

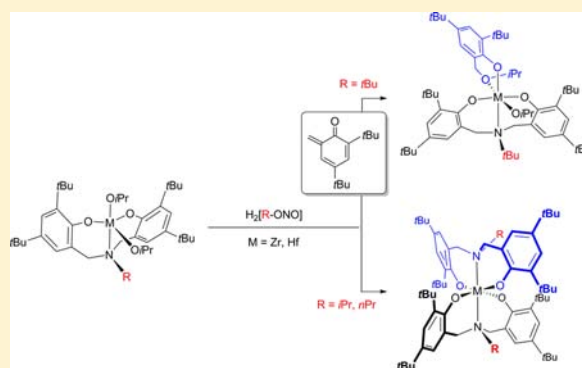
Zirconium and Hafnium Complexes Containing *N*-Alkyl-Substituted Amine Biphenolate Ligands: Unexpected Ligand Degradation and Divergent Complex Constitutions Governed by *N*-Alkyls

Lan-Chang Liang,* Chia-Cheng Chien, Ming-Tsz Chen, and Sheng-Ta Lin

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

Supporting Information

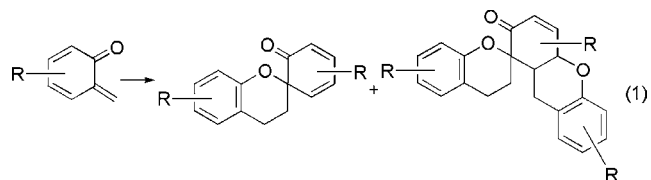
ABSTRACT: The reactivity and thermal stability of zirconium and hafnium complexes containing the *N*-alkyl-substituted amine biphenolate ligands of the type $[\text{RN}(\text{CH}_2\text{-2-O-3,5-C}_6\text{H}_2(\text{tBu})_2)_2]^{2-}$ ($[\text{R-ONO}]^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**), or *n*Pr (**1c**)) were investigated. The reactions of either $[\mathbf{1a}]\text{M}(\text{O}i\text{Pr})_2$ (M = Zr or Hf) with equimolar $\text{H}_2[\mathbf{1a}]$ or $\text{M}(\text{O}i\text{Pr})_4(\text{HO}i\text{Pr})$ (M = Zr or Hf) with 2 equiv of $\text{H}_2[\mathbf{1a}]$ at 25 °C in diethyl ether or 80 °C in toluene afford moderate yields of colorless crystals of $\text{M}[\mathbf{1a}](\text{O}i\text{Pr})_2$ ($\text{M} = \text{Zr}$ (**4a**) or Hf (**5a**)). Controlled experiments revealed that the production of **4a** and **5a** proceeds via unexpected thermal degradation of $\text{H}_2[\mathbf{1a}]$ that produces a highly reactive, transient *ortho*-quinone methide intermediate. Similar reactions employing $\text{H}_2[\mathbf{1b}]$ and $\text{H}_2[\mathbf{1c}]$, however, led to the formation of homoleptic bis-ligand complexes $\text{Zr}[\mathbf{1b}]_2$ (**8b**) and $\text{M}[\mathbf{1c}]_2$ (M = Zr (**8c**) or Hf (**9c**)) as colorless crystals. Decisive factors governing these divergent reaction pathways and complex constitutions are discussed. The X-ray structures of **4a**, **5a**, **8b**, **8c**, and **9c** are presented.



INTRODUCTION

There has been considerable interest in the past decades in amine phenolate complexes of main group and transition metals because of their versatile structural and reaction chemistry. Of particular note are their applications in the construction of tailor-made molecular architectures for specific materials^{1–3} or as catalysts for polymerization of α -olefins^{4–12} or heterocyclic molecules.^{13–22} The amine phenolate ligands are routinely synthesized by traditional Mannich reactions employing appropriate phenols and amines in the presence of formaldehyde.^{23,24} With the incorporation of variable numbers of *N*- and *O*-donors and a wide variety of peripheral substituents on the phenol rings, these phenolic Mannich bases have become conceivably ubiquitous ancillary ligands in coordination chemistry.^{5,25}

ortho-Quinone methides (*o*-QMs) are transient but versatile intermediates that have recently been demonstrated to be competent synthons for natural product synthesis.^{26–28} With inherently highly reactive characteristics, *o*-QMs are susceptible to cycloaddition, typically termed hetero-Diels–Alder reactions, with vinyl substrates.²⁹ Intrinsically, *o*-QMs generally exist as di- or trimers (eq 1).^{30,31} Synthetically, *o*-QMs may be generated by thermal or photochemical processes either from their oligomeric precursors or from phenol derivatives bearing *ortho*-substituted vinyl, hydroxymethyl, (pseudo)halomethyl, etc.²⁷ In contrast, aminophenols such as those that are widely used in exploratory coordination chemistry typically act as “innocent”



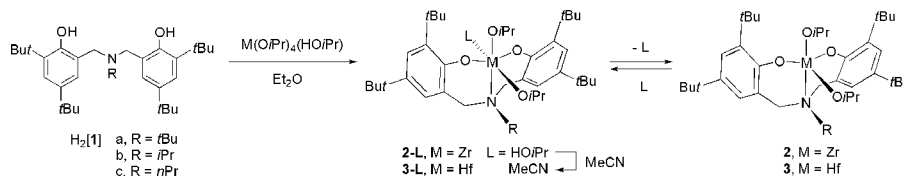
ancillary ligands and usually do not participate in *o*-QM formation.

We are exploring reaction and structural coordination chemistry employing complexes of chelating phenolate ligands.^{32–39} In particular, a series of amine biphenolate ligands of the type $[\text{RN}(\text{CH}_2\text{-2-O-3,5-C}_6\text{H}_2(\text{tBu})_2)_2]^{2-}$ ($[\text{R-ONO}]^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**), or *n*Pr (**1c**)) featuring an *N*-bound tertiary, secondary, or primary alkyl substituent, respectively, has been employed to prepare complexes of group 1, 4, and 13 metals; their corresponding reactivity was explored thereafter.^{40–43} In the course of the preparation of mono-ONO-ligated zirconium and hafnium complexes of $[\mathbf{1}]^{2-}$ (Scheme 1),⁴³ we observed in some cases inevitable generation of either bis-ligated derivatives or unidentified side products, depending on synthetic strategies and use of $\text{H}_2[\mathbf{1}]$. To clarify, we scrutinized these reactions further and found that the amine

Received: April 10, 2013

Published: June 17, 2013

Scheme 1



Scheme 2

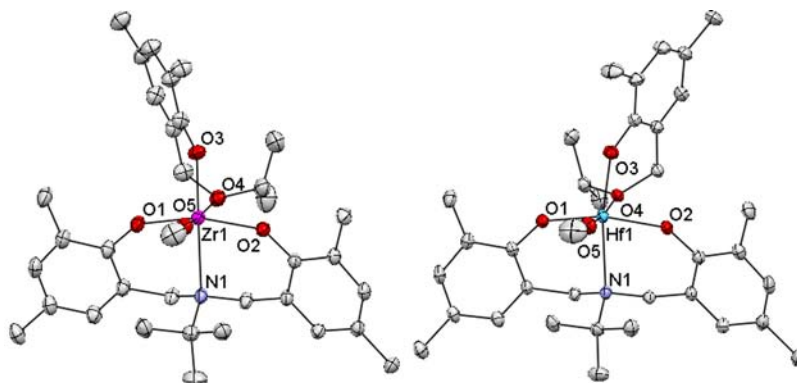
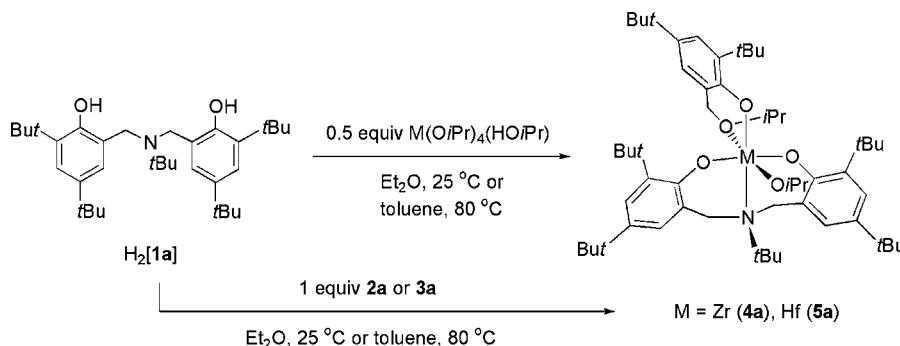


Figure 1. Molecular structures of 4a (left) and 5a (right) with thermal ellipsoids drawn at the 35% probability level. All methyl groups in the aryl *tert*-butyl and isopropoxide are omitted for clarity.

biphenol $H_2[1]$ may degrade to form an *o*-QM derivative, depending on the *N*-alkyl. Though *o*-QMs were first postulated in 1907⁴⁴ and spectroscopically observed in 1971,⁴⁵ it was not until 1998 that their absolute structures were elucidated by Amouri et al. as an η^4 ligand in pentamethylcyclopentadienyl iridium complexes.⁴⁶ In this Article, we present evidence of the presence of *o*-QM in group 4 ONO chemistry as a consequence of amine biphenol degradation and its participation in reactions with reactive metal alkoxides. Parallel studies were also carried out with distinct *N*-alkyl-substituted compounds in order to probe decisive factors for how and why this degradation occurs. These results are intriguing and informative, particularly in view of the current interest in reaction chemistry involving Mannich base-derived metal complexes.

RESULTS AND DISCUSSION

It has been shown that the synthesis of complexes 2a–c and 3a–c is not trivial.⁴³ Though $[1a]Zr(OiPr)_2$ (2a) could be isolated from the reaction of $Zr(OiPr)_4(HOiPr)$ with 1 equiv of $H_2[1a]$ in diethyl ether, some unidentified side products (ca. 10% as judged by ¹H NMR) might concomitantly be produced.⁴³ Attempts to selectively isolate or characterize these side products were not successful. After close scrutiny of

reaction parameters, including reaction solvent, temperature, time, addition sequence, and stoichiometry of starting materials, we found that the same side products could become predominant in the mixture produced as indicated by ¹H NMR spectra when 2-fold $H_2[1a]$ was reacted with $Zr(OiPr)_4(HOiPr)$ either in diethyl ether at 25 °C or in toluene at 80 °C (Scheme 2). Note that this reaction proceeds much faster at elevated temperatures, though the ultimate thermodynamic products are produced in essentially identical ratios. The same results were also observed from the reaction of $H_2[1a]$ with 1 equiv of isolated 2a, indicating unambiguously the participation of a second amine biphenol ligand per zirconium in the generation of this unexpected complex. Similar phenomena were also found for reactions involving $H_2[1a]$, $Hf(OiPr)_4(HOiPr)$, and 3a.

Complexes 4a and 5a were both isolated as colorless crystalline solids in moderate yield with the strategies illustrated in Scheme 2. Colorless crystals of 4a and 5a suitable for X-ray diffraction analysis were grown by layering diethyl ether and acetonitrile on top of a concentrated pentane solution at –35 °C. As depicted in Figure 1, these complexes are six-coordinate, pseudo-octahedral species containing one intact meridional $[1a]^{2-}$ ligand, one isopropoxide, and a novel phenolate ligand

tethered with an isopropyl ethereal donor. Complexes **4a** and **5a** are isostructural to each other, though one is the enantiomer of the other in the established absolute configuration. In accordance with the electron-releasing abilities of substituents at anionic O-donors, the M–O distances for aryloxides are longer than those for alkoxides (Table 1). Without the anionic charge, the isopropyl ethereal donor O(4) lies much farther from the metallic center than other O-donors.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **4a** and **5a**

	4a	5a
M–O(1)	2.013(2)	2.0063(17)
M–O(2)	2.015(2)	2.0094(17)
M–O(3)	1.985(2)	1.9857(18)
M–O(4)	2.469(2)	2.4122(18)
M–O(5)	1.923(2)	1.9132(19)
M–N(1)	2.547(2)	2.492(2)
O(1)–M–O(2)	154.78(9)	156.10(8)
O(1)–M–O(3)	93.69(9)	102.06(7)
O(1)–M–O(4)	83.16(8)	80.94(7)
O(1)–M–O(5)	98.76(10)	101.59(8)
O(1)–M–N(1)	78.68(8)	80.70(6)
O(2)–M–O(3)	101.63(9)	92.28(7)
O(2)–M–O(4)	81.84(8)	84.39(7)
O(2)–M–O(5)	98.12(9)	98.84(8)
O(2)–M–N(1)	79.44(8)	79.33(7)
O(3)–M–O(4)	74.45(8)	75.35(7)
O(3)–M–O(5)	100.14(10)	98.24(8)
O(3)–M–N(1)	156.87(9)	159.42(8)
O(4)–M–O(5)	174.41(8)	172.99(7)
O(4)–M–N(1)	82.93(8)	85.09(6)
O(5)–M–N(1)	102.58(9)	101.59(8)

The solution structures of **4a** and **5a** were elucidated by ^1H , ^{13}C , COSY, and HMQC NMR experiments. Both molecules are *Cs* symmetric on the NMR time scale. The averaged mirror plane coincides approximately with the N–M–O(*i*Pr) plane that contains roughly the ethereal phenolate ring and bisects [**1a**] $^{2-}$. Diagnostically, the aromatic protons resonate as four well-resolved signals with an integral ratio of 2:2:1:1 in the ^1H NMR spectra. The *N*-bound benzylic methylene protons are diastereotopic as evidenced by signals corresponding to an AB spin system, indicating the coordination of the amine nitrogen donor to these group 4 metals.

It has been demonstrated that **2a** is a competent catalyst for ring-opening polymerization (ROP) of ϵ -caprolactone and that the identity of *N*-alkyls in **2** and **3** has a dramatic effect on both coordination chemistry and ROP catalysis.⁴³ The reactivity of **4a** was examined in comparison with its synthetic precursor

(Table 2). While catalytically active, **4a** reacts at a much slower rate than **2a**, producing poly(ϵ -caprolactone) (PCL) with reasonably narrow molecular weight distributions. The slower reaction rate of the former is ascribed to its more sterically encumbered coordination sphere and a presumably less electrophilic metal center when compared to the latter. Though relatively slow, the reactivity of **4a** in ROP catalysis is informative as it suggests that complexes or intermediates derived from thermal degradation may also function as catalytically active species. This result is particularly relevant to systems employing in situ prepared catalysts wherein ligands or additives are used in (slightly) excess amounts. The ^1H NMR analysis of PCL (see Supporting Information) prepared by catalytic **4a** confirmed the presence of an isopropyl ester end group instead of the incorporation of the ethereal phenolate or ONO, suggesting that the initiation of this ROP catalysis selectively involves the zirconium-bound isopropoxide ligand⁴³ rather than chelating phenolates.⁴⁷

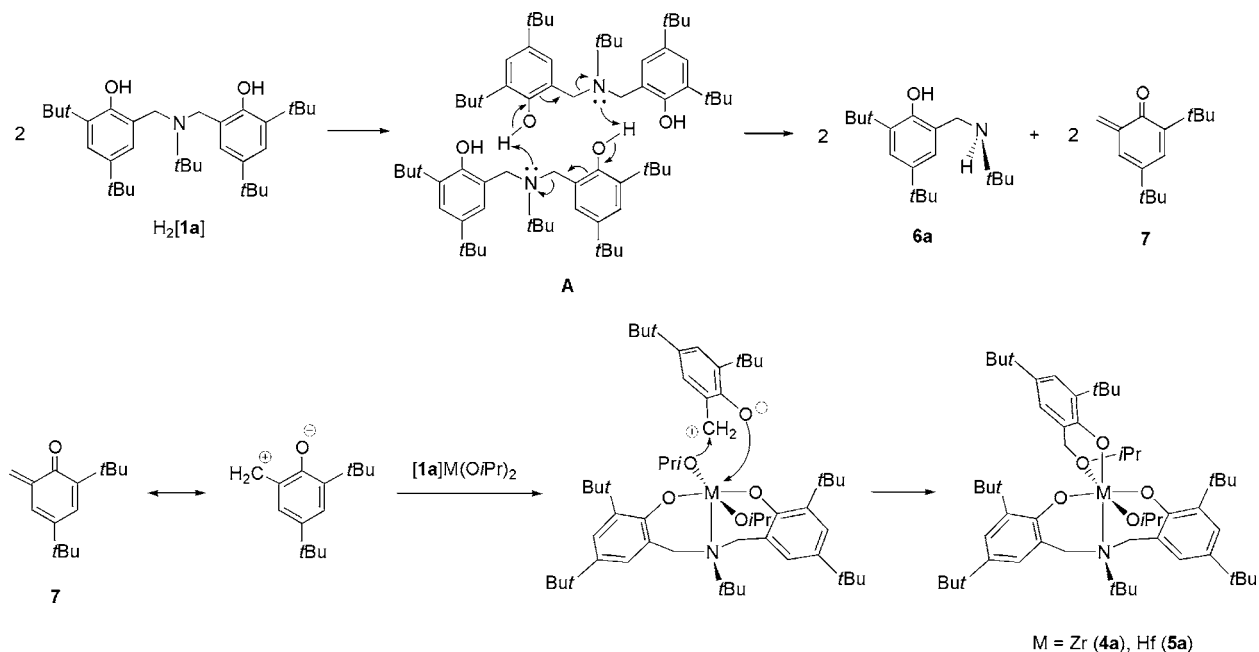
Mechanistically, the formation of **4a** and **5a** may involve either **2a/3a** or H_2 [**1a**] decomposition in view of the incorporation of the ethereal phenolate ligand in these complexes. Controlled experiments showed that both **2a** and **3a** are thermally stable (40 mM in toluene- d_8 at 80 °C for 24 h), thus eliminating the possibility of **4a/5a** evolution from **2a/3a** decomposition under the conditions employed. The ligand precursor H_2 [**1a**], however, decomposes gradually in solutions even at ambient temperature. The disappearance rate of H_2 [**1a**] follows second-order kinetics (rate constant $k = 2.8(5) \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$ at 80 °C; see Supporting Information), suggesting a bimolecular degradation process. Analyses on the thermal decomposition products of H_2 [**1a**] (49 mM in toluene- d_8 at 80 °C) by ^1H NMR and mass spectrometry revealed the presence of 2,4-di-*tert*-butyl-6-(*tert*-butylaminomethyl)phenol (**6a**) accompanied by di- and trimeric di-*tert*-butyl-substituted *o*-QM ($[\text{7}]_x$, $x = 2$ or 3; see Supporting Information) as depicted in Scheme 3. The diagnostic signals of **6a** and oligomeric **7** were also found in reactions used to prepare **4a** and **5a** (Scheme 2) by ^1H NMR and mass spectrometry. Accordingly, we reason that the transient monomeric **7** was produced upon thermolysis of H_2 [**1a**]; subsequent reactions of **7** with **2a** or **3a** took place via insertion of the reactive methylene group of **7** into the M–O(*i*Pr) bond of **2a** or **3a**, thus forming the ethereal phenolate ligand in **4a** or **5a**, respectively. This result is interesting in view of the *formally* nucleophilic substitution of a benzyl amine with an alkoxide. Consistent with these results, thermolysis of H_2 [**1a**] in the presence of 10 equiv of norbornadiene in toluene at 110 °C generates, via hetero-Diels–Alder reactions involving **7**, the anticipated mono- and dicycloaddition products in 12 h as evidenced by EI-MS spectroscopy (see Supporting Information). The involvement of transient *o*-QM was also

Table 2. Catalytic ROP of ϵ -CL^a

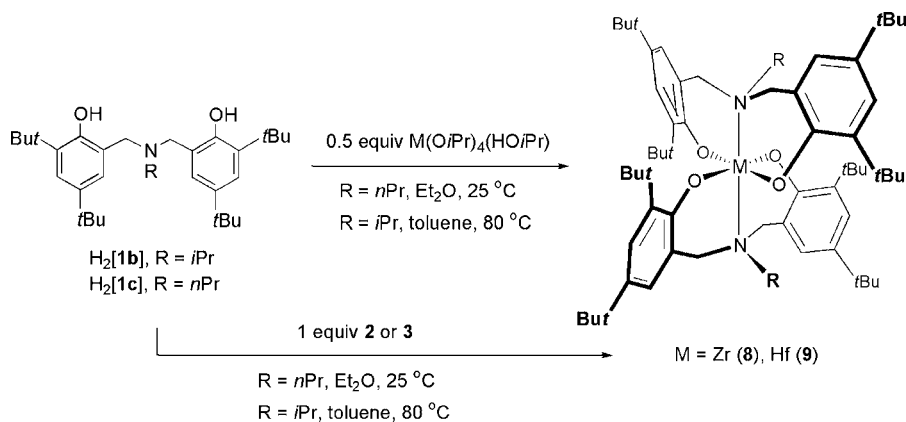
entry	cat.	time (h)	conv (%) ^b	M_n (calcd, kg mol^{-1}) ^c	M_n (exptl, kg mol^{-1}) ^d	corrected M_n (exptl, kg mol^{-1}) ^e	PDI ^d
1 ^f	2a	0.5	69	7.9	6.3	3.5	1.13
2 ^f	2a	1	>99	11.4	10.0	5.6	1.12
3	4a	72	96	11.0	15.7	8.8	1.31

^aUnless otherwise noted, $[\text{cat.}]_0 = 1.0 \text{ mM}$ and $[\epsilon\text{-CL}]_0 = 100 \text{ mM}$ in 10 mL of toluene, 25 °C. ^bDetermined by ^1H NMR analysis. ^cCalculated from $[(\text{fw of } \epsilon\text{-CL}) \times ([\epsilon\text{-CL}]_0/[\text{cat.}]_0) \times \text{conversion}] + (\text{fw of } i\text{PrOH})$, assuming one propagating chain per zirconium atom. ^dMeasured by gel permeation chromatography in tetrahydrofuran, calibrated with polystyrene standards. ^eMultiplied by a factor of 0.56.^{48,49} ^fData selected from reference 43.

Scheme 3



Scheme 4



postulated⁵⁰ in the formation of a yttrium complex containing an *N*-heterocyclic carbene-functionalized phenolate ligand.

Though conformationally similar, $H_2[1a]$ distinguishes itself from $H_2[1b]$ and $H_2[1c]$ as the latter two are both thermally stable as evidenced by 1H NMR studies (40 mM in toluene- d_8 at $80^\circ C$ for 24 h). The thermal stability of these amine biphenol compounds thus depends clearly on the identity of their *N*-alkyl substituents. We reason that the *tert*-butyl-substituted amine in $H_2[1a]$ is substantially more nucleophilic than the isopropyl- and *n*-propyl-substituted amine in $H_2[1b]$ and $H_2[1c]$, respectively, thereby facilitating deprotonation of the phenolic OH, presumably in a reversible manner. Note that X-ray studies of $H_2[1a-c]$ revealed intra- and intermolecular hydrogen bonding of hydroxyl with the amine nitrogen atom and cocrystallized acetonitrile, respectively.⁴⁰ The driving force for $H_2[1a]$ rather than $H_2[1b]$ or $H_2[1c]$ degradation is thus putatively ascribed to the somewhat stabilized protonated ammonium nitrogen in the proposed transition state **A** (Scheme 3) because of the presence of the *tert*-butyl substituent whose electron-donating nature is stronger than that of isopropyl and *n*-propyl substituents. The degradation presum-

ably occurs upon electron release from O to N via the benzyl moiety involving dearomatization, leading to C–N bond cleavage and **6a** and **7** generation. The possibilities involving radical processes were also examined, but these postulations were ruled out as identical results were obtained when reactions depicted in Scheme 2 were conducted in the presence of 2,6-di-*tert*-butyl-4-methylphenol, a common radical scavenger. Another assumption concerns the possible involvement of 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol, as salicyl alcohols are known to react with metal alkoxides to generate ethereal phenolate complexes.⁵¹ Compound 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol could in principle be produced accompanied by **6a** by hydrolysis of $H_2[1a]$. Controlled experiments, however, revealed that 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol⁵² was not produced (1H NMR evidence) from the reactions of $H_2[1a]$ with water ($25^\circ C$ in diethyl ether or $80^\circ C$ in toluene), nor was **4a/5a** generated (1H NMR evidence) from the reactions of **2a/3a** with 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol. Consequently, the participation of 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol in the formation of **4a/5a** was also ruled out. Conceptually, the degradation of $H_2[1a]$ may occur

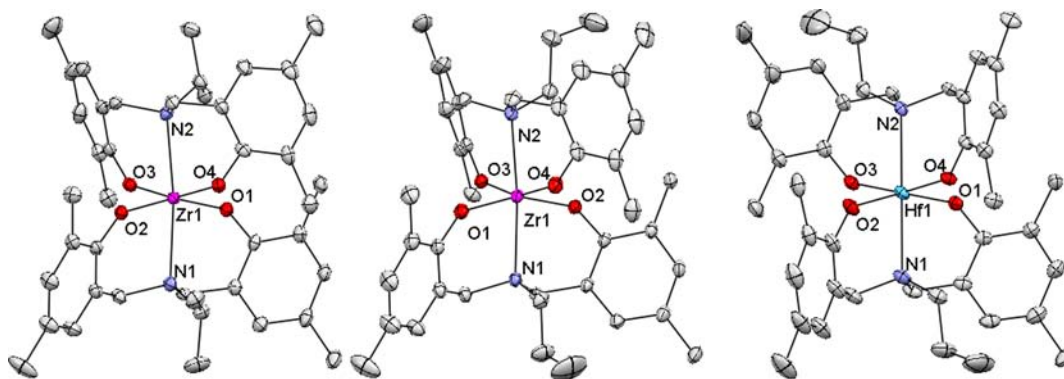


Figure 2. Molecular structures of **8b** (left), **8c** (middle), and **9c** (right) with thermal ellipsoids drawn at the 35% probability level. All methyl groups in the aryl *tert*-butyl are omitted for clarity.

upon nitrogen coordination to the metal center of **2a** or **3a**, but this hypothesis is perhaps unfavorable because the steric size of $H_2[1a]$ is larger than that of $H_2[1b]$ or $H_2[1c]$, with which ligand degradation does not take place in reactions similar to that illustrated in Scheme 2 (*vide infra*).

To better understand the decisive factors for the formation of **4a** and **5a**, parallel studies were performed employing $H_2[1b]$ and $H_2[1c]$ (Scheme 4). In particular, no ligand degradation was found in these reactions. The preparation of **8b** requires prolonged heating at 80 °C, whereas that of **8c** proceeds smoothly even at ambient conditions. No reaction occurs when a toluene- d_8 solution of **2b** with equimolar $H_2[1b]$ was stirred at room temperature for 24 h (1H NMR evidence). The formation rate of **8b** is thus significantly less than that of **8c**, reflecting unambiguously the steric rather than electronic difference of these isomeric *N*-substituents. Interestingly, though **9c** could be synthesized quantitatively with conditions similar to those of **8c** (25 °C, 16 h), attempts to prepare **9b** under even rather harsher conditions (80 °C, 4 days) led to the formation of a mixture containing **3b** and the presumed **9b** (judged by 1H NMR) in a ratio of >10:1. This result is surprising but can be ascribed to an activation barrier for **3b** conversion to **9b** significantly higher than that for **2b** conversion to **8b**. Though rarely encountered, hafnium complexes have in some cases exhibited thermal stability and chemical inertness⁵³ greater than those of their 4d congeners because of inherently stronger metal–ligand bond strengths. In the present study, we propose that the Hf–O*i*Pr bonds in **3b** are relatively inert; thus, their protonation with $H_2[1b]$ becomes more challenging and less effective. These homoleptic complexes are all thermally stable at elevated temperatures (19 mM in toluene- d_8 , 80 °C, 24 h, 1H NMR evidence). In contrast to the mono-ONO-ligated **4a**, the bis-ligated **8c** is inactive for ROP catalysis under similar conditions or in the presence of additional benzyl alcohol.

The solution NMR data of **8b**, **8c**, and **9c** are all indicative of a structure having time-averaged C_2 symmetry. For instance, four distinct singlet resonances are observed in the 1H NMR spectra for aryl *tert*-butyl groups in these molecules. The benzylic methylene moieties are all diastereotopic, so are the *N*-isopropyl methyl groups in **8b** and the *N*- CH_2CH_2Me in **8c** and **9c**. Colorless crystals of **8b**, **8c**, and **9c** suitable for X-ray diffraction analysis were grown from concentrated pentane solutions at –35 °C. Figure 2 depicts the molecular structures of these complexes. Table 3 summarizes selected bond distances and angles. As illustrated, these compounds are

Table 3. Selected Bond Distances (Å) and Angles (deg) for **8b**, **8c**, and **9c**

	8b	8c	9c
M–O(1)	2.005(2)	2.0117(18)	2.007(3)
M–O(2)	2.019(3)	2.0091(18)	2.008(3)
M–O(3)	2.025(3)	2.0128(19)	2.004(2)
M–O(4)	2.028(3)	2.0072(19)	1.995(2)
M–N(1)	2.460(3)	2.399(2)	2.356(3)
M–N(2)	2.449(3)	2.393(2)	2.365(3)
O(1)–M–O(2)	158.78(10)	158.58(8)	159.90(11)
O(1)–M–O(3)	90.89(10)	95.97(8)	95.84(11)
O(1)–M–O(4)	91.16(11)	90.66(8)	90.09(11)
O(1)–M–N(1)	79.82(10)	78.99(7)	79.44(11)
O(1)–M–N(2)	104.90(11)	97.00(8)	97.00(10)
O(2)–M–O(3)	93.87(10)	90.19(8)	90.37(11)
O(2)–M–O(4)	91.88(11)	91.05(8)	90.54(11)
O(2)–M–N(1)	79.12(10)	79.85(7)	80.89(11)
O(2)–M–N(2)	96.30(10)	104.33(8)	102.92(11)
O(3)–M–O(4)	158.60(10)	158.42(8)	159.95(11)
O(3)–M–N(1)	96.26(10)	97.80(7)	96.18(11)
O(3)–M–N(2)	78.78(10)	78.92(8)	79.61(10)
O(4)–M–N(1)	105.07(10)	103.62(8)	103.74(11)
O(4)–M–N(2)	80.11(10)	79.91(8)	80.66(10)
N(1)–M–N(2)	173.09(10)	174.60(7)	174.26(10)

homoleptic complexes, containing two meridional $[ONO]^{2-}$ ligands with the two nitrogen atoms being *trans*-disposed. Similar structural features were also reported by Kol, Goldschmidt, and co-workers for homo- and heteroleptic ONO complexes of titanium.⁵⁴ Davidson and co-workers also reported independently a series of structurally characterized homoleptic group 4 complexes of sterically less demanding ONO ligands.⁵⁵ Though complexes presented herein are essentially isostructural to one another, the M–N bond distances in **8b** are slightly longer than those in **8c** and **9c**. At first glance, this phenomenon appears irrational as both *n*-propyl and isopropyl carry similar electronic characteristics and the steric repulsion between two *N*-bound alkyls should be negligible in view of *trans*-disposed nitrogen donors. Structural scrutiny of these molecules revealed that these *N*-bound alkyls have marginally close contacts with one of the *ortho-tert*-butyl groups on the phenolate rings. A representative drawing is provided in Figure S5 (see Supporting Information), highlighting the steric interaction between the N2-bound isopropyl and the spatially peripheral *tert*-butyl group *ortho* to O1 in **8b**. With less sterically hindered *n*-propyl groups in **8c** and **9c**, the

nitrogen donors thus lie closer to the metal center than those in isopropyl-derived **8b**.

The divergent preferences for the formation of **4a** and **5a** versus **8b–c** and **9b–c** deserve more comments. Though **8b–c** and **9b–c** are all bis-ligand complexes, the preparation of isopropyl-derived **8b** and **9b** requires conditions to acquire reasonable synthetic yields much more severe than those of *n*-propyl-substituted **8c** and **9c** for steric reasons. As mentioned previously, the steric argument is also supported by X-ray structural data of **8b**, **8c**, and **9c**, from which close contacts are found, though marginally, for *N*-alkyls with spatially peripheral *ortho-tert*-butyl substituents on the phenolate rings. With more sterically demanding *tert*-butyl groups at the nitrogen donors, the presumed bis-ligand $M[1a]_2$ ($M = Zr$ (**8a**) or Hf (**9a**)) should be sterically unfavorable and synthetically rather inaccessible. In view of the synthetic conditions employed for **8b–c** and **9b–c**, the preparation of the presumed **8a** and **9a** would require even harsher conditions, that is, prolonged heating at temperatures much higher than 80 °C. On the basis of the reaction conditions employed for the preparation of **4a** and **5a**, the presumed energies of **8a** and **9a** are apparently higher than those of **4a** and **5a**, thus precluding the possibility of **4a** and **5a** evolution from **8a** and **9a**.

The bis-ligand complexes **8b–c** and **9b–c** were prepared from alcoholysis reactions of **2b–c** and **3b–c**, respectively, with their corresponding ligand precursors $H_2[1b–c]$. It is reasonable to propose that these reactions proceed via reversible $H_2[1b–c]$ coordination, either O-bound or N-bound, to the metal center of **2b–c** or **3b–c** followed by proton transfer between oxygen donors to liberate isopropanol and generate **8b–c** and **9b–c**. In view of the Lewis basic characteristics of O and N, the N-bound intermediacy appears more favorable. This hypothesis is also consistent with the observed formation rates of **8b** and **9b** in comparison with those of **8c** and **9c**. With more sterically demanding *tert*-butyl substituents in $H_2[1a]$, **2a**, and **3a**, a similar N-bound intermediacy may be even more unfavorable on steric grounds, though it may conceptually assist $H_2[1a]$ degradation. Interestingly, ligand degradation does not occur for $H_2[1b]$ and $H_2[1c]$, even in the presence of Lewis acidic metal complexes at elevated temperatures, for which the relatively weaker electron-releasing nature of the N-donor in these ligand precursors should be responsible.

As discussed above, we prefer the justification illustrated in Scheme 3 for the formation of **4a** and **5a**. Note that $H_2[1a]$ degrades in solutions at ambient temperature in the presence or absence of **2a** or **3a**. Upon thermal decomposition of $H_2[1a]$, the produced *o*-QM **7** reacts either with other unsaturated molecules, including **7** itself, present in solutions to give cycloaddition products, or with **2a** or **3a** to produce the structurally characterized ethereal phenolate complex **4a** or **5a**, respectively.

CONCLUSIONS

We have demonstrated that the thermal stability of amine biphenol compounds is a function of their incorporated *N*-substituents. With a *tert*-butyl group at the nitrogen donor, the ONO ligand $H_2[1a]$ is susceptible to thermal degradation, unexpectedly producing a transient *o*-QM derivative that, under the conditions employed, reacts subsequently with metal alkoxides to afford a novel ethereal phenolate ligand as observed in complexes **4a** and **5a**. As a result, these reactions involve both C–N bond cleavage and C–O bond formation.

Parallel studies employing either isopropyl- or *n*-propyl-derived ONO ligands gave different results, wherein no ligand degradation was observed. These results are intriguing as the latter ligands are close, lower homologues of the former. The formation rates of homoleptic **8b** and **9b** in comparison with those of **8c** and **9c** highlight the steric effect of these ONO ligands, in spite of the fact that the *N*-alkyl substituents in these ligands are isomeric. Though produced unexpectedly by a process involving thermal degradation of $H_2[1a]$, **4a** is an active catalyst for ϵ -caprolactone polymerization, underscoring the fact that the presumed innocent ligands may under certain circumstances become reactive, providing perhaps misleading conclusions in catalysis. In sharp contrast, the bis-ligated complex **8c** is inactive for ROP catalysis. The comparison in ROP activities of **4a** and **8c** is intriguing, particularly from the standpoint that both complexes are prepared with identical synthetic strategies. These findings are informative and relevant to the structural and reaction chemistry of complexes containing the conceivably ubiquitous Mannich-type ligands.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane. Coupling constants (*J*) are listed in hertz. 1H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 . ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6 . The assignment of the carbon atoms for all new compounds is based on distortionless enhancement by polarization transfer ^{13}C NMR spectroscopy. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer. Gel permeation chromatography analyses were carried out at 45 °C on a JASCO instrument equipped with two Waters Styragel HR columns in series and a JASCO RI-2031 refractive index detector. HPLC grade THF was supplied at a constant flow rate of 1.0 mL/min with a JASCO PU-2080 isocratic HPLC pump. Molecular weights (M_n and M_w) were determined by interpolation from calibration plots established with polystyrene standards.

Materials. Compounds $H_2[1a]$,⁴⁰ $H_2[1b]$,⁴⁰ and $H_2[1c]$ ⁵⁴ were prepared according to literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Crystallographic data for all structurally characterized complexes are available in Supporting Information. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Structures were solved by direct methods and refined by full matrix least-squares procedures against F^2 using SHELXL-97.⁵⁶ All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The structures of **5a**, **8b**, **8c**, and **9c** contain disordered pentane. Attempts to obtain suitable disorder models failed. The SQUEEZE procedure of the Platon program⁵⁷ was used to obtain a new set of $F^2(hkl)$ values for each structure without the contribution of solvent molecules, leading to the presence of significant voids in these structures. The refinement reduced R1 values of **5a**, **8b**, **8c**, and **9c** to 0.0235, 0.0667, 0.0526, and 0.0342, respectively. Structures reported herein also contain disordered *tert*-butyl groups in ONO or methyl groups in isopropoxide that could not be resolved properly, thus giving rise to B-level alerts in checkCIF reports. CCDC entries 910754 (for **4a**), 910755 (for **5a**), 910756 (for **8b**), 910757 (for **8c**), and 910758 (for **9c**) contain the supplementary crystallographic data for this Article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Zr[1a](OiPr)(iPrOCH₂-2-O-3,5-C₆H₂(tBu)₂) (4a).

To a toluene solution (6 mL) of H₂[1a] (200 mg, 0.392 mmol) was added a toluene solution (6 mL) of Zr(OiPr)₄(HOiPr) (76 mg, 0.196 mmol) at room temperature. The solution was heated with stirring in an oil bath at 80 °C for 16 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. The solid residue was washed with acetonitrile (6 mL) to afford the product as an off-white solid. Yield: 98 mg (52%). ¹H NMR (C₆D₆, 500 MHz) δ: 7.50 (d, 2, J = 2.1, ArH), 7.49 (d, 1, J = 2.3, ArH), 7.15 (d, 2, J = 2.1, ArH), 6.68 (d, 1, J = 2.1, ArH), 4.79 (sept, 1, J = 6.1, ZrOCHMe₂), 4.69 (br s, 2, ArCH₂OCHMe₂), 4.43 (sept, 1, J = 6.5, ArCH₂OCHMe₂), 4.14 (d, 2, J = 14.4, ArCH_AH_BN), 3.58 (d, 2, J = 14.5, ArCH_AH_BN), 1.90 (s, 9, ArCMe₃), 1.60 (s, 18, ArCMe₃), 1.38 (s, 18, ArCMe₃), 1.37 (br s, 6, ZrOCHMe₂), 1.30 (s, 9, ArCMe₃), 1.17 (s, 9, NCM₃), 0.74 (d, 6, J = 6.5, ArCH₂OCHMe₂). ¹³C NMR (C₆D₆, 125 MHz) δ: 159.2 (C), 158.5 (C), 140.8 (C), 140.3 (C), 137.5 (C), 137.3 (C), 129.7 (C), 129.6 (C), 124.1 (CH), 123.9 (CH), 123.5 (CH), 122.4 (CH), 75.9 (ArCH₂OCHMe₂), 74.0 (ZrOCHMe₂), 67.4 (ArCH₂OCHMe₂), 62.7 (NCMe₃), 61.9 (ArCH₂N), 36.0 (ArCMe₃), 35.6 (ArCMe₃), 34.7 (ArCMe₃), 34.6 (ArCMe₃), 32.4 (ArCMe₃), 32.3 (ArCMe₃), 30.9 (ArCMe₃), 30.8 (ArCMe₃), 27.7 (NCMe₃), 21.8 (OCHMe₂), 1.8 (ArCH₂OCHMe₂). Anal. Calcd for C₅₅H₈₉NO₅Zr: C, 70.60; H, 9.59; N, 1.50. Found: C, 69.98; H, 9.53; N, 1.53.

Synthesis of Hf[1a](OiPr)(iPrOCH₂-2-O-3,5-C₆H₂(tBu)₂) (5a).

The procedures were similar to those followed for 4a except employing Hf(OiPr)₄(HOiPr) in the place of Zr(OiPr)₄(HOiPr), affording the product as an off-white solid. Yield: 48%. ¹H NMR (C₆D₆, 500 MHz) δ: 7.51 (br s, 2, ArH), 7.50 (br s, 1, ArH), 7.13 (br s, 2, ArH), 6.65 (br s, 1, ArH), 4.87 (sept, 1, J = 6.0, HfOCHMe₂), 4.66 (br s, 2, ArCH₂OCHMe₂), 4.47 (sept, 1, J = 6.2, ArCH₂OCHMe₂), 4.14 (d, 2, J = 14.2, ArCH_AH_BN), 3.57 (d, 2, J = 14.5, ArCH_AH_BN), 1.89 (s, 9, ArCMe₃), 1.59 (s, 18, ArCMe₃), 1.38 (s, 18, ArCMe₃), 1.36 (br s, 6, HfOCHMe₂), 1.31 (s, 9, ArCMe₃), 1.18 (s, 9, NCM₃), 0.73 (d, 6, J = 6.0, ArCH₂OCHMe₂). ¹³C NMR (C₆D₆, 125 MHz) δ: 158.9 (C), 158.6 (C), 140.7 (C), 140.2 (C), 138.1 (C), 138.1 (C), 129.7 (C), 129.3 (C), 124.2 (CH), 123.8 (CH), 123.5 (CH), 122.1 (CH), 76.1 (ArCH₂OCHMe₂), 73.3 (HfOCHMe₂), 67.5 (ArCH₂OCHMe₂), 63.2 (NCMe₃), 61.8 (ArCH₂N), 35.9 (ArCMe₃), 35.6 (ArCMe₃), 34.7 (ArCMe₃), 34.6 (ArCMe₃), 32.5 (ArCMe₃), 32.4 (ArCMe₃), 30.9 (br, ArCMe₃), 27.9 (NCMe₃), 21.7 (OCHMe₂), 1.8 (ArCH₂OCHMe₂). Anal. Calcd for C₅₅H₈₉HfNO₅: C, 64.57; H, 8.77; N, 1.37. Found: C, 64.60; H, 8.87; N, 1.36.

Synthesis of Zr[1b]₂ (8b). The procedures were similar to those followed for 4a except employing H₂[1b] in the place of H₂[1a] and a reaction time of 24 h, affording the product as an off-white solid. Yield: 42%. ¹H NMR (C₆D₆, 500 MHz) δ: 7.51 (d, 2, J = 2.4, ArH), 7.47 (d, 2, J = 2.4, ArH), 7.18 (d, 2, J = 2.3, ArH), 7.09 (d, 2, J = 2.3, ArH), 5.28 (d, 2, J = 10.8, ArCH_AH_B), 5.25 (d, 2, J = 10.7, ArCH_AH_B), 3.66 (d, 2, J = 13.7, ArCH_CH_D), 3.49 (s, 2, J = 13.8, ArCH_CH_D), 3.39 (sept, 2, J = 6.8, NCHMe₂), 1.48 (s, 18, ArCMe₃), 1.42 (s, 18, ArCMe₃), 1.37 (s, 18, ArCMe₃), 1.36 (s, 18, ArCMe₃), 1.22 (d, 6, J = 6.8, NCHMe_AMe_B), 1.06 (d, 6, J = 6.8, NCHMe_AMe_B). ¹³C NMR (C₆D₆, 125 MHz) δ: 159.6 (C), 159.4 (C), 140.9 (C), 140.6 (C), 136.5 (C), 136.0 (C), 126.1 (C), 125.7 (C), 125.4 (br, CH), 124.6 (br, CH), 60.3 (ArCH₂N), 59.9 (ArCH₂N), 51.4 (NCHMe₂), 35.9 (ArCMe₃), 35.2 (ArCMe₃), 34.7 (ArCMe₃), 34.6 (ArCMe₃), 32.8 (ArCMe₃), 32.3 (ArCMe₃), 31.7 (ArCMe₃), 30.8 (ArCMe₃), 18.9 (NCHMe_AMe_B), 18.1 (NCHMe_AMe_B). Anal. Calcd for C₆₆H₁₀₂N₂O₄Zr: C, 73.47; H, 9.54; N, 2.60. Found: C, 73.37; H, 9.59; N, 2.39.

Synthesis of Zr[1c]₂ (8c). To a diethyl ether solution (6 mL) of H₂[1c] (200 mg, 0.404 mmol) was added a diethyl ether solution (6 mL) of Zr(OiPr)₄(HOiPr) (78 mg, 0.202 mmol) at room temperature. The solution was stirred at 25 °C for 16 h, filtered through a pad of Celite, and evaporated to dryness under reduced pressure. The solid residue was washed with pentane (6 mL) to afford the product as an off-white solid. Yield: 214 mg (99%). ¹H NMR (C₆D₆, 500 MHz) δ: 7.53 (d, 2, J = 2.2, ArH), 7.39 (d, 2, J = 2.2, ArH), 7.15 (d, 2, J = 2.2, ArH), 7.12 (d, 2, J = 2.2, ArH), 5.09 (d, 2, J = 13.4, ArCH_AH_B), 4.84 (d, 2, J = 12.8, ArCH_CH_D), 3.57 (d, 2, J = 12.9, ArCH_CH_D), 3.50 (d, 2, J = 13.5, ArCH_AH_B), 3.01 (m, 2, NCH₂CH₂Me), 2.78 (m, 2,

NCH₂CH₂Me), 1.56 (s, 18, ArCMe₃), 1.44 (s, 18, ArCMe₃), 1.37 (s, 18, ArCMe₃), 1.25 (br m, 4, NCH₂CH₂Me), 1.22 (s, 18, ArCMe₃), 0.55 (t, 6, J = 7.3, NCH₂CH₂Me). ¹³C NMR (C₆D₆, 125 MHz) δ: 159.4 (C), 158.9 (C), 140.7 (C), 140.1 (C), 136.6 (C), 135.6 (C), 125.6 (CH), 125.1 (CH), 124.6 (CH), 124.5 (CH), 124.3 (C), 122.6 (C), 59.7 (ArCH₂N), 59.1 (ArCH₂N), 49.6 (NCH₂CH₂Me), 35.4 (ArCMe₃), 35.3 (ArCMe₃), 34.8 (ArCMe₃), 34.6 (ArCMe₃), 32.4 (ArCMe₃), 32.3 (ArCMe₃), 30.9 (ArCMe₃), 30.7 (ArCMe₃), 13.2 (NCH₂CH₂Me), 11.7 (NCH₂CH₂Me). Anal. Calcd for C₆₆H₁₀₂N₂O₄Zr: C, 73.47; H, 9.54; N, 2.60. Found: C, 73.41; H, 9.57; N, 2.62.

Synthesis of Hf[1c]₂ (9c). The procedures were similar to those followed for 8c except employing Hf(OiPr)₄(HOiPr) in the place of Zr(OiPr)₄(HOiPr), affording the product as an off-white solid. Yield: 99%. ¹H NMR (C₆D₆, 500 MHz) δ: 7.57 (d, 2, J = 2.4, ArH), 7.42 (d, 2, J = 2.4, ArH), 7.14 (d, 2, J = 2.4, ArH), 7.11 (d, 2, J = 2.4, ArH), 5.18 (d, 2, J = 13.4, ArCH_AH_B), 4.91 (d, 2, J = 12.9, ArCH_CH_D), 3.56 (d, 2, J = 12.9, ArCH_CH_D), 3.50 (d, 2, J = 13.4, ArCH_AH_B), 3.02 (m, 2, NCH₂CH₂Me), 2.79 (m, 2, NCH₂CH₂Me), 1.57 (s, 18, ArCMe₃), 1.46 (s, 18, ArCMe₃), 1.37 (s, 18, ArCMe₃), 1.25 (br m, 4, NCH₂CH₂Me), 1.22 (s, 18, ArCMe₃), 0.54 (t, 6, J = 7.3, NCH₂CH₂Me). ¹³C NMR (C₆D₆, 125 MHz) δ: 159.4 (C), 159.0 (C), 140.5 (C), 139.8 (C), 137.1 (C), 136.0 (C), 125.5 (CH), 124.9 (CH), 124.7 (CH), 124.6 (CH), 124.1 (C), 122.4 (C), 59.6 (ArCH₂N), 58.8 (ArCH₂N), 49.9 (NCH₂CH₂Me), 35.4 (ArCMe₃), 35.2 (ArCMe₃), 34.8 (ArCMe₃), 34.6 (ArCMe₃), 32.4 (ArCMe₃), 32.3 (ArCMe₃), 30.8 (ArCMe₃), 30.7 (ArCMe₃), 13.2 (NCH₂CH₂Me), 11.8 (NCH₂CH₂Me). Anal. Calcd for C₆₆H₁₀₂HfN₂O₄: C, 67.97; H, 8.82; N, 2.40. Found: C, 68.15; H, 8.55; N, 2.25.

■ ASSOCIATED CONTENT**Supporting Information**

X-ray crystallographic data for all structurally characterized compounds, ¹H NMR spectrum of PCL prepared, and mass spectra and kinetic data of thermolysis of H₂[1a]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION**Corresponding Author**

*E-mail: lcliang@mail.nsysu.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Council of Taiwan for financial support (NSC 99-2113-M-110-003-MY3 and 99-2119-M-110-002), Mr. Ting-Shen Kuo (NTNU) for assistance with X-ray crystallography, and the National Center for High-Performance Computing (NCHC) for the access to chemical databases.

■ REFERENCES

- Winpenney, R. E. P. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 7, pp 125–175.
- MacGillivray, L. R. *Metal-Organic Frameworks: Design and Application*; Wiley: Singapore, 2010.
- Johansson, F. B.; Bond, A. D.; McKenzie, C. J. *Inorg. Chem.* **2007**, *46*, 2224–2236.
- Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462.
- Kol, M.; Tshuva, E. Y.; Goldschmidt, Z. In *Beyond Metallocenes: Next-Generation Polymerization Catalysts*; Patil, A. O., Hlatky, G. G., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2003; Vol. 857, pp 62–75.
- Press, K.; Cohen, A.; Goldberg, I.; Venditto, V.; Mazzeo, M.; Kol, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 3529–3532.

- (7) Gendler, S.; Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Kol, M. J. *Am. Chem. Soc.* **2008**, *130*, 2144–2145.
- (8) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.
- (9) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 11037–11046.
- (10) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257.
- (11) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293–4305.
- (12) Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309–330.
- (13) Darensbourg, D. J.; Karroonnirun, O. *Inorg. Chem.* **2010**, *49*, 2360–2371.
- (14) Darensbourg, D. J.; Choi, W.; Karroonnirun, O.; Bhuvanesh, N. *Macromolecules* **2008**, *41*, 3493–3502.
- (15) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, 6804–6806.
- (16) Silvernail, C. M.; Yao, L. J.; Hill, L. M. R.; Hillmyer, M. A.; Tolman, W. B. *Inorg. Chem.* **2007**, *46*, 6565–6574.
- (17) Nimitsirawat, N.; Gibson, V. C.; Marshall, E. L.; Elsegood, M. R. *J. Inorg. Chem.* **2008**, *47*, 5417–5424.
- (18) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783–4790.
- (19) Stopper, A.; Okuda, J.; Kol, M. *Macromolecules* **2012**, *45*, 698–704.
- (20) Meppelder, G. J. M.; Fan, H. T.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 7378–7388.
- (21) Hung, W. C.; Lin, C. C. *Inorg. Chem.* **2009**, *48*, 728–734.
- (22) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437–1447.
- (23) Blicke, F. F. In *Organic Reactions*; Wiley: New York, 1942; Vol. 1, p 303.
- (24) Cummings, T. F.; Shelton, J. R. *J. Org. Chem.* **1960**, *25*, 419–423.
- (25) Wichmann, O.; Sillanpaa, R.; Lehtonen, A. *Coord. Chem. Rev.* **2012**, *256*, 371–392.
- (26) Rokita, S. E. *Quinone Methides*; Wiley: Hoboken, NJ, 2009.
- (27) Willis, N. J.; Bray, C. D. *Chem.—Eur. J.* **2012**, *18*, 9160–9173.
- (28) Amouri, H.; Le Bras, J. *Acc. Chem. Res.* **2002**, *35*, 501–510.
- (29) Dorrestijn, E.; Pugin, R.; Nogales, M. V. C.; Mulder, P. J. *Org. Chem.* **1997**, *62*, 4804–4810.
- (30) Merijan, A.; Shoulders, B. A.; Gardner, P. D. *J. Org. Chem.* **1963**, *28*, 2148–2149.
- (31) Cavitt, S. B.; Sarrafzadeh, H.; Gardner, P. D. *J. Org. Chem.* **1962**, *27*, 1211–1216.
- (32) Liang, L.-C.; Shih, H.-Y.; Chen, H.-S.; Lin, S.-T. *Eur. J. Inorg. Chem.* **2012**, 298–305.
- (33) Liang, L.-C.; Hsu, Y.-L.; Lin, S.-T. *Inorg. Chem.* **2011**, *50*, 3363–3372.
- (34) Liang, L.-C.; Chang, Y.-N.; Shih, H.-Y.; Lin, S.-T.; Lee, H. M. *Eur. J. Inorg. Chem.* **2011**, 4077–4082.
- (35) Hsu, Y.-L.; Liang, L.-C. *Organometallics* **2010**, *29*, 6201–6208.
- (36) Liang, L.-C.; Cheng, L.-C.; Tsai, T.-L.; Hu, C.-H.; Guo, W.-H. *Inorg. Chem.* **2009**, *48*, 5697–5703.
- (37) Liang, L.-C.; Chang, Y.-N.; Lee, H. M. *Inorg. Chem.* **2007**, *46*, 2666–2673.
- (38) Liang, L.-C.; Chang, Y.-N.; Chen, H.-S.; Lee, H. M. *Inorg. Chem.* **2007**, *46*, 7587–7593.
- (39) Chang, Y.-N.; Liang, L.-C. *Inorg. Chim. Acta* **2007**, 136–142.
- (40) Liang, L.-C.; Lin, S.-T.; Chien, C.-C. *J. Chin. Chem. Soc. (Taipei, Taiwan)* **2013**, 60.
- (41) Liang, L.-C.; Lin, S.-T.; Chien, C.-C. *Polyhedron* **2013**, *52*, 1090–1095.
- (42) Liang, L.-C.; Lin, S.-T.; Chien, C.-C. *Inorg. Chem.* **2013**, *52*, 1780–1786.
- (43) Liang, L.-C.; Lin, S.-T.; Chien, C.-C.; Chen, M.-T. *Dalton Trans.* **2013**, 42, 9286–9293.
- (44) Fries, K. *Liebigs Ann. Chem.* **1907**, 339, 350–356.
- (45) McIntosh, C. L.; Chapman, O. L. *J. Chem. Soc. D* **1971**, 383–384.
- (46) Amouri, H.; Besace, Y.; Le Bras, J. *J. Am. Chem. Soc.* **1998**, *120*, 6171–6172.
- (47) Ejfler, J.; Kobylka, M.; Jerzykiewicz, L. B.; Sobota, P. *Dalton Trans.* **2005**, 2047–2050.
- (48) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889–899.
- (49) Haddad, M.; Laghzaoui, M.; Welter, R.; Dagorne, S. *Organometallics* **2009**, *28*, 4584–4592.
- (50) Wang, Z.-G.; Sun, H.-M.; Yao, H.-S.; Shen, Q.; Zhang, Y. *Organometallics* **2006**, *25*, 4436–4438.
- (51) Wichmann, O.; Sopo, H.; Lehtonen, A.; Sillanpää, R. *Eur. J. Inorg. Chem.* **2011**, 2011, 1283–1291.
- (52) Capanec, I.; Mikuldaš, H.; Vinković, V. *Synth. Commun.* **2001**, *31*, 2913–2919.
- (53) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608–1613.
- (54) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem.* **2001**, *40*, 4263–4270.
- (55) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2006**, 887–889.
- (56) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXA Inc.: Madison, WI, 1998.
- (57) Spek, A. L. *PLATON - A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003.