

# Ligand Metathesis in Surface-Bound Alkoxyzirconium Complexes

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**Abstract:** Aluminum surface-bound alkoxyzirconium complexes undergo smooth ligand metathesis reactions with a variety of phenols to give the corresponding surface-bound phenoxyzirconium complex species. This process enables rapid preparation of members of a family of surface-bound complexes which are synthesized *in situ* from an easy-to-prepare common precursor. Ligand metathesis can be monitored by infrared spectroscopy under ambient conditions or by a combination of infrared and X-ray photoelectron spectroscopic techniques in ultrahigh vacuum.

*In situ* ligand metathesis can provide a general method for the rapid preparation of a large number of surface-bound organometallic species. In this procedure, ligands can be chosen according to their chemical functionality; it provides an alternative to direct organometallic chemical vapor deposition (OM-CVD) processes which may not be feasible, for example, because of difficulties of synthesis or processing of the requisite precursor.<sup>1</sup> We have reported that tetra(*tert*-butoxy)zirconium can be used to prepare an interface between the hydroxylated oxide surface of aluminum and an alkanecarboxylic acid.<sup>2</sup> In this sequence, a surface alkoxyzirconium complex is first formed, and ligand metathesis with the acid generates the new, (alkanecarboxy)zirconium surface species; metathesis is likely driven by the large acidity difference between *tert*-butyl alcohol and the carboxylic acid and by the metal  $\eta^2$ -carboxylate chelate bond strength. We now report that ligand metathesis can occur with phenols in a process which is also likely driven by differences in acidities of the alcoholic species.<sup>3</sup> Ligand metathesis is readily accomplished from the vapor phase; it can be monitored by infrared spectroscopy under ambient conditions or by a combination of infrared and X-ray photoelectron spectroscopic techniques in ultrahigh vacuum. Significantly, it enables rapid, *in situ* synthesis from an easy-to-prepare alkoxyzirconium precursor of numerous surface complexes, in which ligand chemical properties can be chosen and modified systematically.

## Experimental Section

**Reagents.** Tetra(*tert*-butoxy)zirconium (Aldrich) was vacuum distilled and stored under nitrogen prior to use. Phenol (Allied Chemical), *p*-cresol (Aldrich), *p*-methoxyphenol (Aldrich), and *p*-cyanophenol (Acros) were used without further purification. Glass slides were cleaned first in an ultrasonic detergent bath, followed by successive rinsing with hot trichloroethylene, acetone, and hot methanol. Slides were dried at 250 °C prior to aluminum deposition.

**Hydroxylation of the Aluminum/glass Surface.**<sup>2,4</sup> Aluminum coated glass slides were prepared in an Edwards Vacuum Coating

System Model 306A, by evaporating Al wire (99.999%) from a W point source filament (Mathis) at  $<10^{-6}$  Torr. Aluminum layers of between 40 and 50 nm were deposited. The aluminum substrate was hydroxylated by exposure to water vapor at 85 °C for approximately 1 h, followed by drying under vacuum at 95 °C overnight to remove excess surface water.

**Vapor Phase Reaction between an Al Substrate and Tetra(*tert*-butoxy)zirconium.**<sup>2</sup> A hydroxylated aluminum substrate was placed in an evacuable reaction chamber equipped with an inlet port, which was attached *via* a Teflon stopcock to a reservoir of tetra(*tert*-butoxy)zirconium. The assembly was evacuated for 30 min at *ca.*  $10^{-2}$  Torr. With the vessel open to the vacuum system, the stopcock to the reservoir was opened, and vapor of the organometallic was allowed to pass over the substrate for 30 min. The stopcock was then closed, and the vessel was evacuated for approximately 1 h to give Al-[O]-Zr(OBu)<sub>2</sub>.

**Vapor Phase Reaction between Al-[O]-Zr(OBu)<sub>2</sub> and Phenol.** The Al-[O]-Zr(OBu)<sub>2</sub> substrate slide was loaded into an evacuable reaction chamber equipped with an inlet port, which was attached to a reservoir of phenol *via* a Teflon stopcock. The assembly was evacuated at *ca.*  $10^{-2}$  Torr for 30 min. The chamber was then subjected to four cycles of phenol exposure. Each consisted of a 15 min period when the reservoir was opened to both the chamber and the vacuum, followed by a 30 min period during which time the chamber was isolated from the vacuum, but the reservoir was still open. Following the fourth exposure cycle, the reservoir was closed, and the chamber was evacuated for 1 h.

**Vapor Phase Reaction between Al-[O]-Zr(OBu)<sub>2</sub> and *p*-Cresol.** A similar procedure to that used for phenol was employed. In this case, the *p*-cresol reservoir was opened to the chamber under active vacuum for 2 h, then the flask was closed, and the chamber was evacuated for 2 h.

**Vapor Phase Reaction between Al-[O]-Zr(OBu)<sub>2</sub> and *p*-Methoxyphenol.** A similar procedure to that used for phenol was employed. Two 4 h cycles at  $10^{-5}$  Torr and 38 °C were effected. Final evacuation was at  $10^{-5}$  Torr for 2 h.

**Vapor Phase Reaction between Al-[O]-Zr(OBu)<sub>2</sub> and *p*-Cyanophenol.** A similar procedure to that used for phenol was employed. Here, the assembly was evacuated at *ca.*  $10^{-5}$  Torr for 30 min. The substrate was then subjected to 30 min of exposure to *p*-cyanophenol under active vacuum, after which time the chamber was isolated from the vacuum, but with continued substrate exposure, for 1 h. The initial procedure was followed by five more cycles of 30 min active vacuum and 30 min of isolated chamber exposure. After the final cycle the *p*-cyanophenol flask was closed, and the chamber was evacuated for 2 h.

**Specular Reflectance-Fourier Transform Infrared Spectroscopy (SR-FTIR).** A Nicolet 730 FTIR equipped with a Spectra Tech Variable Angle Specular Reflectance attachment was used to obtain all SR-FTIR spectra. A specular reflectance angle of 85° was used,

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) The aggregation and, hence, the volatility of a metal alkoxide is strongly dependent on the structure of the organic unit. See: Bradley, D. C. *Chem. Rev.* **1989**, 89, 1317.

(2) Aronoff, Y. G.; Chen, B.; Lu, G.; Seto, C.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1997**, 119, 259.

(3) Ligand metathesis in solution is well known. See, for example: Maire, J. C. *Ann. Chim. (Paris)* **1961**, 6, 969.

(4) Miller, J. B.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1993**, 115, 8239.

**Table 1.** Ligand Metathesis Accomplished under Moderate Vacuum

phenol (X =)	exposure (cycles)	exposure (min)	some characteristic IR peaks of product (cm <sup>-1</sup> )
H	4	45	2966, 2923, 1590, 1487, 1286
CH <sub>3</sub>	1	120	3018, 2973, 2924, 2856, 1506, 1282
OCH <sub>3</sub>	2 <sup>a</sup>	240	2977, 2930, 1503, 1230
CN	5	90	3035, 2970, 2926, 2854, 2219( $\nu_{\text{CN}}$ ), 1504, 1251

<sup>a</sup> At 38 °C.

and a freshly coated Al slide was used as a reference. Spectral data were collected for 1024 scans at 8 cm<sup>-1</sup> resolution and are given in Table 1.

**Preparation of Surface Al(110)-O-Zr(OBu<sup>t</sup>)<sub>2</sub> and Al(110)-O-Zr(OBu<sup>t</sup>)<sub>3</sub> in UHV.** An Al(110) single crystal surface was cleaned in UHV by Ar<sup>+</sup> ion sputtering, followed by annealing at 600 K for 30 min. XPS spectral analysis of this surface showed a well-defined Al<sub>2p</sub> peak (BE = 72.8 eV); virtually no peaks were detected in the C<sub>1s</sub>, Zr<sub>3d</sub>, and O<sub>1s</sub> regions. The crystal was cooled to 170 K and then dosed with water as previously described.<sup>5</sup> Following saturation hydroxylation,<sup>5</sup> the crystal was cooled to 170 K and exposed to ~15 L of tetra(*tert*-butoxy)zirconium, which gives a thick multilayer of the intact tetraalkoxide on the hydroxylated aluminum surface. XPS analysis showed no Al<sub>2p</sub> signal (the overlayer was too thick to allow substrate photoelectron escape); the C/Zr atomic ratio was measured to be 16:1. FT-RAIRS analysis also showed the intact tetraalkoxide. A TDS profile of the overlayer (monitoring  $m/z = 57$ ) showed three desorption regions: a first peak at 240 K, for desorption of physisorbed multilayers; a second at 340 K, for conversion of Al-(O)-Zr(OBu<sup>t</sup>)<sub>3</sub>; and a final one at ~500 K, for decomposition of Al-(O)-Zr(OBu<sup>t</sup>)<sub>2</sub>. Practically speaking, by heating the sample to either 300 or 400 K, Al-(O)-Zr(OBu<sup>t</sup>)<sub>3</sub> or Al-(O)-Zr(OBu<sup>t</sup>)<sub>2</sub> can be produced, respectively. Characterization of these two surface species has been published elsewhere.<sup>5</sup>

**Ligand Metathesis for Al-(O)-Zr(OBu<sup>t</sup>)<sub>3</sub> (1) and Phenol in UHV.** Ligand metathesis was accomplished by repetitive dosing of the substrate with phenol at 170 K followed by heating to 300 K. The course of ligand metathesis was followed by RAIRS, XPS, and TDS (Table 2).

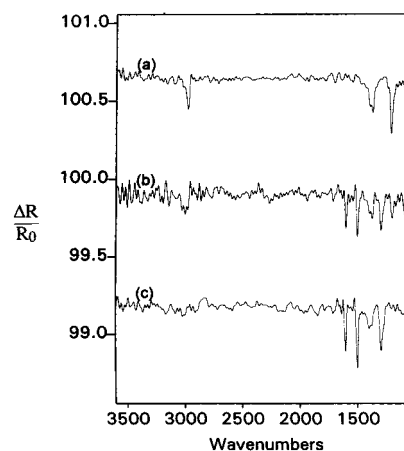
**Ligand Metathesis for Al-(O)-Zr(OBu<sup>t</sup>)<sub>2</sub> (2) and Phenol in UHV.** Ligand metathesis was accomplished as for 1 by repetitive dosing of the substrate with phenol at 170 K followed by warming to 300 K. When 2 was treated with 0.6 L of phenol in this way, FT-RAIRS analysis after one cycle showed the presence of both starting alkoxide and exchanged phenoxy ligands. Analysis after repeating the dose-desorb sequence three more times showed complete ligand exchange (Table 3).

**Ligand Metathesis for Al-(O)-Zr(OBu<sup>t</sup>)<sub>3</sub> (1) and Substituted Phenols in UHV.** Analogous procedures were employed to effect ligand metathesis for 1 and *p*-cresol, *p*-methoxyphenol, and *p*-cyanophenol. Unlike the parent phenol, metathesis reactions using these phenols and 1 were incomplete, even after many dose-desorb cycles. The dosing tube and reservoir were maintained at 100 °C for 4-cyanophenol exposures. Spectral data are collected in Table 2.

**Ligand Metathesis for Al-(O)-Zr(OBu<sup>t</sup>)<sub>2</sub> (2) and Substituted Phenols in UHV.** Analogous procedures were employed to effect ligand metathesis for 2 and *p*-cresol, *p*-methoxyphenol, and *p*-cyanophenol. As for the parent phenol, and in contrast to 1, metathesis reactions using these substituted phenols and 2 were complete after several dose-desorb cycles. Spectral data are collected in Table 3. The dosing tube and reservoir were maintained at 100 °C for 4-cyanophenol exposures.

## Results and Discussion

In a typical metathetical procedure, a surface hydroxylated Al substrate<sup>4</sup> was treated with tetra(*tert*-butoxy)zirconium vapor. Protolytic deposition occurred with loss of *ca.* two alkoxide ligands to give an average stoichiometry, (Al)-O-Zr(*tert*-



**Figure 1.** FT-RAIRS spectra of [Al]-O-Zr(OBu<sup>t</sup>)<sub>2</sub> and its ligand metathesis products with phenol. (a) [Al]-O-Zr(OBu<sup>t</sup>)<sub>2</sub>; (b) one cycle of reaction; and (c) three cycles.

butoxy)<sub>2</sub>.<sup>6</sup> The treated substrate was then placed in an evacuable reaction chamber which was equipped with an inlet port attached to a small vial containing the phenol. Substrate processing conditions for exposure and evacuation depend on the volatility of the particular phenol. For the parent phenol, the reaction assembly was evacuated to approximately 10<sup>-2</sup> Torr for 30 min. The substrate was then subjected to four cycles of exposure (15 min with the reservoir opened to both the reaction assembly and the vacuum; 30 min with the reservoir opened to the reaction assembly, with no evacuation). Following the fourth cycle, the reservoir was isolated, and the chamber was evacuated for 1 h. Procedures using other phenols are given in Table 1. SR-FTIR spectroscopy was used to monitor ligand metathesis; in particular, strong peaks for the *tert*-butoxy ligand (2973 and 1197 cm<sup>-1</sup>) were reduced in intensity, and peaks corresponding to the phenolic ligands grew with each exposure cycle (Table 1).

Alkoxy for phenoxy ligand exchange was also carried out in UHV. Deposition of tetra(*tert*-butoxy)zirconium was accomplished as previously described<sup>5</sup> at 170 K on both lightly hydroxylated and saturation hydroxylated Al(110) surfaces. For both surfaces, a tri(*tert*-butoxy)zirconium species, Al-(O)-Zr(OBu<sup>t</sup>)<sub>3</sub> (1), was initially formed. For the saturation coverage substrate, di(*tert*-butoxy)zirconium species Al-(O)-Zr(OBu<sup>t</sup>)<sub>2</sub> (2) was obtained by mild warming of 1. Metathesis of *tert*-butoxy ligands of 2 with a phenol was accomplished by cycles of exposure at 170 K followed by warming to 300 K. For the parent phenol, FT-RAIRS analysis following one exposure cycle (0.6 L of phenol) showed the presence of both starting material and a new phenoxy complex. Repeating this procedure three more times resulted in complete loss of IR signals for the *tert*-butoxide ligand and an increase in intensity of those of the phenoxy ligand (Figure 1). That simple ligand metathesis and not some other degradation process occurred was demonstrated by XPS analysis of the reaction procedure. In particular, the XPS determined atomic ratio of C to Zr measured prior to treatment with phenol was C/Zr = 8.2 ± 0.5:1 (expected: 8:1); after four cycles of exposure to phenol, C/Zr = 13.0 ± 0.5:1 (expected: 12:1), in good agreement with the stoichiometry, (Al)-O-Zr(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (Scheme 2). Further evidence for metathesis was obtained by analysis of the C<sub>1s</sub> XPS; here, energy resolution is adequate to distinguish C bound directly to O (BE[C<sub>1s</sub>] = 287.1 eV) from C which is bound to C (BE[C<sub>1s</sub>] = 285.3 eV).<sup>7</sup> XPS analysis of the carbon region showed that the atomic ratio of C-O vs C-C changed from 1:3.6 (expected: 1:4) before

(5) Lu, G.; Purvis, K. L.; Schwartz, J.; Bernasek, S. L. *Langmuir* **1997**, *13*, 5791.

(6) Miller, J. B.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **1995**, *117*, 4037.

**Table 2.** Ligand Metathesis From (Al)-O-Zr(OBu)<sub>3</sub> Carried Out in Ultrahigh Vacuum

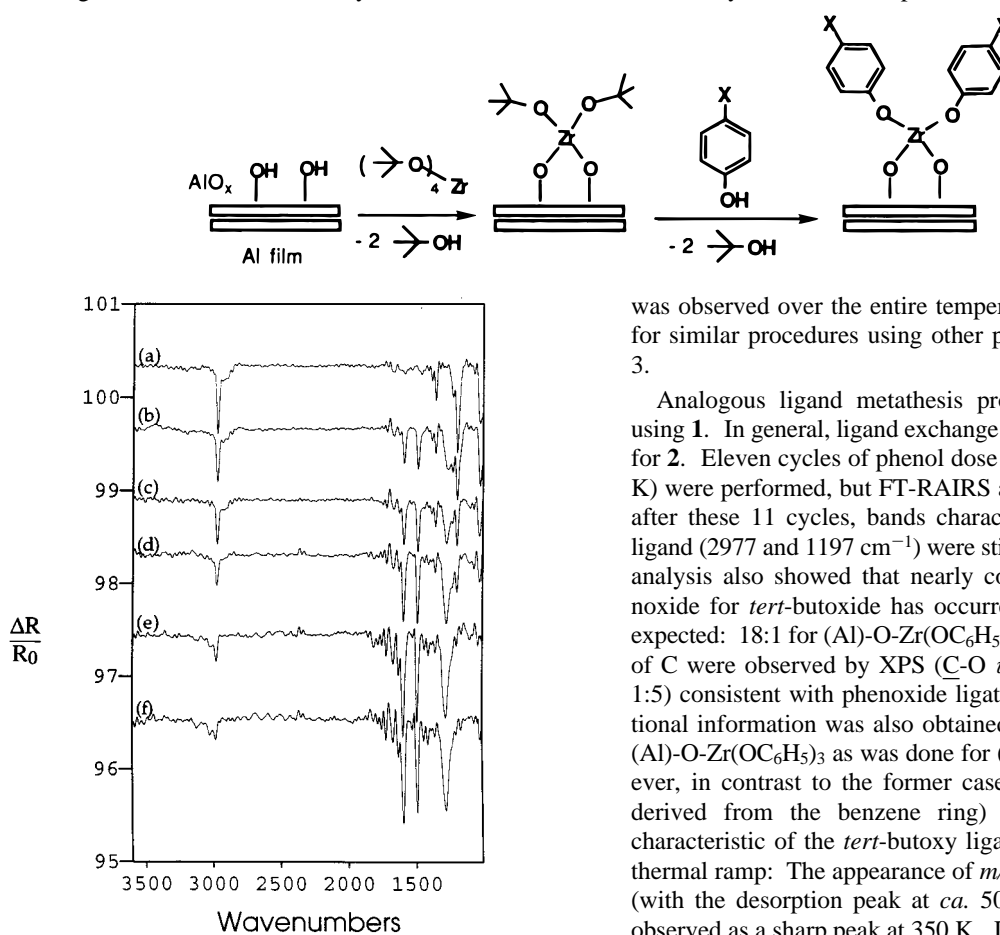
phenol (X =)	exposure (cycles)	exposure per cycle (L) <sup>a</sup>	some characteristic IR peaks of product (cm <sup>-1</sup> )	measd C/Zr atomic ratio (calcd)
H	11	1–3.2	3020, 2978, 1593, 1489, 1281	18.5 (18 <sup>b</sup> )
CH <sub>3</sub>	7	0.6–4.0	2969, 2931, 2877, 1592, 1511, 1454, 1284, 1199	18.1 (21; <sup>b</sup> 18 <sup>c</sup> )
OCH <sub>3</sub>	6	2.2–11.0	2974, 2904, 2835, 1593, 1508, 1268, 1234	18.7 (21; <sup>b</sup> 18 <sup>c</sup> )
CN	6	0.7–1.6	2969, 2927, 2857, 2225, 1596, 1508, 1469, 1307, 1245, 1195, 1168	17.3 (21; <sup>b</sup> 18 <sup>c</sup> )

<sup>a</sup> Exposure was calculated based on ion gauge sample pressure times dosing duration, without pressure calibration. <sup>b</sup> Calculated based on Zr(OC<sub>6</sub>H<sub>4</sub>X)<sub>3</sub> stoichiometry. <sup>c</sup> Calculated based on Zr(OBu)(OC<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> stoichiometry.

**Table 3.** Ligand Metathesis from (Al)-O-Zr(OBu)<sub>2</sub> Accomplished in Ultrahigh Vacuum

phenol (X =)	exposure (cycles)	exposure per cycle (L) <sup>a</sup>	some characteristic IR peaks of product (cm <sup>-1</sup> )	measd C/Zr atomic ratio (calcd)
H	4	0.6–1.2	3016, 1596, 1496, 1392, 1292	13.0 (12)
CH <sub>3</sub>	3	0.6–3.6	2969, 1612, 1511, 1288	14.5 (14)
OCH <sub>3</sub>	3	1.0–1.5	3005, 2897, 2839, 1597, 1512, 1273, 1242	12.4 (14)
CN	3	0.35–0.5	2962, 2931, 2881, 2229, 1600–1477 (br), 1299, 1257	15.0 (14)

<sup>a</sup> Exposure was calculated based on ion gauge sample pressure times dosing duration, without pressure calibration.

**Scheme 1.** Ligand Metathesis Enables Synthesis of Al Film Surface Phenoxyzirconium Complexes

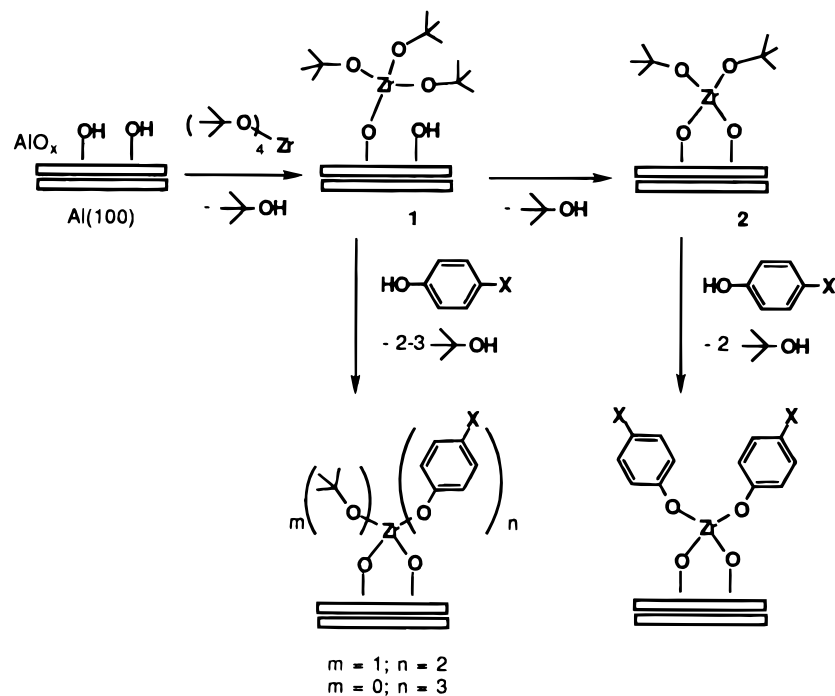
**Figure 2.** FT-RAIRS spectra of [Al]-O-Zr(OBu)<sub>3</sub> and its ligand metathesis products with phenol. (a) [Al]-O-Zr(OBu)<sub>3</sub>; (b) 1 cycle of reaction; (c) 2 cycles; (d) 5 cycles; (e) 9 cycles; and (f) 11 cycles.

phenol exposure to 1:5.4 (expected: 1:5) following ligand metathesis. Qualitative compositional information was also obtained by TDS experiments in which both  $m/z = 39$  ( $C_3H_3^+$ , derived from the benzene ring) and  $m/z = 57$  ( $C_4H_9^+$ , characteristic of the *tert*-butoxy ligand) were monitored during thermal ramp: The appearance of  $C_3H_3^+$  began at *ca.* 400 K (with the desorption peak at *ca.* 500 K); no signal at  $m/z = 57$

(7) (a) Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, 2, 70. (b) Clark, D. T.; Kilcast, D.; Musgrave, W. K. R. *J. Chem. Soc., Chem. Commun.* **1971**, 517.

was observed over the entire temperature range probed. Data for similar procedures using other phenols are given in Table 3.

Analogous ligand metathesis procedures were performed using **1**. In general, ligand exchange occurred more slowly than for **2**. Eleven cycles of phenol dose (170 K) and removal (300 K) were performed, but FT-RAIRS analysis showed that, even after these 11 cycles, bands characteristic of the *tert*-butoxy ligand (2977 and 1197 cm<sup>-1</sup>) were still, barely, observable; XPS analysis also showed that nearly complete exchange of phenoxide for *tert*-butoxide has occurred (C/Zr = 18.5 ± 0.5:1; expected: 18:1 for (Al)-O-Zr(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>) (Scheme 2). Two types of C were observed by XPS ( $\underline{C-O}$  vs  $\underline{C-C}$  = 1:5.0; expected: 1:5) consistent with phenoxide ligation. Qualitative compositional information was also obtained by TDS experiments for (Al)-O-Zr(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> as was done for (Al)-O-Zr(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. However, in contrast to the former case, both  $m/z = 39$  ( $C_3H_3^+$ , derived from the benzene ring) and  $m/z = 57$  ( $C_4H_9^+$ , characteristic of the *tert*-butoxy ligand) were observed during thermal ramp: The appearance of  $m/z = 39$  began at *ca.* 400 K (with the desorption peak at *ca.* 500 K), and  $m/z = 57$  was observed as a sharp peak at *ca.* 350 K. Data for similar procedures using other phenols are given in Table 2; noteworthy is the observation that, with the exception of the parent phenol, incomplete exchange, consistent with replacement of only 2 *tert*-butoxy ligands, was found for (Al)-O-Zr(*tert*-butoxy)<sub>2</sub>. This difference might be due in part to relatively dense packing of ligand groups in (Al)-O-Zr(*tert*-butoxy)(phenoxy)<sub>2</sub>, which impedes further coordination of a phenolic molecule, necessary to complete metathesis. Comparatively, crowding in (Al)-O-Zr(*tert*-butoxy)(phenoxy) may not be so acute. Also interesting is the observation that, while proton transfer is required for ligand metathesis, there is no apparent correlation between phenol acidities and rates of ligand exchange. Instead, rates seem to correlate with phenol melting points, suggesting that, perhaps, ligand mobility on the surface is a controlling factor.

**Scheme 2.** Ligand Metathesis Enable Synthesis of Al Surface Phenoxyzirconium Complexes in UHV

We have shown that the sequence of tetra(*tert*-butoxy)-zirconium OMCVD followed by phenolic ligand metathesis enables the facile preparation of a family of surface organometallic complexes rapidly, from a common, accessible precursor. We are now studying the physical properties of such surface modified materials, in which systematic, subtle variation of ligation properties can be accomplished through appropriate choice of the phenol.

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**Supporting Information Available:** Six figures, including FT-RAIRS spectra for metathesis using *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, and *p*-CN substituted phenols (6 pages). See any current masthead page for ordering and Internet access instructions.

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