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Synthesis and Reactivity of Zinc and Aluminum Alkyl Derivatives Stabilized by Oxygen Tripod Ligands

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Zinc and aluminum alkyl derivatives $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$) and $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ of the oxygen tripod ligand system $L_{OEt} \equiv [CpCo\{P(O)(OEt)_2\}_3]^-$ (Cp = η^5-C_5H_5) have been synthesized by the reactions of the alkyls ZnR_2 and $Al(CH_3)_3$ with TlL_{OEt}. The zinc alkyls $L_{OEt}ZnR$ are precursors for a series of other half-sandwich complexes $L_{OEt}ZnX$ (X = Cl, I, CH_3CO_2, NO_3).

Introduction

We have recently described the use of the nitrogen-donor poly(pyrazolyl)hydroborato ligands[1] to provide well-defined coordination environments for a series of monomeric alkyl and hydride derivatives of the s- and p-block metals.[2] Here we report the use of the related oxygen-donor tripod ligand system $L_{OEt} \equiv [CpCo\{P(O)(OEt)_2\}_3]^-$ (Cp = η^5-C_5H_5), recently introduced by Kläui,[3] for the synthesis of alkyl derivatives of zinc and aluminum.

Results

The thallium derivative TlL_{OEt}, prepared by metathesis of $TlNO_3$ with NaL_{OEt}, is a useful reagent for the synthesis of half-sandwich zinc alkyl derivatives $L_{OEt}ZnR$. Thus, the complexes $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$) are readily prepared by the metathesis of ZnR_2 with TlL_{OEt} (eq 1). The alkyl derivatives $L_{OEt}ZnR$ are yellow crystalline solids that are soluble in hydrocarbons. ^1H and ^{13}C NMR spectra are in accord with the proposed formulation, and the ^1H NMR spectrum of $L_{OEt}ZnCH_3$, illustrated in Figure 1, is provided as a repesentative example. Selected NMR data (in which only the cyclopentadienyl resonances of the L_{OEt} ligand are reported) for all new complexes are presented in Table I, while a complete table of spectroscopic data is available as supplementary material.

$$ZnR_2 \xrightarrow{TlL_{OEt}} L_{OEt}ZnR \tag{1}$$

$Al(CH_3)_3$ reacts with TlL_{OEt} (or NaL_{OEt}) to give a binuclear complex of composition $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$, in which the tripod ligand is proposed to be coordinated to two different aluminum alkyl centers (eq 2). Evidence for the formulation of $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ is provided by the ^1H NMR spectrum (Figure 2), which shows three singlets due to aluminum methyl groups in the ratio 1:1:3. The two singlets in the ratio 1:1 are assigned to inequivalent methyl groups of the $[Al(CH_3)_2]$ group, with the remaining singlet due to coordinated $[Al(CH_3)_3]$. Furthermore, the observation of three sets of triplet resonances assigned to the methyl groups of the L_{OEt} ligand indicates that the C_3 symmetry of the tripod ligand has been reduced to C_s upon coordination. A *tentative* structure for $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ that is consistent with the NMR data is shown in Figure 2, in which a mirror plane passes through Co and the two Al atoms.

$$Al(CH_3)_3 \xrightarrow{TlL_{OEt}} L_{OEt}Al(CH_3)_2[Al(CH_3)_3] \tag{2}$$

The reactions of the zinc alkyl complexes $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3) with HCl, CH_3CO_2H, and HNO_3 result in elimination of alkane and formation of the corresponding zinc derivative $L_{OEt}ZnX$ (X = Cl, O_2CCH_3, NO_3). The iodide derivative $L_{OEt}ZnI$ is obtained from the reaction of $L_{OEt}ZnR$ with I_2. The $L_{OEt}ZnX$ complexes (X = Cl, I, CH_3CO_2, NO_3) may also be obtained independently by the reaction of ZnX_2 with 1 equiv of ML_{OEt} (M = Na, Tl) as shown in eq 3.

$$ZnX_2 + ML_{OEt} \rightarrow L_{OEt}ZnX + MX \tag{3}$$

The molecular structures of the chloride and nitrato derivatives, $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$, have been determined by X-ray diffraction. Unfortunately, the tripod ligands in $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ are disordered in a manner similar to that for previously reported structures,[4] so that detailed analyses of the structures are not warranted. However, the constitutions of the molecules are clearly supported by the structure determinations, as illustrated by Figures 3 and 4 in which only one of the disordered configurations is shown in each case.

Discussion

The zinc alkyl derivatives $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$) are conveniently obtained by the metathesis of ZnR_2 with TlL_{OEt}. The decomposition of [TlR], depositing metallic thallium, provides an effective driving force for the reaction, in a manner similar to that observed in the reactions of ZnR_2 and MgR_2 with (poly(pyrazolyl)hydroborato)thallium complexes.[2] Although the mononuclear 4-coordinate zinc alkyl complexes are analogous to those obtained for the tris(pyrazolyl)hydroborato ligand system,[2b,c] the product obtained from the reaction of $Al(CH_3)_3$ with TlL_{OEt} (or NaL_{OEt}) is proposed to be a binuclear complex of composition $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$, in which the tripod ligand is coordinated to two different aluminum alkyl centers. Precedence for coordination of the L_{OEt} ligand to more than one metal center is provided by the structures of the sodium and lithium complexes $Na_3(L_{OEt})_3(H_2O)_2$[5] and $[LiL_{OEt}]_2$.[6]

The reactivity of the zinc alkyl complexes $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3) is illustrated in Scheme I. Reactions with HCl, CH_3CO_2H, and HNO_3 result in elimination of alkane accompanied by formation of the corresponding zinc derivative $L_{OEt}ZnX$ (X = Cl, CH_3CO_2, NO_3). The iodide derivative $L_{OEt}ZnI$ may be obtained from the reaction of $L_{OEt}ZnR$ with I_2. Thus, a series of half-sandwich derivatives $L_{OEt}ZnX$ (X = Cl, I, CH_3CO_2, NO_3), which complement the very stable sandwich complex $(L_{OEt})_2Zn$,[7] may be prepared directly from the zinc alkyl complexes $L_{OEt}ZnR$. Alternatively, the half-sandwich complexes $L_{OEt}ZnX$ (X = Cl, I, CH_3CO_2, NO_3) may be obtained independently by the reaction of ZnX_2 with 1 equiv of ML_{OEt} (M = Na, Tl).

The molecular structures of the chloride and nitrato derivatives, $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$, have been determined by X-ray diffraction, as shown in Figures 1 and 2. Although the tripod

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Table I. Selected Spectroscopic Data[a-c]

	^{1}H NMR			^{13}C NMR		
compd	assgnt	δ, ppm	coupling, Hz	assgnt	δ, ppm	coupling, Hz
$L_{OEt}ZnCH_3$	η^5-C_5H_5	4.96	s	η^5-C_5H_5	89.6	d, $^1J_{C-H}$ = 181
	$Zn-CH_3$	0.01	s	$Zn-CH_3$	−16.9	q, $^1J_{C-H}$ = 120
$L_{OEt}ZnCH_2CH_3$	η^5-C_5H_5	4.96	s	η^5-C_5H_5	89.6	d, $^1J_{C-H}$ = 181
	$Zn-CH_2CH_3$	0.92	q, $^3J_{H-H}$ = 8	$Zn-CH_2CH_3$	−2.4	t, $^1J_{C-H}$ = 119
	$Zn-CH_2CH_3$	1.91	t, $^3J_{H-H}$ = 9			q, $^2J_{C-H}$ = 4
				$Zn-CH_2CH_3$	13.7	q, $^1J_{C-H}$ = 123
						t, $^2J_{C-H}$ = 5
$L_{OEt}ZnCH(CH_3)_2$	η^5-C_5H_5	4.96	s	η^5-C_5H_5	89.6	d, $^1J_{C-H}$ = 181
	$Zn-CH(CH_3)_2$	1.35	spt, $^3J_{H-H}$ = 7	$Zn-CH(CH_3)_2$	10.7	d, $^1J_{C-H}$ = 119
	$Zn-CH(CH_3)_2$	1.95	d, $^3J_{H-H}$ = 7	$Zn-CH(CH_3)_2$	24.9	q, $^1J_{C-H}$ = 121
$L_{OEt}ZnI$	η^5-C_5H_5	4.84	s	η^5-C_5H_5	89.8	d, $^1J_{C-H}$ = 181
$L_{OEt}ZnCl$	η^5-C_5H_5	4.84	s	η^5-C_5H_5	89.8	d, $^1J_{C-H}$ = 182
$L_{OEt}Zn(\eta^2$-$O_2NO)$	η^5-C_5H_5	4.85	s	η^5-C_5H_5	89.8	d, $^1J_{C-H}$ = 182
$L_{OEt}ZnCO_2CH_3$	η^5-C_5H_5	4.91	s	η^5-C_5H_5	89.7	d, $^1J_{C-H}$ = 182
	$Zn-CO_2CH_3$	2.11	s	$Zn-CO_2CH_3$	180.7	s
				$Zn-CO_2CH_3$	21.3	q, $^1J_{C-H}$ = 127
$(L_{OEt})_2Zn$	η^5-C_5H_5	5.16	s	η^5-C_5H_5	89.1	d, $^1J_{C-H}$ = 181
$L_{OEt}AlMe_2[AlMe_3]$	η^5-C_5H_5	4.95	s	η^5-C_5H_5	91.5	d
	$Al(CH_3)_2Al(CH_3)_3$	−0.37	s	$Al(CH_3)_2[Al(CH_3)_3]$	−7.6	q
		−0.48	s		−9.3	q
	$Al(CH_3)_2Al(CH_3)_3$	−0.20	s	$Al(CH_3)_2[Al(CH_3)_3]$	−5.9	q

[a] In C_6D_6. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and spt = septet. [b] Only cyclopentadienyl resonances are given for the L_{OEt} ligand. [c] NMR assignments are consistent with observed integrations.

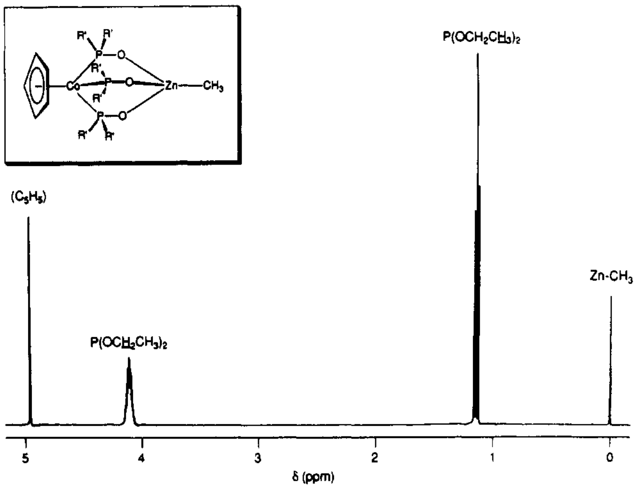

Figure 1. ^{1}H NMR spectrum of $L_{OEt}ZnCH_3$ (R′ = OEt).

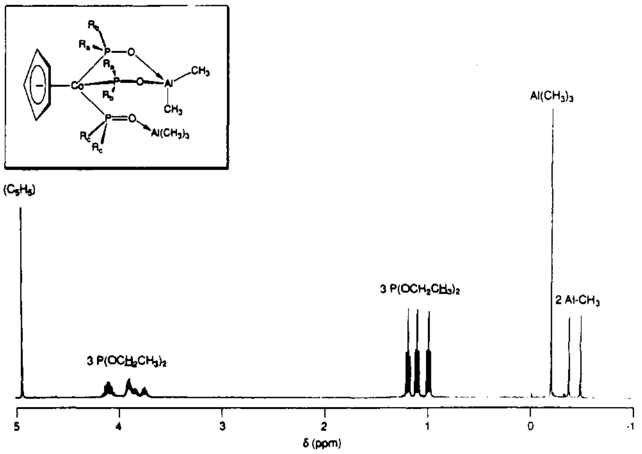

Figure 2. ^{1}H NMR spectrum of $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ (R = OEt; a–c subscripts indicate chemically equivalent groups).

ligand in these molecules is disordered, the coordination environment about the zinc center in the chloride derivative $L_{OEt}ZnCl$ can be seen to be closely analogous to that in the related 4-coordinate complex {η^3-HB(3-Bu^{t}pz)$_3$}ZnCl (3-Bu^{t}pz = $C_3N_2Bu^tH_2$).[8] Thus, the Zn–Cl bond distance (2.163 (2) Å),

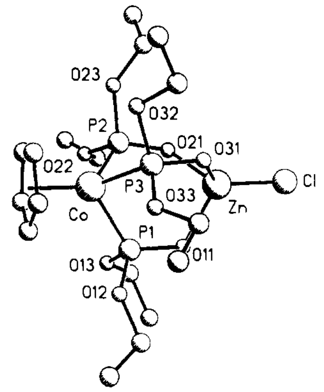

Figure 3. Ball and stick drawing of $L_{OEt}ZnCl$ showing only one of the disordered configurations (see text).

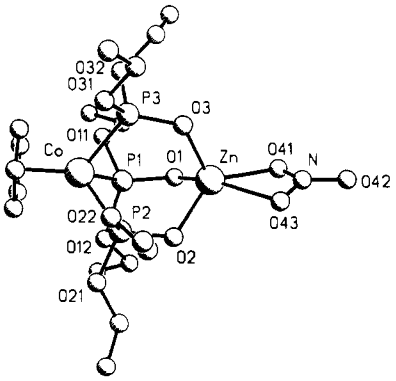

Figure 4. Ball and stick drawing of $L_{OEt}Zn(\eta^2$-$O_2NO)$ showing only one of the disordered configurations (see text).

the Zn–O distances (average = 1.97 Å), and O–Zn–Cl bond angles (average = 119°) in $L_{OEt}ZnCl$ may be compared with the Zn–Cl bond distance (2.183 (2) Å), the Zn–N distances (average = 2.05 Å), and N–Zn–Cl bond angles (average = 122°) in {η^3-HB(3-Bu^{t}pz)$_3$}ZnCl. However, the oxygen tripod ligand L_{OEt} is significantly less sterically demanding than the tris(3-*tert*-butylpyrazolyl)hydroborato ligand, as indicated by the ready formation of the 5-coordinated complexes $L_{OEt}Zn(\eta^2$-$O_2NO)$ and L_{OEt}Zn-

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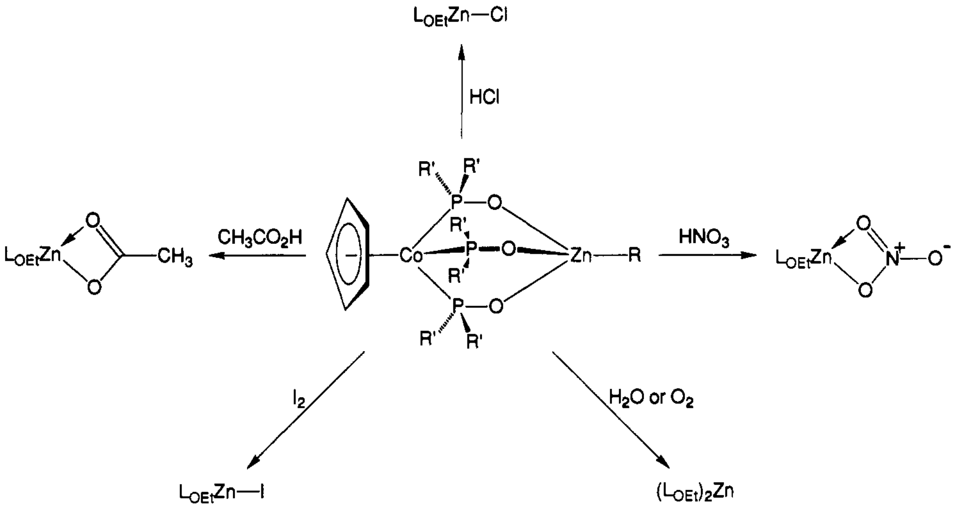
Scheme I. Reactivity of $L_{OEt}ZnR$ (R′ = OEt)



(η^2-O_2CCH_3). Although 5-coordination is not common for zinc, several other complexes that possess 5-coordinate zinc centers have been reported.[9] Indeed, the zinc *N*-benzoylglycinate pentahydrate complex, $Zn(C_6H_5CONHCH_2CO_2)_2{\cdot}5H_2O$,[9a] is similar to $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ in that the zinc coordination sphere of both compounds is comprised of only oxygen ligation.

A further illustration of the relatively small steric requirements of the L_{OEt} ligand is the observation that the 6-coordinate sandwich complex $(L_{OEt})_2Zn$[7] may be obtained as the product of the reactions of $L_{OEt}ZnR$ with a variety of substrates, including O_2 and H_2O. In this regard the oxygen tripod ligand L_{OEt} more closely resembles the unsubstituted tris(pyrazolyl)hydroborato ligand than the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand system.

In summary, alkyl derivatives of zinc and aluminum, $L_{OEt}ZnR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$) and $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$, that are stabilized by the oxygen tripod ligand system L_{OEt} may be readily synthesized. The zinc complexes are analogous to those of the tris(pyrazolyl)hydroborato ligand system, whereas the binuclear aluminum complex $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ is unique. The reactions of the zinc alkyls $L_{OEt}ZnR$ result in the formation of a variety of other half-sandwich derivatives $L_{OEt}ZnX$ (X = Cl, I, CH_3CO_2, NO_3).

Experimental Details

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques.[10] Solvents were purified and degassed by standard procedures. ^1H NMR spectra were measured on a Varian VXR 200 spectrometer. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (NH_3) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $Na[CpCo\{P(O)(OEt)_2\}_3]{\cdot}xH_2O$ was prepared by the literature method.[11] NMR data for all new complexes are given in Table I.

Synthesis of TlL_{OEt}. A solution of $TlNO_3$ (10 g, 37.6 mmol) in H_2O (125 mL) was added to a solution of NaL_{OEt} (10 g, 17.9 mmol) in H_2O (90 mL), resulting in the formation of a yellow precipitate. The mixture was stirred for 6 h at room temperature, and the water was removed under reduced pressure. The residue was extracted into CH_2Cl_2 (2 × 100 mL) and filtered. The solvent was removed under reduced pressure, giving TlL_{OEt} as a yellow solid (11.7 g, 88%). Anal. Calcd for $C_{17}H_{35}O_9P_3CoTl$: C, 27.6; H, 4.8. Found: C, 27.6; H, 4.6.

Synthesis of $L_{OEt}ZnCH_3$. $Zn(CH_3)_2$ (1.2 mL of a 1.1 M solution in pentane, 1.32 mmol) was added to a stirred solution of TlL_{OEt} (400 mg, 0.54 mmol) in C_6H_6 (15 mL), resulting in the immediate formation of a precipitate of Tl metal. The mixture was stirred overnight at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}ZnCH_3$ as a yellow solid (200 mg, 60%). $L_{OEt}ZnCH_3$ was recrystallized by addition of pentane to a concentrated benzene solution. Anal. Calcd for $C_{18}H_{38}O_9P_3CoZn$: C, 35.1; H, 6.2. Found: C, 35.3; H, 5.9. MS: *m/e* 615 (M^+ + 1).

Synthesis of $L_{OEt}ZnCH_2CH_3$. $Zn(CH_2CH_3)_2$ (0.73 mL of a 1.1 M solution in hexane, 0.80 mmol) was added to a stirred solution of TlL_{OEt} (300 mg, 0.4 mmol) in C_6H_6 (25 mL), resulting in the immediate formation of a precipitate of Tl metal. The mixture was stirred for 1 h at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}ZnCH_2CH_3$ as a yellow solid (218 mg, 86%), which was recrystallized from pentane at −78 °C. Anal. Calcd for $C_{19}H_{40}O_9P_3CoZn$: C, 36.2; H, 6.4. Found: C, 36.0; H, 6.2.

Synthesis of $L_{OEt}ZnCH(CH_3)_2$. $Zn[CH(CH_3)_2]_2$ (1.0 mL of a 0.2 M solution in pentane, 0.20 mmol) was added to a stirred solution of TlL_{OEt} (150 mg, 0.20 mmol) in C_6H_6 (20 mL), resulting in the immediate formation of a precipitate of Tl metal. The mixture was stirred for 2 h at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}ZnCH(CH_3)_2$ as a yellow solid (40 mg, 31%), which was recrystallized from pentane at −78 °C. Anal. Calcd for $C_{20}H_{42}O_9P_3CoZn$: C, 37.3; H, 6.6. Found: C, 38.1; H, 6.1. MS: *m/e* 644 (M^+).

Synthesis of $L_{OEt}ZnI$. A solution of NaL_{OEt} (250 mg, 0.45 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of ZnI_2 (143 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) and stirred overnight at room temperature. The mixture was filtered, giving a yellow solution, and the solvent was removed under reduced pressure, giving $L_{OEt}ZnI$ as a yellow solid (160 mg, 49%). $L_{OEt}ZnI$ was recrystallized from a mixture of benzene/pentane. Anal. Calcd for $C_{17}H_{35}O_9P_3CoZnI$: C, 28.1; H, 4.9. Found: C, 28.3; H, 4.8. MS: *m/e* 726 (M^+ − 1).

Reaction of $L_{OEt}ZnR$ (R = CH_2CH_3, $CH(CH_3)_2$) with I_2. A solution of $L_{OEt}ZnR$ (R = CH_2CH_3, $CH(CH_3)_2$) (20 mg) in C_6D_6 (0.7 mL) was treated with I_2 (ca. 10 mg). $L_{OEt}ZnI$ and RI were formed quantitatively after 10 min at room temperature, as observed by ^1H NMR spectroscopy.

Synthesis of $L_{OEt}ZnCl$. A solution of NaL_{OEt} (200 mg, 0.36 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of $ZnCl_2$ (49 mg, 0.36 mmol) in CH_2Cl_2 (10 mL) and stirred overnight at room temperature. The mixture was filtered, giving a yellow solution, and the solvent was removed under reduced pressure, giving $L_{OEt}ZnCl$ as a yellow solid (120 mg, 52%). $L_{OEt}ZnCl$ was recrystallized from a mixture of benzene/pentane. Single crystals for X-ray diffraction were obtained from acetone. Anal. Calcd for $C_{17}H_{35}O_9ClCoZn$: C, 32.1; H, 5.6. Found: C, 32.2; H, 5.3. MS: *m/e* 634 (M^+).

Reaction of $L_{OEt}ZnCH_2CH_3$ with HCl(aq). A solution of $L_{OEt}ZnCH_2CH_3$ (350 mg, 0.55 mmol) in C_6H_6 (15 mL) was treated with HCl(aq) (60 μL of a 12 M solution, 0.72 mmol). The mixture was stirred for 2 h at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}ZnCl$ as a yellow solid (125 mg, 35%).

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Table II. Summary of Crystal and Intensity Collection Data

	$L_{OEt}Zn(\eta^2\text{-}NO_3)$	$L_{OEt}ZnCl$
formula	$C_{17}H_{35}NO_{12}P_3CoZn$	$C_{17}H_{35}O_9P_3ClCoZn$
fw	662.7	636.2
lattice	monoclinic	monoclinic
cell consts		
a, Å	11.923 (2)	11.882 (2)
b, Å	20.352 (4)	20.017 (4)
c, Å	12.170 (2)	12.204 (2)
β, deg	103.31 (1)	106.49 (1)
V, Å^3	2873.8 (8)	2783.2 (7)
Z	4	4
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ(calcd), g cm^{-3}	1.53	1.52
GOF[a]	1.848	1.841
R[a]	0.0627	0.0524
R_w[a]	0.0775	0.0723

[a] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = \{[\sum(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; GOF $= \{[\sum w(F_o - F_c)^2]/[N_{data} - N_{params}]\}^{1/2}$; $w = [\sigma^2(F) + gF^2]^{-1}$.

Synthesis of $L_{OEt}Zn(\eta^2\text{-}O_2NO)$. A solution of TlL_{OEt} (500 mg, 0.68 mmol) in THF (20 mL) was added to a suspension of $Zn(NO_3)_2{\cdot}6H_2O$ (200 mg, 0.68 mmol) in THF (6 mL), resulting in the formation of a white precipitate. The mixture was stirred overnight at room temperature and was filtered, giving a yellow solution, and the solvent was removed under reduced pressure, giving $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ as a yellow solid (345 mg, 77%). $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ was recrystallized from a mixture of benzene/pentane. Single crystals of X-ray diffraction were obtained from THF. Anal. Calcd for $C_{17}H_{35}O_{12}NP_3CoZn$: C, 30.8; H, 5.3; N, 2.1. Found: C, 30.8; H, 5.1; N, 2.1. MS: m/e 660 ($M^+ - 1$).

Reaction of $L_{OEt}ZnCH_2CH_3$ with HNO_3(aq). A solution of $L_{OEt}ZnCH_2CH_3$ (130 mg, 0.21 mmol) in C_6H_6 (10 mL) was treated with HNO_3(aq) (15 μL of a 15.6 M solution, 0.23 mmol). The mixture was stirred for 2 h at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ as a yellow solid (100 mg, 74%).

Synthesis of $L_{OEt}Zn(\eta^2\text{-}O_2CCH_3)$. A solution of TlL_{OEt} (250 mg, 0.34 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (74 mg, 0.34 mmol) in CH_2Cl_2 (10 mL), resulting in the formation of a white precipitate. The mixture was stirred overnight at room temperature and was filtered, giving a yellow solution, and the solvent was removed under reduced pressure, giving $L_{OEt}Zn(\eta^2\text{-}O_2CCH_3)$ as a yellow solid (100 mg, 45%). $L_{OEt}Zn(\eta^2\text{-}O_2CCH_3)$ was recrystallized from a mixture of toluene/pentane. Anal. Calcd for $C_{19}H_{38}O_{11}P_3CoZn$: C, 34.6; H, 5.8. Found: C, 34.6; H, 5.8.

Reaction of $L_{OEt}ZnCH_2CH_3$ with CH_3CO_2H. A solution of $L_{OEt}ZnCH_2CH_3$ (770 mg, 1.22 mmol) in C_6H_6 (30 mL) was treated with CH_3CO_2H (110 μL, 1.93 mmol). The mixture was stirred overnight at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}Zn(\eta^2\text{-}O_2CCH_3)$ as a yellow solid (700 mg, 87%).

Synthesis of $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$. $Al(CH_3)_3$ (600 μL of a 2 M solution in hexane, 1.20 mmol) was added to a stirred solution of TlL_{OEt} (200 mg, 0.27 mmol) in pentane (10 mL), resulting in the immediate formation of a precipitate of Tl metal. The mixture was stirred for 1 h at room temperature and filtered, giving a yellow solution. The solvent was removed under reduced pressure, giving $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$ as a yellow solid (100 mg, 56%). Anal. Calcd for $C_{22}H_{50}Al_2CoO_9P_3$: C, 39.8; H, 7.6. Found: C, 39.8; H, 7.5.

Reaction of $L_{OEt}ZnCH_2CH_3$ with O_2. A solution of $L_{OEt}ZnCH_2CH_3$ (100 mg, 0.16 mmol) in benzene (10 mL) was stirred for 5 min under O_2 (1 atm). The mixture was filtered and the solvent removed under reduced pressure to give $(L_{OEt})_2Zn$ as a yellow solid (50 mg).

Reaction of $L_{OEt}ZnCH_2CH_3$ with H_2O. A solution of $L_{OEt}ZnCH_2CH_3$ (20 mg) in C_6D_6 (0.7 mL) was treated with H_2O (14 μL). Over the period of 1 day $L_{OEt}ZnCH_2CH_3$ was converted to the complex $(L_{OEt})_2Zn$ as shown by ^{1}H NMR spectroscopy.

Synthesis of $(L_{OEt})_2Zn$. The following synthesis is adapted from the original report.[6] A solution of NaL_{OEt} (200 mg, 0.36 mmol) in CH_2Cl_2 (15 mL) was added to a stirred suspension of $ZnCl_2$ (24 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred overnight at room temperature. The mixture was filtered and the solvent removed under reduced pressure, giving $(L_{OEt})_2Zn$ (40 mg, 20%).

X-ray Structure Determination of $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$. Crystal data, data collection, and refinement parameters are summarized in Table II. Single crystals of $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ were mounted in glass capillaries and placed on a Nicolet R3m diffractometer. The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structures was solved using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[12] Systematic absences were consistent with the space group $P2_1/n$ (No. 14) for both crystals. A 2-fold disorder of the $[P(O)(OEt_2)_2]$ groups of the L_{OEt} ligand about the Co–Zn vector was evident for both structures, analogous to that previously reported.[4] The 2-fold disorder is such that the OEt groups of both orientations become coincident (or nearly so), so that in effect only two orientations of the [P(O)] group were observed. The disorder was therefore modeled by refining the occupancies of the P and O atoms of the two sets of [P(O)] groups. The site occupancy factors refined to 0.56 and 0.44 for $L_{OEt}Zn(\eta^2\text{-}NO_3)$, and 0.69 and 0.31 for $L_{OEt}ZnCl$. Tables of atomic coordinates and thermal parameters are available as supplementary material.

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Registry No. TlL_{OEt}, 137942-96-2; $L_{OEt}ZnCH_3$, 137942-97-3; $L_{OEt}ZnCH_2CH_3$, 137942-98-4; $L_{OEt}ZnCH(CH_3)_2$, 137942-99-5; $L_{OEt}ZnI$, 137943-00-1; $L_{OEt}ZnCl$, 137943-01-2; $L_{OEt}Zn(\eta^2\text{-}O_2NO)$, 137943-02-3; $L_{OEt}Zn(\eta^2\text{-}O_2CCH_3)$, 137943-03-4; $L_{OEt}Zn$, 58438-24-7; $L_{OEt}Al(CH_3)_2[Al(CH_3)_3]$, 137943-04-5.

Supplementary Material Available: Table SI, listing spectroscopic data for all the new complexes, Tables SII–SV, listing crystal and intensity collection data and atomic coordinates for $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$, and ORTEP drawings (11 pages); listings of calculated and observed structure factors for $L_{OEt}ZnCl$ and $L_{OEt}Zn(\eta^2\text{-}O_2NO)$ (27 pages). Ordering information is given on any current masthead page.

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(12) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.