Inorg. Chem. **2005**, *44*, 8188–8190

Inorganic Chemistry
Communication

Group IV Complexes of a Tetradentate Amine Mono(phenolate) Ligand: a Second Side-Arm Donor Stabilizes Cationic Species

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Received August 17, 2005

An amine mono(phenolate) ligand bearing two side-arm donors led to octahedral trialkoxo and trialkyl group IV metal complexes, in which one of the donors was unbound, and to exceptionally stable cationic complexes in which the two side-arm donors were tightly bound.

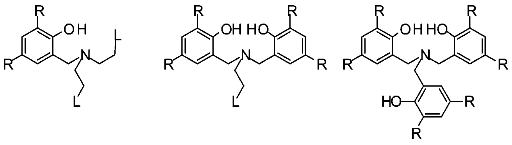
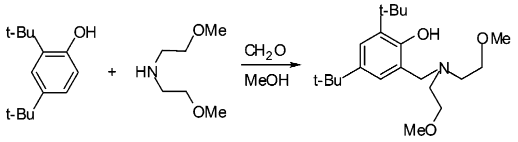


Figure 1. Tetradentate amine phenolate ligand family.

Scheme 1. Synthesis of the Amine Mono(phenolate) Ligand Precursor



Currently, there is considerable interest in early-transition-metal complexes of the chelating tetradentate amine phenolate ligands.[1−5] These ligands bind strongly to those oxophilic metals, leading to well-defined geometries at the metal centers and allowing a precise control of the complex structure and activity. Thus far, this family included two subclasses: the trianionic amine tris(phenolate) ligands[1,2] and the dianionic amine bis(phenolate) ligands,[3−5] possessing an additional "side-arm" donor. Conceptually, an additional subclass of this family is feasible: the monoanionic amine mono(phenolate) ligands that should possess two neutral side-arm donors to be tetradentate (Figure 1). Among other manifestations, this second side-arm donor may stabilize cationic M^{IV} metal centers. To our knowledge, no early-transition-metal complexes of such ligands have been previously reported.[6,7] Herein, we describe the synthesis and structure of neutral and cationic group IV metal complexes of an amine mono(phenolate) ligand bearing two side-arm donors. The latter complexes exhibit remarkable stability.

Aiming at complexes of the $LigMX_3$ and $LigMX_2^+$ types, we chose a ligand featuring methoxy side-arm donors in view of the strong binding of this donor[4c] and bulky *tert*-butylphenolate substituents to minimize the formation of unwanted products.[4d] The ligand precursor (LigH) was prepared by a Mannich condensation between 2,4-di-*tert*-butylphenol, bis(2-methoxyethyl)amine, and formaldehyde (Scheme 1). This method may lead to a broad range of amine mono(phenolate) ligand precursors.

The group IV metal alkoxides, $Ti(O^iPr)_4$ and $Zr(O^tBu)_4$, reacted with LigH at room temperature (RT) to give the corresponding complexes $LigTi(O^iPr)_3$ (**1**) and $LigZr(O^tBu)_3$ (**2**) in high yields. Both complexes feature a single amine phenolate ligand and three alkoxo groups, according to the relative peak integration. The two OMe donors and the three

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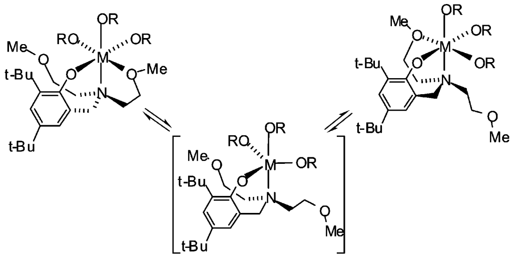
10.1021/ic051400w CCC: $30.25

Scheme 2. Proposed Equilibration Processes for the Alkoxide Complexes **1** and **2**



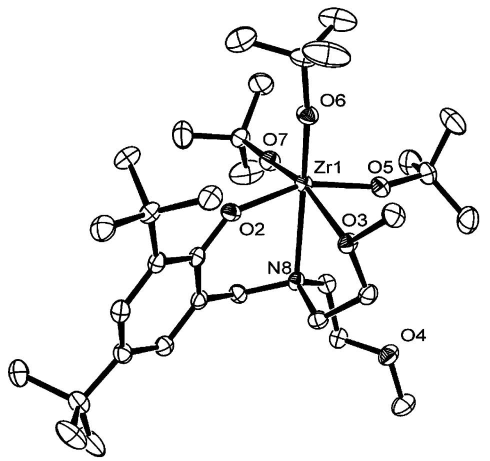


Figure 2. Crystal structure of **2**. ORTEP representation, 50% probability. Selected bond distances (Å) and angles (deg): Zr1−O2, 1.928(2); Zr1−O3, 2.403(2); Zr1−O5, 1.984(2); Zr1−O6, 1.936(2); Zr1−O7, 1.928(2); Zr1−N8, 2.500(2); O2−Zr1−O5, 156.26(7); O3−Zr1−O7, 161.51(7); N8−Zr1−O6, 162.46(7); O2−Zr1−O3, 81.28(6); O5−Zr1−O7, 9.05(7).

alkoxo groups are each identical in the spectra of **1** and **2**. Variable-temperature NMR experiments indicated that both **1** and **2** undergo a dynamic process equilibrating the side-arm donors. For **1**, a single set of two triplets for the [NCH_2CH_2O] protons of the two side arms and a sharp singlet for the benzylmethylene protons at RT signify an averaged C_s-symmetric complex on the NMR time scale. For **2**, this equivalence is apparent only at elevated temperatures. Cooling down both complexes to ca. 230−240 K results in more complex ^{1}H NMR spectra, displaying, among others, two different peaks for the OMe groups and an AB system for the benzylmethylene protons. $\Delta G^{\ddagger}$ values of 50 and 53 kJ mol^{-1} for **1** and **2**, respectively, were extracted from the coalescence temperatures of the $-OCH_3$ peaks in the ^{1}H NMR spectra.[8] The process that equilibrates the side-arm donors can be envisioned as "hopping" of the metal between the two donors (Scheme 2) accompanied by a "flip" of the phenolate ring, which explains the equivalence of the benzylmethylene protons at higher temperatures. This process probably proceeds via a pentacoordinate intermediate ("intramolecular dissociative" mechanism), in which the scrambling of the alkoxo groups takes place.

X-ray structure determinations were carried out for both **1** and **2** (for the structure of Zr complex **2**, see Figure 2).[9] In both structures, in agreement with the spectroscopic data, the second side arm is unbound, resulting in an octahedral geometry at the metal center. The coordination mode of the ligand is *fac*, imposing a *fac* coordination of the three alkoxo groups. The bond distances of Zr−O^{t}Bu are different [1.984(2) Å vs 1.928(2) and 1.936(2) Å], probably because of the different trans influence of the OPh function versus the neutral amine and methoxy donors, respectively. The structure of the Ti complex **1** is analogous to the structure of the Zr complex **2**.

Reports of cationic early-transition-metal alkoxo species are scarce,[10] even though such species may be of great importance because they should exhibit higher electrophilicity than the analogous uncharged species. We anticipated that the "extra" donor in the ligand framework will bind to the metal center upon abstraction of one of the three alkoxo groups, therefore stabilizing the cationic bis(alkoxo) species. Upon reaction of the tris(alkoxo) complexes **1** and **2** with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], a clean formation of monocationic complexes (whose counteranion is tetrakis(pentafluorophenyl)borate, **3** and **4**, respectively) was observed. Compounds **3** and **4** are highly soluble in common organic solvents such as diethyl ether, benzene, and toluene. These compounds were found to be exceptionally stable in solution at RT (no apparent decomposition was observed in a period of several days to several weeks). The cationic alkoxo complexes possess a rigid C_1 symmetry at RT, consistent with coordination of both donors to the metal. The structure of these unusual cationic complexes was confirmed by an X-ray structure determination (for **4**, see Figure 3).[11] As anticipated, both side arms are bound to the metal center [Zr−O3, 2.383(2) Å; Zr−O4, 2.268(2) Å], completing the octahedral geometry at Zr. Overall, the cationic complex presents slightly more compressed bond distances for all donor atoms in comparison to the neutral species (**2**): For example, the PhO−Zr bond is 2.080(2) Å in **2** and 1.973(2) Å in **4**. In **4**, the "second" methoxy group is trans to the phenolate oxygen, having replaced the most weakly bound *tert*-butoxide group. In this disposition, all of the neutral donors are trans to the anionic (σ and π) donors (alkoxo and phenolate oxygens).

Metal alkyl cationic species are known to be highly unstable, often yielding poorly defined mixtures upon isolation attempts. In addition, weakly coordinating counteranions may lead to the formation of dinuclear species.[12] One possible role of an "extra" donor is the stabilization of mononuclear metal alkyl cationic compounds. The reaction of LigH with titanium tetrabenzyl was not successful, leading to a complex mixture of products. On the other hand, the reaction of LigH with zirconium tetrabenzyl formed the

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(8) $\Delta G^{\ddagger} = 19.14T_c[9.97 + \log(T_c/\delta\nu)]$. See: Günther, H. *NMR spectroscopy—an Introduction*; Wiley: New York, 1980.

(9) Crystal data for **2**: $C_{33}H_{63}NO_6Zr$, $M = 661.06$, monoclinic, $C2/c$, $a = 27.186(2)$ Å, $b = 13.295(1)$ Å, $c = 20.779(2)$ Å, $\beta = 90.692(5)°$, $V = 7509.8(9)$ Å^3, $Z = 8$, $D_c = 1.169$ g cm^{-1}, $T = 110$ K, 8663 unique reflns, R1 = 0.046, wR2 = 0.1064 for 6249 reflns with $I > 2\sigma(I)$.

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(11) Crystal data for **4**: $C_{53}H_{54}BF_{20}NO_5Zr$, $M = 1267.00$, monoclinic, $P2_1/n$, $a = 19.9790(5)$ Å, $b = 10.9770(4)$ Å, $c = 26.8330(7)$ Å, $\beta = 109.905(2)°$, $V = 5533.2(3)$ Å^3, $Z = 4$, $D_c = 1.521$ g cm^{-1}, $T = 110$ K, 13 315 unique reflns, R1 = 0.0592, wR2 = 0.1447 for 7896 reflns with $I > 2\sigma(I)$.

(12) For example, see: Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

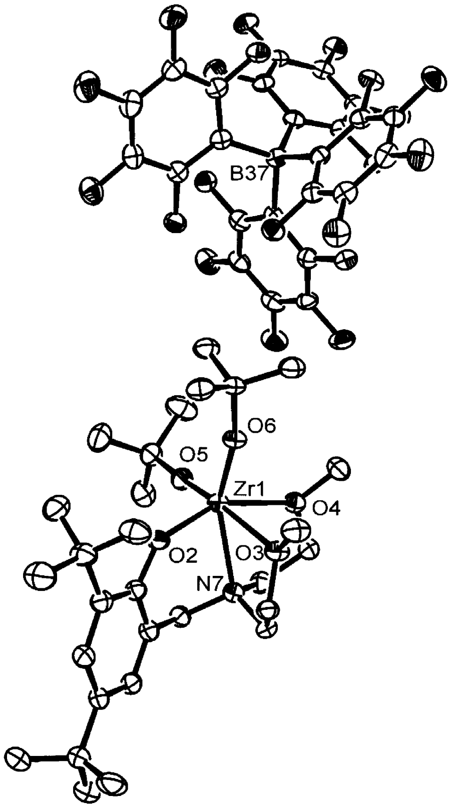
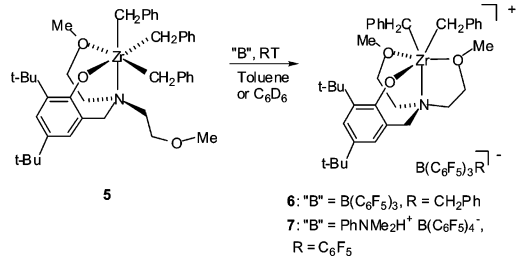


Figure 3. Crystal structure of **4**. ORTEP representation, 40% probability. Selected bond distances (Å) and angles (deg): Zr1−O2, 1.973(2); Zr1−O3, 2.383(2); Zr1−O4, 2.268(2); Zr1−O5, 1.909(2); Zr1−O6, 1.919(2); Zr1−N7, 2.413(3); O2−Zr1−O4, 152.45(9); O5−Zr1−O3, 163.23(10); O6−Zr1−N7, 154.04(9); O2−Zr1−O3, 86.60(9).

desired LigZr(Bn)$_3$ complex **5**, quantitatively, whose spectral data supported a structure analogous to those of complexes **1** and **2**. Upon the addition of a benzene solution of the strong Lewis acid B(C$_6$F$_5$)$_3$ to a solution of **5**, a yellow homogeneous solution formed immediately. According to ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies, formation of a single species (**6**) took place. A 2:1 ratio of the benzyl (phenyl) peaks in **6** implies that the activation of one of the benzyl groups took place. The methylene protons at 3.40 ppm and the broad signal for the carbon atom at ca. 32 ppm are consistent with a Ph−CH$_2$−B fragment of a counteranion. Moreover, the ^{19}F NMR absorptions for the meta and para fluorines (−163.75 and −166.73 ppm, respectively) indicate that the counteranion does not coordinate to the metal.[4c,13] Thus, we suggest that **6** is a well-separated ion pair (Scheme 3). We propose that the "extra" donor binds to the metal in this electron-deficient cationic species.

To further validate the structure of the cationic dibenzyl complex, we reacted the tribenzyl complex **5** with a different activator, [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. Because the activation mechanism by this compound relies on protonation of one of the benzyl groups to form toluene, the formation of a well-separated ion pair should be unequivocally anticipated in this case. This reaction led to the formation of compound **7** (Scheme 3) and was accompanied by toluene liberation. The ^{1}H NMR spectra corresponding to the cationic species of both **6** and **7** are very similar.[14] Most significantly, the cation is stable in solution for a prolonged period of time (no decomposition was observed after a period of 4 days for **7** in C$_6$D$_6$ at RT). We attribute this remarkable stability to the binding of the "extra" donor to the metal.[15]

Scheme 3. Synthesis and Proposed Structure of the Monocationic Dialkylzirconium Complex in **6** and **7**



The structure of the dibenzyl cationic complex deserves some consideration. The overall structure of the cation is consistent with a rigid C_s-symmetric complex, in which the methylene protons of the two identical benzyl groups are diastereotopic, appearing as an AB spin system. Namely, the mirror plane reflects, rather than bisects, the two benzyl groups. This symmetry is not consistent with the "octahedral" C_s-coordination mode, typical of the amine bis(phenolate) ligands.[4] An alternative structure features a "tripodal" binding of the tetradentate ligand, with the two mirror-plane-reflected benzyl groups occupying the C_s-symmetric cavity above the three oxygen donors. An analogous structure was previously reported for the "[N$_3$N]TaR$_2$"-type complexes (see Scheme 3).[16] Thus, the cationic dialkoxo complexes and the cationic dialkyl complexes exhibit a different binding mode. The origin of this difference may lie in the presence of two strong (σ and π) donor ligands (alkoxo groups) in **3** and **4** versus two σ donors only (benzyl ligands) in **6** and **7**.

In summary, we introduced the first member of a new class of tetradentate amine phenolate ligands to the early-transition-metal chemistry realm. This ligand led, on the one hand, to flexible neutral complexes, in which one of the side-arm donors is not bound to the metal, and, on the other hand, to exceptionally stable cationic alkoxo and alkyl complexes, in which the two side-arm donors bind to the metal. The straightforward synthetic pathway and the well-defined coordination modes hint on the rich chemistry that these ligands may sustain.

Acknowledgment. We thank the Israel Science Foundation for financial support.

Supporting Information Available: Experimental procedures, spectroscopic, and crystallographic details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) For example, the methoxy groups give rise to a single peak at 2.95 ppm (**7**) and 2.97 ppm (**6**), and the remaining benzyl groups give rise to an AB system at 2.12 and 2.02 ppm in **7** and 2.22 and 2.09 ppm in **6**. The ^{t}Bu signals and the ligand phenyl signals are essentially identical in these complexes.

(15) The aniline could be removed almost completely by pentane washings without affecting other signals in the ^{1}H NMR spectrum; this further supports the binding of both side-arm donors in this electron-deficient complex.

(16) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *118*, 3643.