMR spectroscopy in micromolar scale reactions performed in benzene-d_6, the majority of **3** remained unreacted at room temperature over 1 day. After 2 days at room temperature, a signal at 10.86 ppm assigned to a 2H-imidazolium moiety was observed as part of the major product suggesting protonation of the carbene.

Conclusions

We have described the preparation of a new heteroleptic monoanionic scorpionate ligand that contains two oxazoline donors and one *N*-heterocyclic carbene donor. There are some similarities between the tris(oxazolinyl)borate $[To^M]^-$ and the bis(oxazolinyl)(carbene)borate in the facile metalation reactions of H[ligand] by dialkylzinc reagents. Both ligands support four-coordinate monoalkyl zinc compounds. In addition, both To^MZnMe and $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnMe$ compounds are inert toward O_2, whereas both To^MZnEt and $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnEt$ react with O_2 to give isolable zinc alkylperoxides. Unlike To^MZnEt, $\{PhB(Ox^{Me2})_2Im^{Mes}\}ZnEt$ does not provide an isolable [Zn]OO*t*-Bu in its reaction with *t*-BuOOH. The ancillary ligand $[PhB(Ox^{Me2})_2Im^{Mes}]^-$ is only the second example of a ligand that supports a monometallic zinc alkylperoxide formed from O_2. Notably, the carbene moiety is inert toward O_2 as well as any $^{\bullet}$OOR present during the radical chain process that gives {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnOOEt. Additionally, a significant and systematic structural distortion of the compounds {PhB(Ox^{Me2})$_2$Im^{Mes}}ZnX has been observed, where the X group (Me, Et, OOEt) is distorted away from the carbene ligand in three structures determined by X-ray crystallographic diffraction studies. However, this distortion, or the substitution of an oxazoline in the To^{M}ZnR compounds with a carbene donor does not appear to affect the reactivity of zinc methyl or ethyl toward O_2, either by increasing the reactivity of the zinc methyl or decreasing the reactivity of the zinc ethyl toward O_2.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental data and spectra for compounds **1**·LiCl, **2**-**4**. Crystallographic data files (995354-995357) are available from the CCDC. Computational coordinates and energies. See DOI: 10.1039/b000000x/

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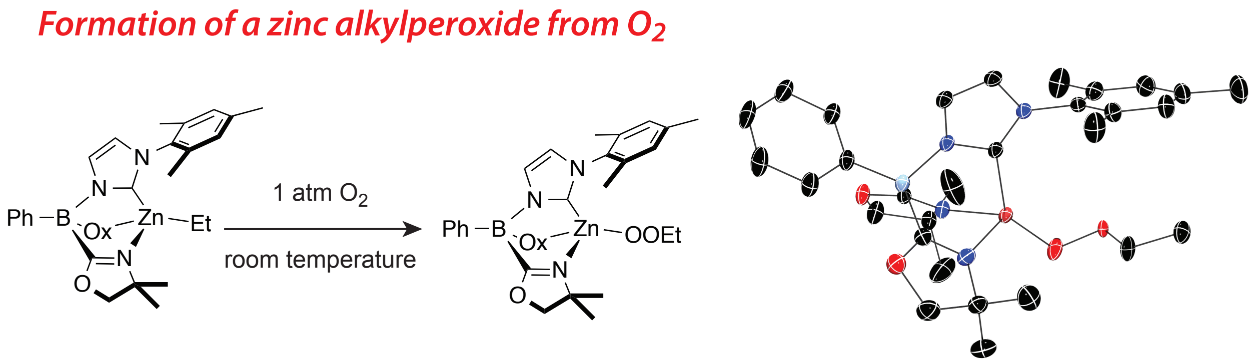

A oxazolinyl-carbene borate zinc ethyl compound reacts with O_2 at room temperature to provide a monometallic zinc ethylperoxide.