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Mixed Alkyl Hydrido Complexes of Zinc: Synthesis, Structure, and Reactivity

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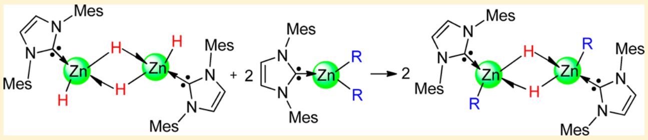
Ⓢ *Supporting Information*



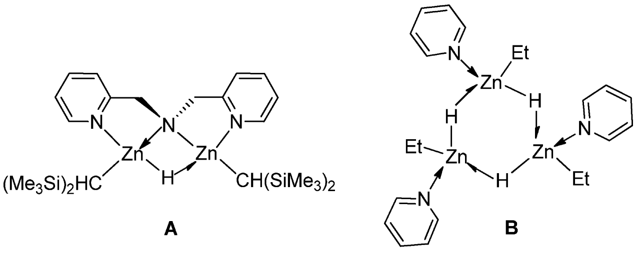
ABSTRACT: The (NNNN)-type macrocycle 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane (Me_3TACD, 1,4,7-Me_3[12]-aneN_4) reacted with 1 equiv of $ZnEt_2$ under ethane elimination to give the mononuclear ethyl complex [(Me_3TACD)ZnEt] (**1**). Upon treatment of (Me_3TACD)H with 2 equiv of $ZnEt_2$, the dinuclear complex [(Me_3TACD)(ZnEt)($ZnEt_2$)] (**2**) was formed, which was converted with an additional 1 equiv of (Me_3TACD)H to **1**. Reaction of **1** with $PhSiH_3$ led to the formation of a tetranuclear ethyl hydrido complex [{(Me_3TACD)ZnEt}$_2$(ZnEtH)$_2$] (**3**). Single-crystal X-ray diffraction study revealed **3** to be a centrosymmetric dimer featuring two [(Me_3TACD)ZnEt] units coordinated to a [Zn(μ-H)$_2$Zn] core via amido nitrogen atoms of the Me_3TACD ligands. Substitution of the two [(Me_3TACD)ZnEt] units in **3** by N-heterocyclic carbene IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] gave [(IMes)ZnEtH]$_2$ (**4b**). The mixed alkyl hydrido complexes [(IMes)ZnRH]$_2$ (R = Me, **4a**; Et, **4b**) were alternatively synthesized in quantitative yield by reacting [(IMes)ZnR$_2$] (R = Me, Et) with [(IMes)ZnH$_2$]$_2$ in 2:1 ratio. Methyl complex **4a** reacted with CO_2 ($p(CO_2) = 0.5$ bar) under facile insertion of CO_2 into Zn−H bonds to give dinuclear formate complex [(IMes)ZnMe(O_2CH)]$_2$ (**5a**). Treatment of **4b** with CO_2 ($p(CO_2) = 0.5$ bar) afforded a mixture of di- and trinuclear formate complexes [(IMes)ZnEt(O_2CH)]$_2$ (**5b**) and [(IMes)$_2$Zn$_3$Et$_3$(O_2CH)$_3$] (**6**) under elimination of one IMes as CO_2 adduct **IMes·CO$_2$**.

■ INTRODUCTION

Zinc hydrides have been mainly used as reducing agents in organic synthesis,[1] as models for zinc-containing enzymes,[2] and as molecular precursors in material science.[3] More recently, molecular zinc hydrides have received much attention as nonprecious metal catalysts for silane coupling with protic substrates,[4a,b] for hydrogenation of imines,[4c] and for homogeneous hydrosilylation of carbon dioxide,[4a] ketones, nitriles,[4d] and activated alkenes.[4e] As a result of poor solubility and low thermal stability of polymeric zinc dihydride $(ZnH_2)_n$,[5] more stable zinc hydride derivatives have been sought over the last decades.[6,7] Compounds of general formula [(LX)ZnH] were stabilized by using chelating monoanionic ligands such as nacnac,[6a,b] tris(4,4-dimethyl-2-oxazolinyl)phenylborate,[6c] [tris-(2-pyridylthio)methyl],[6d] and phenolate diamine ligands.[6e] We have recently isolated the thermally robust molecular zinc dihydrides containing neutral NHC ligands of composition [(L)ZnH$_2$]$_2$ (L = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IMes; 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr).[7]

Well-defined zinc complexes that feature both alkyl and hydrido ligands are rare. Most of the stable neutral derivatives reported to date contain chelating alkyl ligands such as tris(2-pyridylthio)methyl,[6d] HC(SiMe$_3$)$_2$(SiMe$_2$hpp) (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine),[8a] and methylidyne-3,3′-bis(*N*-*tert*-butylimidazol-2-ylidene).[4e] Alkyl hydrido complexes with nonchelating alkyl groups (CH_3, CH_2SiMe_3) of the di(2-pyridylmethyl)amide ligand undergo either decomposition (for CH_3) or dismutation/redistribution (for CH_2SiMe_3) to give higher clusters.[8b] The zinc alkyl hydrido complexes of 1,3-bis(2-pyridylmethyl)acetamidinato ligand decompose readily at room temperature.[8c] A more stable complex **A** (Chart 1) was obtained by using the bulky CH(SiMe$_3$)$_2$ group.[8b] In 1978, De Koning *et al.* have reported the formation of the only known neutral ethyl hydrido complex of zinc of tentative composition [(py)ZnEtH]$_3$, **B** (Chart 1), by treating $(ZnH_2)_n$ with $ZnEt_2$ in the presence of pyridine in THF or C_6H_6. This compound was not crystallographically characterized.[9] No further zinc alkyl hydrides of this type became known, although the parent [ZnMeH] was charac-

Chart 1. Stable Neutral Complexes of Zinc Featuring Nonchelating Alkyl and Hydrido Ligands



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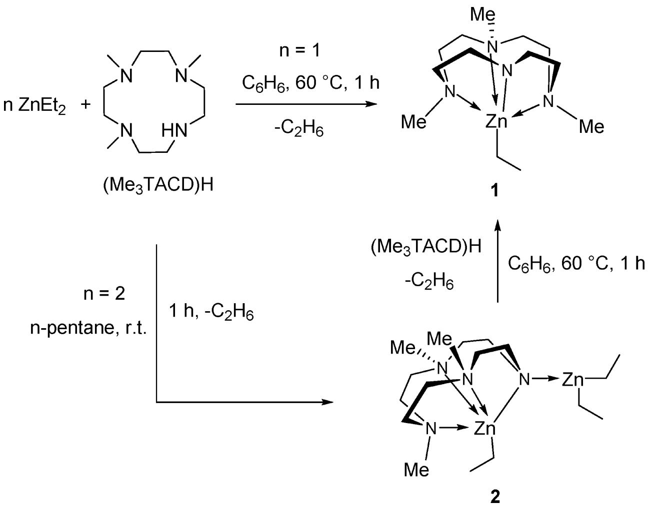
terized in an argon matrix.[8d] We have found out that the monoanionic macrocyclic Me_3TACD ligand[10] is suitable for stabilizing several lanthanide, early transition, and main group metal hydrides.[11] As most of the zinc hydrides reported to date are also stabilized by a monoanionic chelating ligand,[6] we became interested in using the Me_3TACD ligand to support zinc hydride species. Herein we describe the synthesis and characterization of a zinc alkyl hydrido complex containing the Me_3TACD ligand $[\{(Me_3TACD)ZnEt\}_2(ZnEtH)_2]$. We also describe a straightforward synthesis and characterization of mixed alkyl hydrido complexes $[(IMes)ZnRH]_2$ (R = Me, Et) stabilized by a IMes ligand, as well as their reactivity toward carbon dioxide.

■ RESULTS AND DISCUSSION

Zinc Ethyl Complexes. Reaction of 1 equiv of $ZnEt_2$ with $(Me_3TACD)H$[10] in benzene at 60 °C for 1 h afforded the mononuclear complex $[(Me_3TACD)ZnEt]$ (**1**) (Scheme 1).

Scheme 1. Zinc Ethyl Complexes Supported by a Me_3TACD Ligand



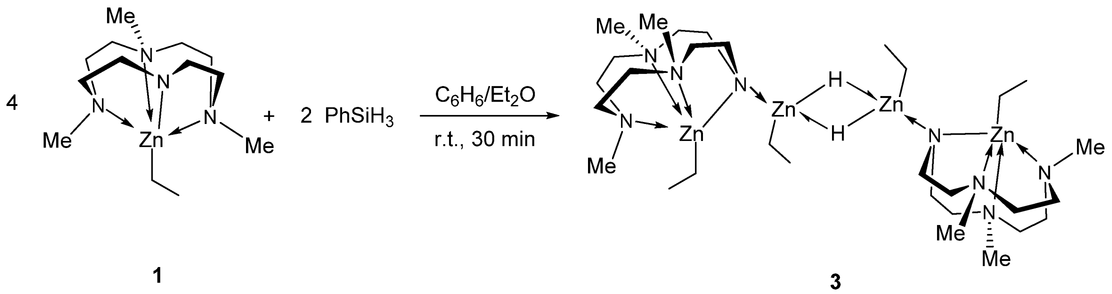
Whereas the treatment of $(Me_3TACD)H$ with 1 equiv of $ZnEt_2$ in *n*-pentane at room temperature give a dinuclear complex $[(Me_3TACD)(ZnEt)(ZnEt_2)]$ (**2**) in less than 50% yield with 0.5 equiv of $(Me_3TACD)H$ remaining unreacted, the yield increased to 90% by using 2 equiv of $ZnEt_2$ (Scheme 1). Reaction of isolated **2** with an additional 1 equiv of $(Me_3TACD)H$ in benzene at 60 °C for 1 h gave the mononuclear complex **1** in 98% yield (Scheme 1). While **1** is soluble in all common polar as well as nonpolar organic solvents, **2** is soluble only in polar organic solvents but not in aliphatic hydrocarbons. The formation of two different products **1** and **2** in benzene and *n*-pentane may be due to the insolubility of **2** in *n*-pentane. When the reaction was performed in *n*-pentane, **2** precipitated out of the reaction mixture, preventing further reaction. On the other hand, solubility of the intermediate **2** in benzene facilitates the reaction to proceed further at higher temperature to give **1**. Both **1** and **2** were characterized by elemental analysis and multinuclear NMR spectroscopy.

The ^1H NMR spectrum of **1** in C_6D_6 shows one set of signals at δ 0.41 (q, 2H) and 1.79 (t, 3H) ppm for an ethyl group, in agreement with the formulation of a mononuclear complex of composition $[(Me_3TACD)ZnEt]$. The ^1H NMR spectrum of **2** in C_6D_6 shows two distinct sets for two nonequivalent ethyl groups at δ 0.73 (q, 4H) and 2.07 (t, 6H) ppm as well as at δ 0.24 (q, 2H) and 1.66 (t, 3H) ppm in 2:1 ratio, corresponding to the formulation $[(Me_3TACD)(ZnEt)(ZnEt_2)]$. A similar type of bridging by an amide N atom to two metal centers has been observed previously for metal complexes containing a Me_3TACD ligand[11f,12a] or the related dianionic 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (Me_2TACD) ligand.[12b−d] Several sets of signals for the CH_2 resonances of the Me_3TACD ligand backbone were observed for both complexes **1** and **2** in the range of δ 1.1−3.0 ppm. The N-Me groups of the Me_3TACD ligand are recorded as two singlets at δ 1.88 and 2.14 ppm for **1** and at δ 1.69 and 1.99 ppm for **2**. The DFT geometry optimization on **1** leads to a monomeric molecule with a zinc center coordinated by the tetradentate Me_3TACD and a terminal ethyl ligand (see Supporting Information).

Zinc Ethyl Hydrido Complex. Several metal alkyl complexes of Me_3TACD ligands reacted with aromatic silanes or dihydrogen to form metal hydrides stabilized by the Me_3TACD ligand.[11] This makes ethyl complexes **1** and **2** possible precursors for zinc hydride species. Treatment of **2** with $PhSiH_3$ did not lead to any clean reactions. The mono(ethyl) complex **1** reacted with $PhSiH_3$ in C_6H_6/Et_2O at room temperature to give a colorless crystalline precipitate of $[\{(Me_3TACD)ZnEt\}_2(ZnEtH)_2]$ (**3**) (Scheme 2). This was isolated within 30 min in 70% yield (based on Zn) to prevent further reaction to an unidentified yellow product mixture. Complex **3** is highly soluble in THF, but only moderately soluble in aromatic hydrocarbons. In THF solution, the decomposition of **3** is probably caused by the reduction of Zn(II) to metallic zinc together with the oxidation of hydride to dihydrogen. **3** is stable for months as a solid at −35 °C. **3** was characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction.

The ^1H NMR spectrum of **3** in THF-d_8 shows two sets of signals at δ −0.07 (q) and −0.04 (q) ppm for the CH_2 moieties, whereas resonances for the CH_3 moieties of the ethyl groups

Scheme 2. Mixed Zinc Ethyl Hydrido Complex Stabilized by a Me_3TACD Ligand



appear at δ 1.21 ppm. The *N*-Me groups of the Me_3TACD ligand were identified by two singlets at δ 2.34 and 2.37 ppm. The CH_2 resonances of the Me_3TACD ligand backbone were observed as several sets of broad signals in the range δ 2.3−3.1 ppm. The Zn−H resonance was not reliably assigned due to overlap with the Me_3TACD ligand backbone signals. Two sets of signals were observed for the Me_3TACD ligand in the $^{13}C\{^1H\}$ NMR spectrum. The ν_{Zn-H} absorption for **3** could not be reliably assigned due to overlap with the Me_3TACD ligand stretching modes.

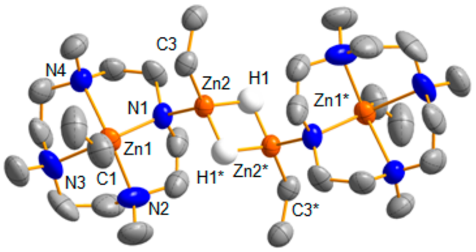


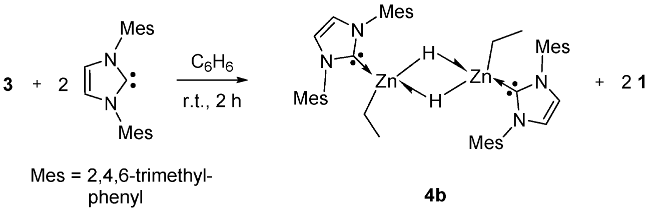
Figure 1. Molecular structure of **3** with displacement parameters at the 50% probability level. Hydrogen atoms except the hydride connected to zinc are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−N1 = 2.047(5), Zn1−N2 = 2.259(7), Zn1−N3 = 2.387(6), Zn1−N4 = 2.367(6), Zn2−N1 = 2.064(5), Zn1−C1 = 2.008(9), Zn2−C3 = 2.023(7), Zn2−H1 = 1.66(7), Zn2−H1* = 1.74(7), Zn2···Zn2* = 2.5374(14); Zn2−H1−Zn2* = 97(2), H1−Zn2−H1* = 83(3), N1−Zn2−C3 = 115(2), N1−Zn2−H1 = 109(2), H1−Zn2−C3 = 121(2).

Single crystals were obtained from C_6H_6/Et_2O at room temperature. As shown in Figure 1, the molecular structure consists of a centrosymmetric dimer with an inversion center at the centroid of the Zn_2H_2 core. The Zn1 centers are coordinated by one ethyl ligand (X-type) and one tetradentate amido triamine Me_3TACD ligand (L_3X-type). The coordination geometry of the five-coordinated Zn1 centers can be regarded as either trigonal bipyramidal (considering N2 and N4 in axial positions) or distorted square-based pyramidal. The distorted tetrahedral Zn2 is surrounded by an amido N1 atom, one ethyl group, and two bridging hydrido ligands. The distances between the amido nitrogen N1 and the zinc centers are significantly shorter (Zn1−N1 = 2.047(5), Zn2−N1 = 2.064(5) Å) than the dative bonds between N2−N4 and the zinc center (average distance: 2.34 Å). The average $Zn-C_{ethyl}$ bond length of 2.02 Å is comparable to other zinc ethyl complexes.[4e,13] The average Zn−(μ-H) bond length of 1.70 Å is comparable to 1.766 Å found in $[\{HC(CMeNR)_2\}ZnH]_2$ (R = 2,6-$Me_2C_6H_3$).[6a] Two zinc atoms Zn2 and Zn2* are bridged by hydrido ligands via three-center two-electron bonds. The Zn2···Zn2* distance of 2.5374(14) Å is comparable to the value of 2.4513(9) Å in $[\{HC(CMeNR)_2\}ZnH]_2$.[6a]

In the reaction of **1** with $PhSiH_3$, most likely one $[Me_3TACD^-]$ unit is first replaced, and the resulting "zinc ethyl hydrido" fragments are then stabilized via coordination to the amido N atoms of Me_3TACD ligands of another molecule of the remaining $[(Me_3TACD)ZnEt]$ as **3**. Replacement of the $[Me_3TACD^-]$ unit in **1** by $PhSiH_3$ is indicated by the ^1H NMR spectroscopic analysis of the reaction mixture after precipitation of **3**. The resonances at δ 3.91 (Si−H), 6.98−7.11 (Ph), and 7.53−7.60 (Ph) ppm in THF-d_8 correspond to a $PhSiH_2$ group, suggesting the formation of $[(Me_3TACD)SiH_2Ph]$, which could not be isolated in pure form. In the synthesis of alkyl hydrido species from other zinc alkyl complexes, amides were found to be more reactive toward $PhSiH_3$ than alkyl ligands.[8b,c]

Mixed Zinc Alkyl Hydrido Complexes of a NHC Ligand. Due to the higher σ-donor ability of an N-heterocyclic carbene (NHC)[14] as compared to neutral N-donors, it was expected that the $[(Me_3TACD)ZnEt]$ units in **3** can be replaced by an NHC ligand. **3** reacted with 2 equiv of IMes at room temperature in C_6H_6 for 2 h to give the mixed alkyl hydrido complex $[(IMes)ZnEtH]_2$ (**4b**) in 66% yield (Scheme 3) along with $[(Me_3TACD)ZnEt]$ (**1**), which was detected by ^1H NMR spectroscopic analysis of the washing solution. The sterically more crowded IPr [1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] ligand did not substitute the $[(Me_3TACD)ZnEt]$ fragments in **3** under the same condition, probably due to the steric bulk of IPr compared to that of IMes.

Scheme 3. Zinc Ethyl Hydrido Complex Stabilized by a NHC Ligand



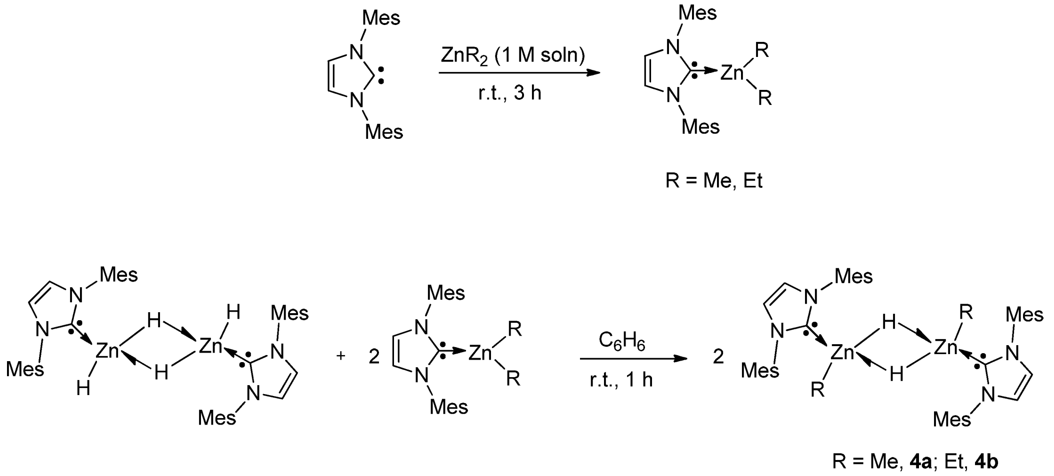
Comproportionation of the $[(IMes)ZnH_2]_2$[7] with $[(IMes)ZnR_2]$ (R = Me, Et) turned out to be a more efficient route to synthesize the mixed alkyl hydrido complexes $[(IMes)ZnRH]_2$ (R = Me, Et). Reaction of $[(IMes)ZnH_2]_2$ with 2 equiv of $[(IMes)ZnR_2]$ (R = Me, Et), synthesized from IMes and a 1 M solution of ZnR_2, for 1 h at room temperature in C_6H_6 readily gave the complexes $[(IMes)ZnRH]_2$ (R = Me, **4a**; R = Et, **4b**) in quantitative yield (Scheme 4).

Most of the isolated stable alkyl hydrido complexes of zinc reported to date contain chelating alkyl ligands.[6d,8a,4e] A structurally characterized stable alkyl hydrido complex featuring nonchelating alkyl groups was achieved only by using the bulky $CH(SiMe_3)_2$ group.[8b] As for $[(IMes)ZnH_2]_2$,[7] NHC ligand IMes enabled us to prepare the simplest alkyl hydrido complexes of type [(L)ZnRH] (R = Me, Et).

Complexes **4a** and **4b** are highly soluble in all common polar organic solvents but not in aliphatic hydrocarbons and are stable at room temperature in C_6D_6 solution over a week. Complexes **4a** and **4b** were fully characterized by elemental analysis and multinuclear NMR spectroscopy and also by single-crystal X-ray diffraction for **4b**. Exposure of **4a** and **4b** in C_6D_6 to D_2 (1 bar) showed no significant H−D exchange at ambient temperature over 1 week. Other zinc hydride compounds $[(L)ZnH_2]_2$ (L = IMes, IPr) are also found to be inert.[7]

The ^1H NMR spectra of **4a** and **4b** in C_6D_6 show the hydride signals at δ 2.75 (**4a**) and 2.78 ppm (**4b**) along with the typical pattern for the IMes ligand.[7] The methyl group signals of **4a** are found as two broad signals at δ −0.51 and −0.77 ppm. The broadness of the ^1H NMR resonances of **4b** and the appearance of two sets of signals for the alkyl groups in **4a** and **4b** at 25 °C might be due to a monomer−dimer equilibrium. In order to obtain some insight, we performed variable-temperature ^1H NMR studies of **4b** in toluene-d_8 in the temperature range of −60 to +75 °C (see Figure S12 in the Supporting Information).

Scheme 4. Mixed Zinc Alkyl Hydrido Complexes Stabilized by an NHC Ligand



At 75 °C, one set of sharp signals was observed, suggesting the presence of only the monomer. Gradually cooling the sample to −60 °C led to a new set of signals with a hydride resonance at δ 2.52 ppm, probably due to the dimer formation. Another set of signals with a hydride resonance at δ 3.78 ppm was also observed. Others have observed temperature-dependent monomer−dimer equilibria for zinc hydride complexes.[6b,e] In the $^{13}C\{^{1}H\}$ NMR spectra, the characteristic carbene carbon resonances are found at δ 190.70 (4a) and 191.19 ppm (**4b**), in agreement with other NHC compounds of zinc(II).[4e,7] The ν_{Zn-H} absorptions for **4a** and **4b** could not be reliably assigned due to overlap with the aromatic vibrations of the NHC ligands.[7,15]

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a saturated solution of **4b** in toluene at room temperature. The molecular structure of **4b** shows a noncrystallographic C_2 axis passing through the H1−H2 vector (Figure 2). The zinc centers are tetrahedrally coordinated by one ethyl, one IMes, and two bridging hydrido ligands. The average Zn−$C_{(ethyl)}$ bond length of 2.02 Å is similar to that found in **3**. The average Zn−(μ-H) bond length of 1.78 Å is comparable to that in **3** (1.70 Å) and $[\{HC(CMeNR)_2\}ZnH]_2$ (R = 2,6-$Me_2C_6H_3$) (1.77 Å).[6a] The Zn1···Zn2 distance of 2.5066(5) Å is comparable with that in **3** (2.537(14) Å); the Zn−C_{NHC} bond lengths (Zn1−C1 2.084(3), Zn2−C24 2.081(3) Å) are similar to those in $[(IMes)ZnH_2]_2$ (2.052(3)−2.054(3) Å).[7]

The DFT-optimized geometry of complex **4b** matches well with the experimental one (see Supporting Information). In particular, the Zn1−C1 and Zn2−C24 distances (2.128 and 2.124 Å computed vs 2.084(3) and 2.081(3) Å experimental) and the Zn1−C22 and Zn2−C45 bond distances (2.022 and 2.020 Å calculated vs 2.009(3) and 2.024(3) Å experimental) are well reproduced. The Zn_2H_2 core is also well represented by the employed method with calculated Zn−H distances of 1.765 Å (Zn1−H1), 1.784 Å (Zn1−H2), 1.767 Å (Zn2−H1), and 1.786 Å (Zn2−H2) as well as a Zn1···Zn2 distance of 2.535 Å.

Reaction of 4a and 4b with CO_2. The mixed alkyl hydrido complexes **4a** and **4b** readily reacted with excess CO_2 ($p(CO_2)$ = 0.5 bar) at ambient temperature to give formate species **5a** and **5b·6**, respectively (Scheme 5). ^{1}H NMR spectroscopic analysis showed that all hydrido ligands reacted within 30 min, but the zinc alkyl bonds remained inert for several days under these conditions. Zinc alkyls ZnR_2 (R = Me, Et) and $ZnCp^*_2$ are reported to react with heterocumulenes and CO_2 only at elevated temperatures to give insertion products,[16a−e] whereas $[(NHC)ZnCp^*(C_6F_5)]$ (Cp* = C_5Me_5) reacts with CO_2 at room temperature to give insertion products.[16f] Both formates are soluble in common polar organic solvents, but insoluble in aliphatic hydrocarbons. They were fully characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction.

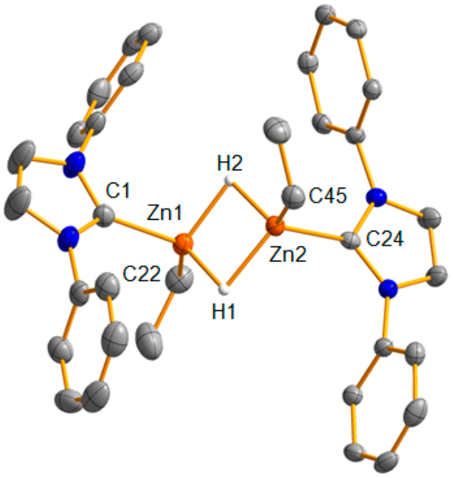
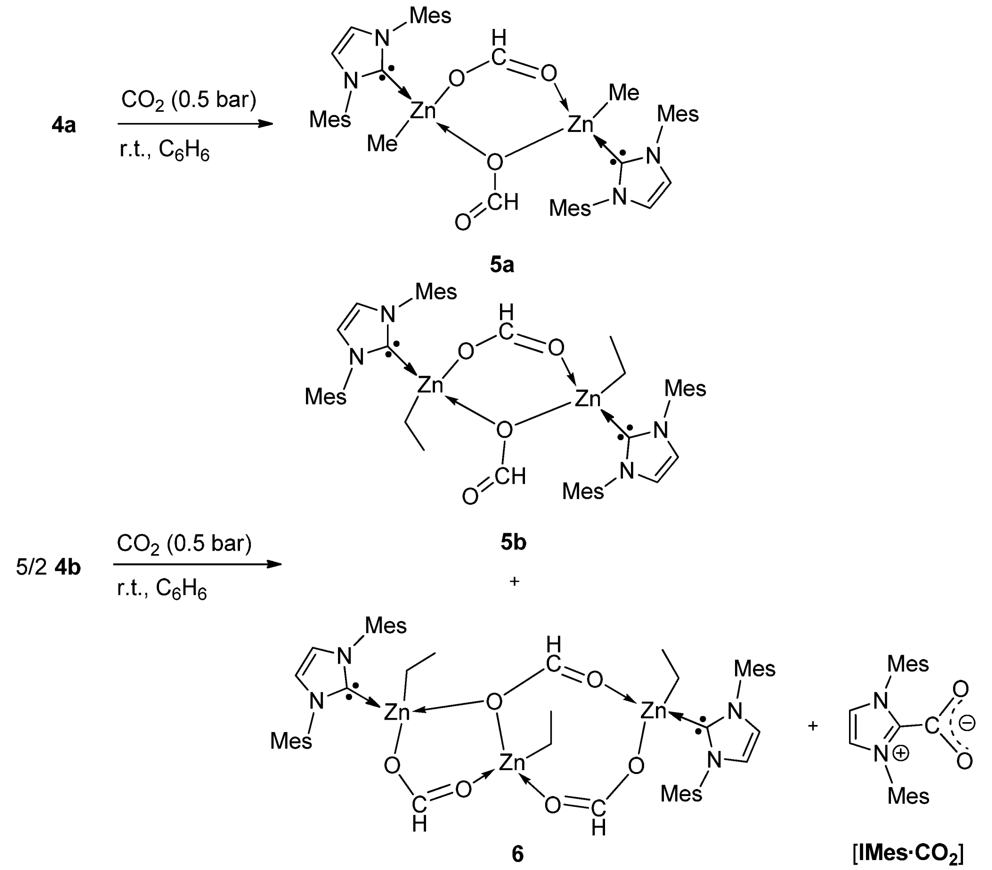


Figure 2. Molecular structure of **4b** with displacement parameters at the 50% probability level. All methyl groups of the mesityl moieties and hydrogen atoms except hydrides connected to the zinc atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C1 = 2.084(3), Zn2−C24 = 2.081(3), Zn1−C22 = 2.009(3), Zn2−C45 = 2.024(3), Zn1−H1 = 1.73(3), Zn1−H2 = 1.77(3), Zn2−H1 = 1.82(3), Zn2−H2 = 1.78(3), Zn1···Zn2 = 2.5066(5); Zn1−H1−Zn2 = 90(1), H2−Zn1−H1 = 91.6(12), C1−Zn1−C22 = 117.81(13), C1−Zn1−H1 = 111.4(8), C1−Zn1−H2 = 103(8).

The formate units in **5a** are characterized by one broad singlet at δ 7.59 in the ^{1}H NMR spectrum and by a signal at δ 167.16 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum in C_6D_6. These chemical shifts are similar to those reported for formate ligands in $[(IMes)Zn(O_2CH)_2]_2$.[7] The ^{1}H NMR integration ratio of formate:IMes:Me group of 1:1:1 in **5a** agrees with the formation of a diformate as a result of CO_2 insertion into the Zn−H bonds (Scheme 5).

Single crystals of **5a** were obtained from Et_2O/hexane at room temperature as colorless blocks. **5a** is a dinuclear

Scheme 5. Reaction of 4a and 4b with CO_2



diformate (Figure 3). The zinc centers are unsymmetrically bridged by one bidentate formate μ_2-O_2CH-κO,O′ ligand; the other formate is bridging in the monodentate μ_2-OCH(=O)-κO coordination mode in the solid state. A similar coordination mode where two metal centers are bridged by two formate ligands was reported before.[17c] The C−O bond lengths indicate localized single and double bonds within the η^1-formate ligand (1.303(4) and 1.217(4) Å, respectively). The appearance of a single resonance in the ^1H NMR spectrum of **5a** may be due to the dissociation into a monomeric complex and/or rapid exchange between both the coordination modes. DFT calculations showed that the symmetrically bridged (η^2−η^2) dimer would be more stable than the experimentally observed unsymmetrical dimer with (η^2−η^1) bridging modes by 0.43 kcal/mol (see Supporting Information). This suggests a rapid exchange between the two coordination modes in solution at ambient temperature.

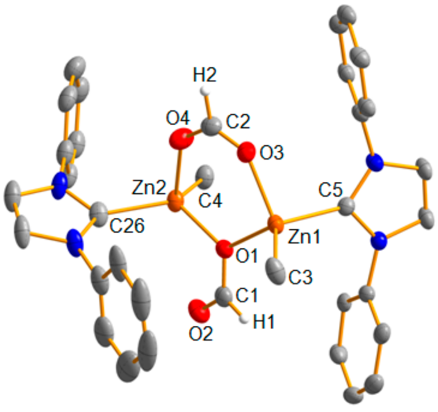


Figure 3. Molecular structure of **5a**·$C_4H_{10}O$ with displacement parameters at the 50% probability level. All methyl groups of the mesityl moieties, hydrogen atoms except for those of the formate units, and the cocrystallized solvent molecule Et_2O are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C5 = 2.066(3), Zn2−C26 = 2.066(3), Zn1−C3 = 2.02(3), Zn2−C4 = 1.981(3), C1−O1 1.303(4), C1−O2 1.217(4), Zn2···O2 2.918(3), Zn1···Zn2 = 3.6784(9); C3−Zn1−C5 = 118.54(14), C3−Zn1−O1 = 112.5(12), C3−Zn1−O3 = 115.24(13), O1−Zn1−O3 = 98.49(9), O1−C1−O2 = 124.9(4), O3−C2−O4 = 129.4(4).

The formate units in the product obtained from the reaction of **4b** with CO_2 give rise to a broad signal at δ 7.97 ppm in the ^1H NMR spectrum and a signal at δ 168.88 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H NMR integration ratio of formate:IMes:Et group and the formation of the byproduct **IMes·CO$_2$** via dissociation of a IMes ligand in **4b** indicate a composition different from that of the dinuclear diformate **5a**. To conclusively determine the structure of the product, crystals of composition **5b**·**6**·$C_4H_{10}O$ suitable for X-ray diffraction were grown from Et_2O/hexane at −35 °C. In the solid state, the dinuclear complex **5b** was found to cocrystallize with the trinuclear complex **6** in 1:1 ratio (Figure 4). Although two distinct sets of signals corresponding to **5b** and **6** were not observed in the ^1H NMR spectrum at 25 °C, the integration ratio of 5:4:5 for the formate:IMes:Et group suggests the existence of **5b** and **6** in 1:1 ratio in solution as well. Cooling the sample led to the appearance of several sets of signals in the ^1H NMR spectra in toluene-d_8 (see Figure S17 in the

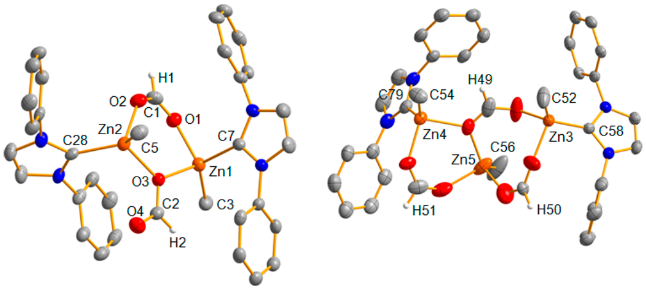


Figure 4. Molecular structure of **5b·6**·$C_4H_{10}O$ with displacement parameters at the 50% probability level. The ethyl groups are shown only with their methylene carbon atom. All methyl groups of the mesityl moieties and hydrogen atoms except for those of the formate units, as well as the cocrystallized solvent molecule Et_2O, are omitted for clarity. Selected bond lengths (Å) and angles (deg): range Zn−C_{NHC} = 2.028(5)−2.064(5), range Zn−$C_{(ethyl)}$ = 1.973(5)−2.015(6), C2−O3 1.295(5), C2−O4 1.209(5), Zn2···O4 3.061(3), Zn1···Zn2 = 3.6498(8) Å, Zn3···Zn5 = 4.1778(11), Zn4···Zn5 = 3.6727(9); C7−Zn1−C3 = 124.79(19), C7−Zn1−O1 = 104.52(16), C7−Zn1−O3 = 104.04(15), O1−Zn1−O3 = 97.16(13), O2−C1−O1 = 130.7(5), O3−C2−O4 = 126.1(5).

Supporting Information). Due to similar solubility of **5b** and **6**, it was not possible to separate them, but 1:1 cocrystals were obtained reproducibly from Et_2O/hexane. Two bridging modes, μ_2-OCH(=O)-κO and μ_2-O_2CH-κO,O′, were found for the formate ligands in **5b**, whereas another type, μ_3-O_2CH-κO,O′, was observed in **6** in the solid state. The first two bridging modes have been observed previously,[7,17] but the μ_3-O_2CH-κO,O′ bridging mode in **6** is unprecedented for zinc formate or acetate complexes. In **6** all zinc atoms are tetrahedrally coordinated by two formate units, one IMes ligand, and one ethyl group except for Zn5, which is coordinated by three formato ligands and one ethyl group. No bonding interaction of the η^1-formate CH(=O) ligand with the zinc center was observed (Zn2···O4 3.061(3) Å); localized single and double (C−O) bonds of 1.295(5) and 1.209(5) Å, respectively, were observed within the η^1-formato ligand.

The Zn···Zn distances in **5b** and **6** are significantly longer than found in the precursor hydride **4b** (2.5066(5) Å). These vary depending on the formate bridge; for example, Zn1···Zn2 (3.6498(8) Å) and Zn4···Zn5 (3.6727(9) Å) distances, where zinc centers are bridged by one η^1 and one η^2 bridging formate, are significantly shorter than the Zn3···Zn5 distance (4.1778(11) Å), where zinc centers are bridged by two η^2 formates. The Zn−C_{NHC} and Zn−C_{ethyl} bond lengths are comparable with that in **4b**. The only known zinc ethyl formate complex is [(dmpzm)ZnEt(O_2CH)] (dmpzm = bis(3,5-dimethylpyrazolyl)methane).[18]

The IR spectrum of **5a** (KBr) shows two distinct intense absorptions for ν_{asy}(C=O) (HCO_2) at 1605 and 1651 cm^{-1} for the η^2 and η^1 formate moieties. The IR spectrum of **5b·6** shows a broad intense band for ν_{asy}(C=O) (HCO_2) absorption at 1608 cm^{-1}, shifted to 1574 cm^{-1} for the corresponding ^{13}C isotopomer. The ν_{sy}(C=O) (HCO_2) absorptions for both **5a** and **5b·6** are not reliably assigned due to overlap with the aromatic stretching modes of the NHC ligands.

The DFT calculations show that the diformate **5a** is more stable by 13.7 kcal/mol than a hypothetical triformate, related to **6**, which was not experimentally observed (see Supporting Information). On the other hand, the diformate **5b** and triformate **6** differ only by 1.2 kcal/mol in energy at room temperature, which explains why both species are formed.

CONCLUSION

Deprotonation of the (NNNN)-type macrocycle (Me_3TACD)-H by $ZnEt_2$ gives the mono(ethyl) complex [(Me_3TACD)-ZnEt] (**1**) under ethane elimination. Formation of the $ZnEt_2$ adduct of **1**, [(Me_3TACD)(ZnEt)($ZnEt_2$)] (**2**), indicates that the amido nitrogen of Me_3TACD is rather basic.[11f,12] The mononuclear complex **1** reacted with $PhSiH_3$ under redistribution of Me_3TACD to the dimeric ethyl hydrido complex [{(Me_3TACD)ZnEt}$_2$(ZnEtH)$_2$] (**3**), which can be regarded as a "[ZnEt(μ-H)]$_2$" unit trapped by the basic amido nitrogen atoms of the Me_3TACD ligands in [(Me_3TACD)ZnEt]. IMes was found to substitute both [(Me_3TACD)ZnEt] units in **3** to give [(IMes)ZnEtH]$_2$ (**4b**) due to the strong σ-donor property of NHC.[14] The mixed alkyl hydrido complexes **4a** and **4b** can also be synthesized in high yields by comproportionation of the dihydride [(IMes)ZnH_2]$_2$ with the dialkyl [(IMes)ZnR_2] (R = Me, Et). **4a** and **4b** reacted with CO_2 to give formate complexes. The relatively common structural motif of an unsymmetrical diformate bridge in **5a** and **5b** was found.[7,17c] The formation of the trinuclear complex **6** is explained by the increased lability of the IMes ligand at the zinc center of **4b** compared to **4a**.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under argon atmosphere using standard Schlenk or glovebox techniques. All glassware was dried at 130 °C in an oven overnight. The solvents used for the synthesis and NMR experiments were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were performed on a Bruker Avance II 400 or on a Bruker Avance III 400 spectrometer at 25 °C. The chemical shifts in the ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. IR spectra were measured using an AVATAR 380 FT-IR spectrometer. Abbreviations for intensities in the IR spectra: w (weak), m (medium), and s (strong). The starting materials (Me_3TACD)H,[10] $PhSiD_3$,[19] IMes,[20] [(IMes)$ZnEt_2$],[13] and [(IMes)-ZnH_2]$_2$[7] were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used as received without further purification. Elemental analyses and mass spectral analyses were performed in the Microanalytical Laboratory of this department.

[(Me_3TACD)ZnEt] (1). To a solution of **2** (1.432 g, 3.32 mmol) in benzene (5 mL) was added a solution of (Me_3TACD)H (0.710 g, 3.32 mmol) in benzene (1 mL), and the reaction mixture was stirred at 60 °C for 1 h. Then the reaction mixture was evaporated to dryness under vacuum and washed with a small amount of cold *n*-pentane; yield: 2.00 g (6.50 mmol, 98%). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.41 (q, $^3J_{HH}$ = 8.2 Hz, 2H, CH_2CH_3), 1.63−1.70 (m, 4H, CH_2), 1.79 (t, $^3J_{HH}$ = 8.2 Hz, 3H, CH_2CH_3), 1.88 (s, 3H, NCH_3), 1.95−2.01 (m, 2H, CH_2), 2.14 (s, 6H, NCH_3), 2.23−2.31 (m, 4H, CH_2), 2.85−3.03 (m, 4H, CH_2), 3.45−3.49 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (100.1 MHz, C_6D_6, 298 K): δ −1.97 (CH_2CH_3), 15.51 (CH_2CH_3), 44.12 (NCH_3), 46.53 (NCH_3), 50.83 (CH_2), 54.59 (CH_2), 56.27 (CH_2), 61.63 (CH_2). Anal. Calcd for $C_{13}H_{30}N_4Zn$ (307.79 g/mol): C, 50.73; H, 9.82; N, 18.21. Found: C, 50.43; H, 10.10; N, 17.92.

[(Me_3TACD)(ZnEt)($ZnEt_2$)] (2). To a solution of (Me_3TACD)H (0.856 g, 4.00 mmol) in *n*-pentane (10 mL) was slowly added a 1 M solution of $ZnEt_2$ in hexane (8 mL, 8.00 mmol). Then the reaction mixture was stirred for 1 h at room temperature. A white solid precipitated during this time, which was isolated by filtration, washed with *n*-pentane, and dried under vacuum; yield: 1.548 g (3.59 mmol, 90%). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.24 (q, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_2CH$_3$), 0.73 (q, $^{3}J_{HH}$ = 8.2 Hz, 4H, CH_2CH$_3$), 1.42−1.48 (m, 2H, CH$_2$), 1.53−1.59 (m, 2H, CH$_2$), 1.63−1.68 (m, 2H, CH$_2$), 1.66 (t, $^{3}J_{HH}$ = 8.2 Hz, 3H, CH$_2$CH_3), 1.69 (s, 3H, NCH$_3$), 1.76−1.82 (m, 2H, CH$_2$), 1.97−2.02 (m, 2H, CH$_2$), 1.99 (s, 6H, NCH$_3$), 2.07 (t, $^{3}J_{HH}$ = 8.2 Hz, 6H, CH$_2$CH_3), 2.28−2.33 (m, 4H, CH$_2$), 3.09−3.14 (m, 2H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100.1 MHz, C_6D_6, 298 K): δ −0.75 (CH_2CH_3), 5.67 (CH_2CH_3), 15.21 (CH_2CH_3), 15.29 (CH_2CH_3), 44.24 (NCH$_3$), 44.56 (NCH$_3$), 50.82 (CH$_2$), 53.12 (CH$_2$), 54.16 (CH$_2$), 57.04 (CH$_2$). Anal. Calcd for $C_{17}H_{40}N_4Zn_2$ (431.29 g/mol): C, 47.34; H, 9.35; N, 12.99. Found: C, 44.59; H, 8.50; N, 13.02; a satisfactory value for carbon was not obtained even after several attempts. Low values for carbon have been reported previously for other zinc complexes.[21] MS (ESI, positive ions): *m/z* 307.1842 (calcd for [M − ZnEt$_2$ + H]$^+$ 307.1840), 277.1338 (calcd for [M − ZnEt$_2$ − Et]$^+$ 277.1370).

[{(Me$_3$TACD)ZnEt}$_2$(ZnEtH)$_2$] (3). To a solution of **1** (0.369 g, 1.20 mmol) in 10 mL of Et$_2$O/benzene (4:1) was slowly added a solution of PhSiH$_3$ (0.130 g, 1.20 mmol) in Et$_2$O (2 mL). Colorless crystals started to precipitate. After stirring the reaction mixture for 30 min at room temperature, the precipitate was isolated, washed with Et$_2$O/benzene (5:1), and dried under vacuum; yield: 0.169 g (0.21 mmol, 70% based on Zn). ^{1}H NMR (400.1 MHz, THF-d_8, 298 K): δ −0.07 (q, $^{3}J_{HH}$ = 8.2 Hz, 4H, CH_2CH$_3$), −0.04 (q, $^{3}J_{HH}$ = 8.0 Hz, 4H, CH_2CH$_3$), 1.21 (t, $^{3}J_{HH}$ = 8.1 Hz, 12H, CH$_2$CH_3), 2.32−2.39 (m, 4H, CH$_2$), 2.34 (s, 6H, NCH$_3$), 2.37 (s, 12H, NCH$_3$), 2.48−2.79 (30H, CH$_2$ and Zn−H, was not reliably assigned), 3.02−3.09 (m, 4H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100.1 MHz, THF-d_8, 298 K): δ −1.17 (CH_2CH_3), 4.32 (CH_2CH_3), 14.88 (CH_2CH_3), 44.51 (br, NCH$_3$), 44.55 (NCH$_3$), 45.29 (br, NCH$_3$), 45.40 (br, NCH$_3$), 51.51 (CH$_2$), 52.82 (br, CH$_2$), 52.99 (CH$_2$), 53.21 (br, CH$_2$), 54.92 (CH$_2$), 55.62 (CH$_2$), 57.92 (CH$_2$), 58.97 (br, CH$_2$). IR (KBr): The $\nu_{Zn\text{-}\mu\text{-}H}$ absorptions could not be reliably assigned. Anal. Calcd for $C_{30}H_{72}N_8Zn_4$ (806.476 g/mol): C, 44.68; H, 9.00; N, 13.90. Found: C, 44.08; H, 8.98; N, 13.90.

[{(Me$_3$TACD)ZnEt}$_2$(ZnEtD)$_2$] (3-D$_2$). This compound was prepared using **1** (0.062 g, 0.20 mmol) and PhSiD$_3$ (0.022 g, 0.20 mmol) instead of PhSiH$_3$ and obtained in 64% yield based on zinc (0.026 g, 0.032 mmol). IR data (KBr): The $\nu_{Zn\text{-}\mu\text{-}D}$ absorptions could not be reliably assigned.

[(IMes)ZnMe$_2$] (ref 22). To a solution of IMes (0.182 g, 0.60 mmol) in toluene (2 mL) was added a 1.2 M solution of ZnMe$_2$ in toluene (0.5 mL, 0.60 mmol). After stirring for 2 h at ambient temperature, the reaction mixture was evaporated to dryness. The residue was washed with cold *n*-pentane (1 mL) and dried in vacuo; yield: 0.228 g (0.57 mmol, 95%). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ −0.49 (s, 6H, CH$_3$), 2.05 (s, 6H, *p*-CH$_3$), 2.06 (s, 12H, *o*-CH$_3$), 6.11 (s, 4H, Im-H), 6.70 (s, 8H, *m*-Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ −8.0 (CH$_3$), 17.94 (*o*-CH$_3$), 21.38 (*p*-CH$_3$), 121.82 (Im-C), 129.79 (*m*-Ph), 135.48 (*o*-Ph), 135.92 (*i*-Ph), 139.45 (*p*-Ph), 192.15 (carbene-C) ppm.

[(IMes)ZnMeH]$_2$ (4a). To a solution of [(IMes)ZnMe$_2$] (0.200 g, 0.50 mmol) in benzene (4 mL) was added a solution of [(IMes)ZnH$_2$]$_2$ (0.186 g, 0.25 mmol) in benzene (4 mL). After stirring for 1 h at ambient temperature, the reaction mixture was evaporated to dryness in vacuo. The residue was washed with *n*-pentane (3 mL) and dried under vacuum; yield: 0.376 g (0.49 mmol, 98%). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ −0.51 (br s, 3H, CH$_3$), −0.77 (br s, 3H, CH$_3$), 2.06 (s, 24H, *o*-CH$_3$), 2.21 (s, 12H, *p*-CH$_3$), 2.75 (br s, 2H, Zn-H), 6.07 (br s, 4H, Im-H), 6.69 (br s, 8H, *m*-Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ −12.32 (CH$_3$), −8.03 (CH$_3$), 18.47 (*p*-CH$_3$), 21.60 (*o*-CH$_3$), 121.76 (Im-C), 129.42 (*m*-Ph), 135.94 (*o*-Ph), 136.86 (*i*-Ph), 137.90 (*p*-Ph), 190.70 (carbene-C) ppm. IR (KBr): $\nu_{Zn\text{-}H}$ absorptions were not reliably assigned due to overlap with the aromatic stretching frequencies of the ligands. Anal. Calcd for $C_{44}H_{56}N_4Zn_2$ (771.69 g/mol): C, 68.48; H, 7.31; N, 7.26; Zn 16.94. Found: C, 68.37; H, 7.29; N, 7.20; Zn, 17.34.

[(IMes)ZnEtH]$_2$ (4b). Method A: To a suspension of **3** (0.040 g, 0.05 mmol) in benzene (2 mL) was slowly added IMes (0.037 g, 0.12 mmol) dissolved in benzene (1 mL). The reaction mixture was stirred for 3 h at room temperature. The mixture was concentrated to 1 mL, and hexane (3 mL) was added. The precipitate was isolated by filtration, washed with hexane, and dried in vacuo; yield: 0.026 g (0.033 mmol, 66%). Method B: To a solution of [(IMes)ZnEt$_2$] (0.170 g, 0.40 mmol) in benzene (2 mL) was added a solution of [(IMes)ZnH$_2$]$_2$ (0.149 g, 0.20 mmol) in benzene (2 mL). After stirring for 1 h at ambient temperature, the reaction mixture was evaporated to dryness in vacuo. The colorless residue was washed with *n*-pentane (2 mL) and dried under vacuum; yield: 0.312 g (0.39 mmol, 97%). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.01−0.40 (br m, 4H, CH_2CH$_3$), 1.42−1.61 (br m, 6H, CH$_2$CH_3), 2.10 (br s, 24H, *o*-CH$_3$), 2.19 (br s, 12H, *p*-CH$_3$), 2.78 (br s, 2H, Zn-H), 6.08 (br s, 4H, Im-H), 6.73 (br s, 8H, *m*-Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ 1.54 and 2.17 (CH_2CH_3), 16.58, 16.83 (CH_2CH_3), 18.58 (*o*-CH$_3$), 21.55 and 21.60 (*p*-CH$_3$), 121.77 (Im-C), 121.93 (Im-C), 129.42 (*m*-Ph), 135.90 (*o*-Ph), 136.76 (*i*-Ph), 138.01 (*p*-Ph), 191.19 (carbene-C) ppm. IR (KBr): The $\nu_{Zn\text{-}H}$ absorptions were not reliably assigned due to overlap with the aromatic vibration of the ligands. Anal. Calcd for $C_{46}H_{60}N_4Zn_2$ (799.94 g/mol): C, 69.08; H, 7.56; N, 7.01; Zn, 16.35. Found: C, 68.83; H, 7.42; N, 6.95; Zn, 15.92.

Reaction of 4a with CO$_2$. A solution of **4a** (0.046 g, 0.06 mmol) in 2 mL of benzene was pressurized with 0.5 bar of CO$_2$ at room temperature for 10 min, resulting in the precipitation of a small amount of colorless solid within 2 h. The solution was filtered, and the filtrate was evaporated to dryness to give a colorless compound, **5a**; yield: 0.043 g (0.05 mmol, 83%). Crystals of **5a** suitable for X-ray diffraction analysis were grown by layering hexane over a saturated solution of **5a** in Et$_2$O at room temperature. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ −0.88 (s, 6H, CH$_3$), 2.08 (s, 24H, *o*-CH$_3$), 2.11 (s, 12H, *p*-CH$_3$), 5.97 (s, 4H, Im-H), 6.76 (s, 8H, *m*-Ph), 7.59 (br s, 2H, OCHO). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ −12.86 (br, CH$_3$), 18.19 (*o*-CH$_3$), 21.43 (*p*-CH$_3$), 122.38 (Im-C), 129.70 (*m*-Ph), 135.95, 136.06, 139.14, 167.16 (OCHO), 182.68 (carbene-C) ppm. IR data (KBr): 3165 (w), 3140 (w), 2954 (w), 2922 (m), 2859 (w), 2820 (w), 1651 (s, ν_{asy}(C=O), HCO$_2$), 1605 (s, ν_{asy}(C=O), HCO$_2$), 1488 (s), 1461 (w), 1401 (w), 1380 (m), 1363 (m), 1276 (w), 1259 (m), 1233 (s), 1161 (w), 1099 (m), 1035 (m), 931 (m), 852 (s), 790 (w), 754 (m), 743 (w), 734 (w), 698 (w), 641 (m), 571 (m), 509 (m) cm^{-1}. Anal. Calcd for $C_{46}H_{56}N_4O_4Zn_2$ (859.708 g/mol): C, 64.26; H, 6.57; N, 6.52; Zn, 15.21. Found: C, 63.56; H, 6.78; N, 6.03; Zn, 15.41.

Reaction of 4b with CO$_2$. A solution of **4b** (0.048 g, 0.06 mmol) in benzene (3 mL) was pressurized with 0.5 bar of CO$_2$ at room temperature for 10 min, which resulted in the precipitation of colorless crystals. After 2 h, the crystals were isolated, washed with 1 mL of benzene, and dried under reduced pressure to give **IMes·CO$_2$**, identified by comparing NMR spectroscopic data with those reported in the literature.[23] The combined filtrates were evaporated to dryness, triturated with *n*-pentane, and dried under vacuum to give a colorless compound; yield: 0.038 g (0.02 mmol, 83% based on Zn). Crystals suitable for X-ray diffraction were grown by layering hexane over a saturated solution of **5b** and **6** in Et$_2$O at −35 °C. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.08−0.24 (br m, 8H, CH_2CH$_3$), 1.12 (t, 6H, (CH_3CH$_2$)$_2$O), 1.42 (br t, $^{3}J_{HH}$ = 7.3 Hz, 12H, CH$_2$CH_3), 2.06 (s, 48H, *o*-CH$_3$), 2.09 (s, 24H, *p*-CH$_3$), 3.27 (q, 4H, (CH$_3$CH_2)$_2$O), 5.98 (s, 8H, Im-H), 6.76 (s, 16H, *m*-Ph), 7.97 (br s, 5H, OCHO). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ 1.29 (br, CH_2CH_3), 13.99 (CH_2CH_3), 18.01 (*o*-CH$_3$), 21.39 (*p*-CH$_3$), 122.56 (Im-C), 129.73 (*m*-Ph), 135.77 (*o*-Ph and *i*-Ph), 139.55 (*p*-Ph), 168.88 (OCHO), 181.59 (carbene-C) ppm. IR (KBr): 3158 (w), 3130 (w), 2922 (m), 2882 (m), 2841 (m), 2726 (w), 1608 (br s, ν_{asy}(C=O), HCO$_2$), 1488 (m), 1462 (w), 1400 (w), 1378 (m), 1364 (m), 1318 (w), 1276 (w), 1236 (m), 1162 (w), 1107 (w), 1036 (m), 1016 (w), 984 (w), 964 (w), 931 (m), 851 (s), 786 (w), 757 (m), 697 (w), 601 (m), 575 (m), 502 (m) cm^{-1}. Anal. Calcd for $C_{99}H_{126}O_{10}N_8Zn_5$ (1914.98 g/mol): C, 62.09; H, 6.63; N, 5.85; Zn, 17.07. Found: C, 62.87; H, 6.44; N, 5.79; Zn 17.55.

Reaction of 4b with ^{13}CO$_2$. This compound was prepared using **4b** (0.040 g, 0.05 mmol) and ^{13}CO$_2$ (0.5 bar) instead of CO$_2$ and isolated as a mixture of **5b-(^{13}C)$_2$** and **6-(^{13}C)$_3$** in 80% yield based on Zn (0.031 g, 0.016 mmol). IR (KBr): 3158 (w), 3129 (w), 2922 (m), 2883 (w), 2843 (m), 2732 (w), 1574 (br s, ν_{asy}(^{13}C═O), $H^{13}CO_2$), 1488 (m), 1462 (w), 1405 (m), 1379 (m), 1344 (m), 1296 (w), 1237 (m), 1163 (w), 1110 (w), 1082 (w), 1036 (m), 1016 (w), 982 (w), 964 (w), 931 (m), 852 (s), 753 (m), 699 (w), 602 (m), 575 (m), 507 (m) cm^{-1}.

X-ray Crystallography. Data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (monolayer optics, λ = 0.71073 Å) using ω scans.[24a] The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT; absorption corrections were applied with SADABS (**3**, **4b**, and **5b·6**) or MULABS (**5a**).[24b,c] The structures were solved by direct methods (SIR-92)[24d] and refined against F^2 using all reflections with the SHELXL-97 as implemented in the WinGX program system.[24e,f] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and treated as riding except for the hydride atoms H1 in **3** and H1 and H2 in **4b** as well as the hydrogen atoms H1 and H2 of the formate unit in **5a** that were located in difference Fourier maps and refined in their position. Compound **3** shows crystallographic inversion symmetry. Complexes **5a** and **5b·6** crystallized with an additional diethyl ether in the lattice. The latter was included with split positions and isotropic displacement parameters in **5a** (due to disorder). Distance restraints were used for this molecule. A distance restraint was also used for the refinement of the bond C1−C2 in **3**. The graphical representations were performed with the program DIAMOND.[24g]

Computational Details. Zinc was treated with a Stuttgart−Dresden pseudopotential in combination with its adapted basis set.[25] The basis set has been augmented by a set of polarization functions (f for Zn).[26] All other atoms have been described with a 6-31G(d,p) double-ζ basis set.[27] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[28,29] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the *extrema* (minimum) was verified with analytical frequency calculations. All computations have been performed with the Gaussian 03[30] suite of programs. The bonding situation was analyzed using the NBO technique.[31]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **1−6**; DFT-optimized structure of [(Me$_3$TACD)ZnEt] (**1**) and Cartesian coordinates of the calculated structures; crystallographic data and refinement details for **3**, **4b**, **5a**·$C_4H_{10}O$, and **5b**·**6**·$C_4H_{10}O$; CIF files giving crystallographic data for compounds **3**, **4b**, **5a**·$C_4H_{10}O$, and **5b**·**6**·$C_4H_{10}O$. 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 interest.

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■ REFERENCES

(1) (a) Gao, Y.; Urabe, H.; Sato, F. *J. Org. Chem.* **1994**, *59*, 5521−5523. (b) Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* **1995**, *60*, 290−291. (c) Uchiyama, M.; Furumoto, F.; Saiko, M.; Kondo, Y.; Sakamato, T. *J. Am. Chem. Soc.* **1997**, *119*, 11425−11433.

(2) Rombach, M.; Brombacher, H.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2002**, 153−159.

(3) Marciniak, W.; Merz, K.; Moreno, M.; Driess, M. *Organometallics* **2006**, *25*, 4931−4933.

(4) (a) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134*, 17462−17462. (b) Mukherjee, D.; Thompson, R. R.; Ellern, A.; Sadow, A. D. *ACS Catal.* **2011**, *1*, 698−702. (c) Jochmann, P.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 9831−9835. (d) Boone, C.; Korobkov, I.; Nikonov, G. I. *ACS Catal.* **2013**, *3*, 2336−2340. (e) Rit, A.; Spaniol, T. P.; Okuda, J. *Chem. Asian J.* **2014**, *9*, 612−619.

(5) (a) Finholt, A. E.; Bond, A. C., Jr.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 1199−1203. (b) Watkins, J. J.; Ashby, E. C. *Inorg. Chem.* **1974**, *13*, 2350−2354. (c) Ashby, E. C.; Watkins, J. J.; Greig, D.; Shriver, D. F. *Inorg. Synth.* **1977**, *17*, 6−8.

(6) (a) Hao, H.; Cui, C.; Roesky, H. W.; Bai, G.; Schmidt, H.-G.; Noltemeyer, M. *Chem. Commun.* **2001**, 1118−1119. (b) Spielmann, J.; Piesik, D.; Wittkamp, B.; Jansen, G.; Harder, S. *Chem. Commun.* **2009**, 3455−3456. (c) Mukherjee, D.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 7582−7583. (d) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 9708−9711. (e) Brown, N. J.; Harris, J. E.; Yin, X.; Silverwood, I.; White, A. J. P.; Kazarian, S. G.; Hellgardt, K.; Shaffer, M. S. P.; Williams, C. K. *Organometallics* **2014**, *33*, 1112−1119.

(7) Rit, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 5228−5246.

(8) (a) Coles, M. P.; El-Hamruni, S. M.; Smith, J. D.; Hitchcock, P. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 10147−10150. (b) Kahnes, M.; Görls, H.; González, L.; Westerhausen, M. *Organometallics* **2010**, *29*, 3098−3108. (c) Kahnes, M.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2011**, *696*, 1618−1625. (d) Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8180−8187.

(9) De Koning, A. J.; Boersma, J.; Van Der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *155*, C5−C7.

(10) Abinet, E.; Martin, D.; Standfuss, S.; Kulinna, H.; Spaniol, T. P.; Okuda, J. *Chem.—Eur. J.* **2011**, *17*, 15014−15026.

(11) (a) Ohashi, M.; Konkol, M.; Rosal, I. D.; Poteau, R.; Maron, L.; Okuda, J. *J. Am. Chem. Soc.* **2008**, *130*, 6920−6921. (b) Venugopal, A.; Fegler, W.; Spaniol, T. P.; Maron, L.; Okuda, J. *J. Am. Chem. Soc.* **2011**, *133*, 17574−17577. (c) Martin, D.; Kleemann, J.; Abinet, E.; Spaniol, T. P.; Maron, L.; Okuda, J. *Eur. J. Inorg. Chem.* **2013**, 3987−3992. (d) Kulinna, H.; Spaniol, T. P.; Maron, L.; Okuda, J. *Inorg. Chem.* **2012**, *51*, 12462−12472. (e) Kulinna, H.; Spaniol, T. P.; Maron, L.; Okuda, J. *Chem.—Eur. J.* **2013**, *19*, 9468−9471. (f) Jochmann, P.; Davin, J. P.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 4452−4455.

(12) (a) Standfuss, S.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2010**, 2987−2991. (b) Cui, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2013**, *32*, 1176−1182. (c) Cui, P.; Spaniol, T. P.; Maron, L.; Okuda, J. *Chem.–Eur. J.* **2013**, *19*, 13437−13444. (d) Cui, P.; Spaniol, T. P.; Maron, L.; Okuda, J. *Chem. Commun.* **2014**, *50*, 424−426.

(13) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13−18.

(14) For reviews on N-heterocyclic carbenes, see: (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172. (b) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810−8849.

(15) (a) Zhu, Z.; Wright, R. J.; Olmstead, M.; Rivard, M. E.; Brynda, M.; Power, P. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5807−5810. (b) Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, W. A.; Rivard, E.; Wolf, R.; Fettinger, J. C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 10847−10857.

(16) (a) Münch, M.; Flörke, U.; Bolte, M.; Schulz, S.; Gudat, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1512−1514. (b) Schulz, S.; Münch, M.; Flörke, U. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2221−2225. (c) Schmidt, S.; Gondzik, S.; Schulz, S.; Bläser, D.; Boese, R. *Organonetallics* **2009**, *28*, 4371−4376. (d) Schmidt, S.; Schäper, R.; Schulz, S.; Bläser, D.; Wölper, C. *Organometallics* **2011**, *30*, 1073−1078. (e) Schulz, S.; Schmidt, S.; Bläser, D.; Wölper, C. *Eur. J. Inorg. Chem.* **2011**, 4157−4160. (f) Jochmann, P.; Stephan, D. W. *Organonetallics* **2013**, *32*, 7503−7508.

(17) (a) Clegg, W.; Little, I. R.; Straughan, B. P. *J. Chem. Soc., Chem. Commun.* **1985**, 73−74. (b) Chen, X.-M.; Tong, Y.-X.; Mak, T. C. W. *Inorg. Chem.* **1994**, *33*, 4586−4588. (c) Schulz, S.; Eisenmann, T.; Schmidt, S.; Bläser, D.; Westphal, U.; Boese, R. *Chem. Commun.* **2010**, *46*, 7226−7228.

(18) Cheng, M.-L.; Li, H.-X.; Liu, L.-L.; Wang, H.-H.; Zhang, Y.; Lang, J.-P. *Dalton Trans.* **2009**, 2012−2019.

(19) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700−4703.

(20) (a) Fegler, W.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2010**, *39*, 6774−6779. (b) Fegler, W.; Saito, T.; Mashima, K.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2010**, *695*, 2794−2797.

(21) Chisholm, M. H.; Gallucci, J. C.; Yin, H.; Zhen, H. *Inorg. Chem.* **2005**, *44*, 4777−4785.

(22) Schnee, G.; Fliedel, C.; Avilés, T.; Dagorne, S. *Eur. J. Inorg. Chem.* **2013**, 3699−3709.

(23) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112−113.

(24) (a) Bruker. *SAINT-Plus*; Bruker AXS Inc.: Madison, WI, USA, 1999. (b) Bruker. *SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2004. (c) Spek, A. L. *Acta Crystallogr. D* **2008**, *65*, 148−155. (d) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350. (e) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122. (f) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838. (g) Brandenburg, K. *Diamond*; Crystal Impact GbR: Bonn, Germany, 2004.

(25) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123−141.

(26) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111−114.

(27) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(29) Burke, K.; Perdew, J. P.; Yang, W. *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F.; Vignale, G.; Das, M. P., Eds.; Springer: Heidelberg, 1998.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowswi, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*, D-02 ed.; Gaussian Inc.: Pittsburgh, PA, 2006.

(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.