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Organometallic chemistry at the interface with materials science

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Abstract

Metal alkoxides are precursors of interfacial species which can be used to enhance interactions between dissimilar components of a composite. Metal alkoxides can react with surface hydroxyl groups of metal oxides or oxidized metals to give covalently bound surface alkoxide species through protolytic loss of one or several alkoxide groups. Because of the reactivity of any remaining alkoxide ligands in the coordination sphere of these surface complexes, a variety of composites can be prepared by ligand exchange. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metal alkoxides; Metathesis; Surface organometallic chemistry; Organometallic chemical vapor deposition; Quartz crystal microbalance

1. Introduction

New developments in materials science create new opportunities for organometallic chemists: problems of interface synthesis and optimization may be addressed using methodologies of surface organometallic chemistry which have already been developed for implementation in catalysis-related fields. Our work focuses on the use of surface organometallic chemistry to interface dissimilar materials, e.g. a surface-oxidized metal or a "bulk" oxide and an organic. We describe below how surface organometallic complex chemistry can address problems in interface synthesis relating to the preparation of species with possible application to fields as diverse as the preparation of new electronic or even "biomedical" materials. Our approach to interface synthesis and optimization involves three general issues:

- *Synthesis*. How are surface organometallic complexes prepared? What factors govern rates and stoichiometries for reaction between an organometallic complex starting material and a surface-activated substrate? How can these surface complexes be modified? Which reagents are best for surface complex synthesis and modification?
- *Structure*. How can we characterize (if only partially) the complex–surface interface?
- *Function*. How do structural features of a surface organometallic complex affect desired properties of the ensemble comprising our designed interface? Can systematic variation of species at the interface predictably affect these ensemble properties?

1.1. The general approach

Our approach to interface synthesis follows the general sequence of (1) surface activation, (2) surface complex deposition, and (3) surface complex elaboration. This sequence enables creation of a variety of novel substrate–organic and substrate–inorganic ensembles through systematic modification of a common interfacial surface complex (Scheme 1). In this methodology, a simple organometallic complex is first chemically bonded to a substrate surface by

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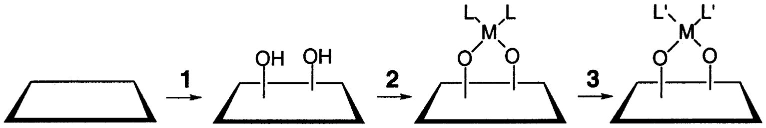


Scheme 1. The general scheme for surface activation and modification.

exploiting reactive functionality both of the surface and of the organometallic. Ligand modification in the resulting surface complex provides for the preparation of a range of types of products, according to the desired properties of the ensemble. Thus, the surface organometallic complex can be viewed as a "universal linker" in that a particular species may react with a range of substrate surfaces and, through ligand exchange (metathesis), variety in surface speciation is effected. This sequence of deposition–metathesis is conceptually different from surface modification methodologies involving serial preparation of members of families of surface modification reagents, each one of which must be prepared individually for a given application (e.g. silane [1] surface modification reagents) (Scheme 1).

2. Surface complex formation

2.1. The mechanism of surface complex formation

Understanding the mechanism of complex deposition can facilitate development of efficient surface modification synthesis protocols, and probing the kinetics of surface–complex reactions can provide such useful mechanistic analysis. One such probe might involve analysis of the rate of formation of volatile products of organometallic chemical vapor deposition (OMCVD) procedures; this analysis provides information about complex "chemisorption" on the surface from the "perspective" of the depositing reagent. However, we have chosen to study the mechanism of OMCVD from the perspective of the surface, itself. We showed [2–4] that it is possible to adapt well-known quartz crystal microbalance (QCM) technology [5] to the analysis of the kinetics of organometallic complex surface chemisorption. The QCM technique exploits the relationship between the resonant frequency of a thin piezoelectric quartz crystal and the mass of the electrodes deposited upon it [6]. If the electrode surface were chemically reactive, the rate of organometallic complex chemisorption would be related to the rate of electrode net mass change, which could be measured by monitoring the resonant frequency of the QCM system in real time [7].Vapor-deposited aluminum QCM electrodes can be oxidized using H_2O to introduce surface OH groups [2–4]. These OH groups can react with protolytically labile organometallic compounds to give surface-bound complexes by ejection of protonated organic ligands, and direct rate data for reaction between an organometallic and the hydroxylated surface can be obtained by measuring the QCM frequency change as a function of time [7]. Similarly, aluminum QCM electrodes can be oxidized with D_2O, yielding surface OD groups. Comparing rate constants for reaction between tetra(*neo*-pentyl)zirconium (**1**) and [Al]–OH versus [Al]–OD gave the kinetic isotope effect for chemisorption: $k_H/k_D = 8.5$. The large magnitude of the kinetic isotope effect for the reaction between **1** and the hydroxylated aluminum surface shows that proton transfer is rate determining, and is consistent with a pathway in which reversible surface complexation of the organometallic reagent (likely to a surface OH or OD group) is followed by rate determining proton transfer from the surface OH (or OD) to the metal–ligand bond [3]. We believe that proton transfer is slow compared with desorption because such proton transfer to the Zr–C bond requires re-hybridization at carbon. Now consider an alkoxide structural analog of **1**: tetra(*tert*-butoxy)zirconium (**2**). In this latter case, a similar surface reaction could involve proton transfer to an oxygen lone pair of the Zr–O unit, and no re-hybridization at O is required for this process. Therefore, a lower kinetic barrier to proton transfer to the alkoxide versus the alkyl would be expected. Indeed, we find that the rate for deposition of **2** increased by an order of magnitude over that for **1**, and the magnitude of the kinetic isotope effect fell ($k_H/k_D = 1.7$). Thus, in contrast to "intuition" based on thermodynamic considerations

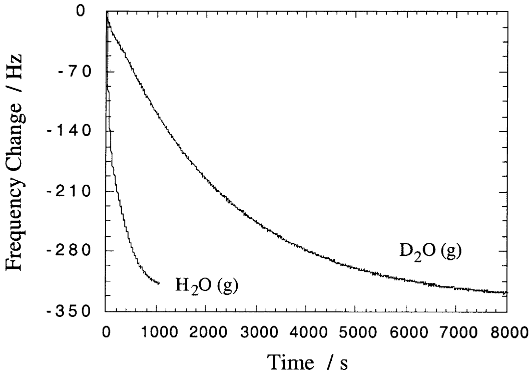


Fig. 1. QCM measurement of the reaction of **2** with Al–OH or Al–OD.

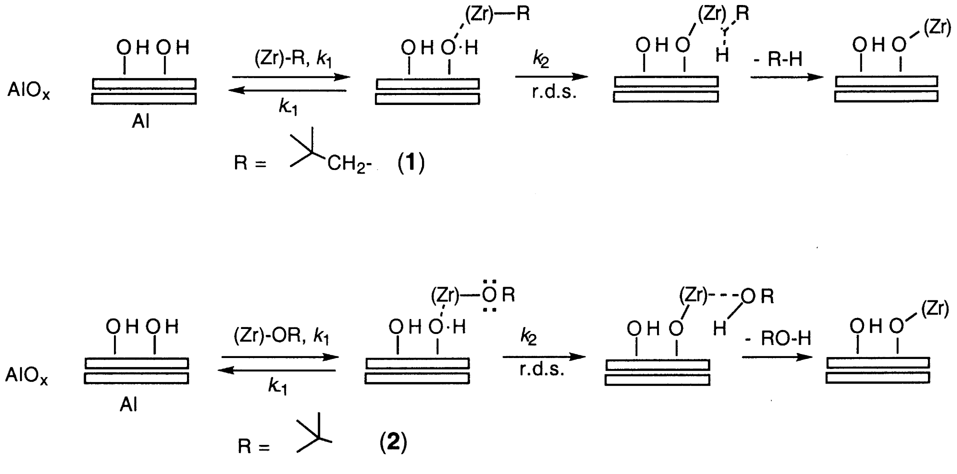
of basicity, the alkoxide is kinetically favored over the alkyl complex for OMCVD. Indeed, this simple QCM experiment demonstrates the importance of understanding the mechanism of surface deposition as a means to facilitate reagent design for OMCVD (see Fig. 1, Scheme 2).

2.2. Studying chemisorption using ultrahigh vacuum techniques

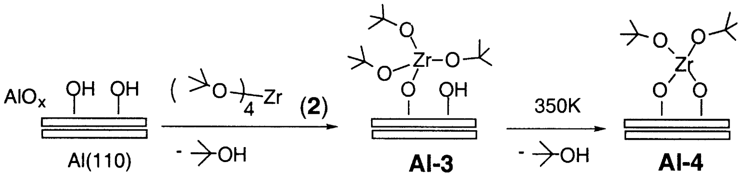
We have adapted several of the classical techniques of ultrahigh vacuum (UHV) surface science, including thermally programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and Fourier transform reflectance–absorbance infrared spectroscopy (FT-RAIRS), to the analysis of reactions between organometallics and a variety of surface-oxidized metals. Whereas the aims of classical UHV surface science have been primarily to explain observed phenomena, we use these techniques instead to guide us in the synthesis of new bulk materials: UHV surface science allows for exquisite control of reaction conditions and for near "real-time" analysis of surface materials as they are prepared.

2.3. The reaction of 2 with surface hydroxylated Al in UHV

We studied the reaction between **2** and hydroxylated Al in UHV [8–10]. The initial product of chemisorption is characterized as tris(*tert*-butoxy)Zr surface species **Al-3**, which is formed by protonolysis of one alkoxide ligand of **2** by a surface OH group. The thermal evolution of **Al-3** depends on the degree of initial surface hydroxylation of the metallic substrate [9]: If surface hydroxylation is extensive, warming **Al-3** yields **Al-4**. This bis(*tert*-butoxy)Zr surface species is formed by protonolysis of a metal–alkoxide bond of **Al-3** by a second surface OH group. However, if surface hydroxylation is dilute, then thermal treatment of **Al-3** gives only decomposed materials. Apparently, under these surface hydroxylation conditions, additional proton transfer reactions cannot compete



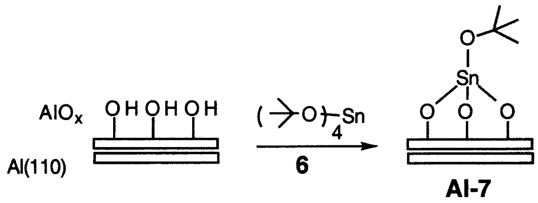
Scheme 2. Comparative mechanisms for reaction of the hydroxylated aluminum surface with tetra(*neo*-pentyl)zirconium (top) or tetra(*tert*-butoxy)zirconium (bottom).



Scheme 3. The reaction of tetra(*tert*-butoxy)zirconium with the hydroxylated Al surface in UHV.

kinetically with simple ligand thermolysis to ZrO_2 (Scheme 3).

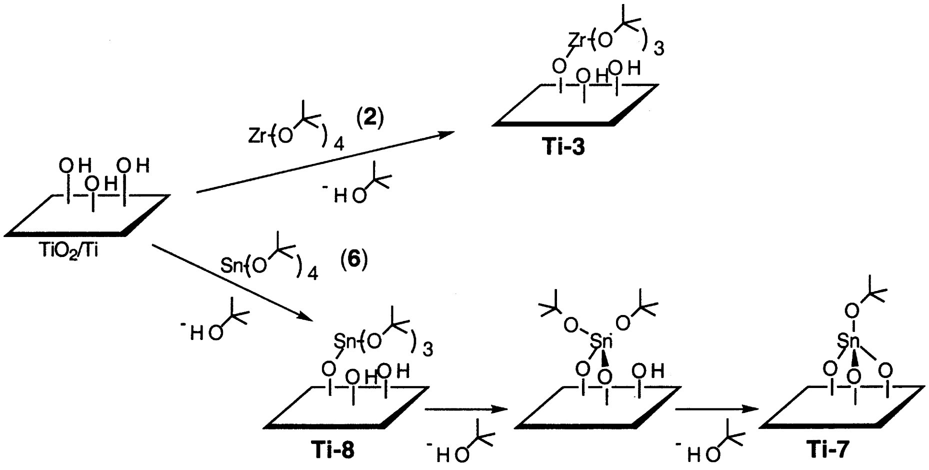
The titanium analog of **2**, tetra(*tert*-butoxy)titanium (**5**), also reacts with surface hydroxylated-oxidized Al [9], but the yield for this deposition reaction (as measured by relative FT-RAIRS intensities for *tert*-butoxy ligand absorbance) is lower for **5** than for **2**. We believe deposition proceeds less readily for **5** than for **2** because of size considerations for the metals and the requirement for surface OH group coordination as a precursor to chemisorption. Tin analog **6** also reacts with surface hydroxylated Al [11]; reactivity is quite high and, even at room temperature, only mono(*tert*-butoxy)Sn surface complex **Al-7** is observed. It may be that any tin analogs of **3** or **4** formed on hydroxylated Al simply react with a third surface OH group to give **Al-7**. We attribute the high relative chemisorptive reactivity of surface tin species to high affinity of that metal for coordination of OH groups, by analogy with crystallographic analyses of Sn and Zr alkoxide–alcohol adducts [12,13]. Thus, a simple series for surface hydroxyl reactivity tendencies is: $Sn(OBu^t)_4 > Zr(OBu^t)_4 > Ti(OBu^t)_4$ (Scheme 4).



Scheme 4. The reaction of tetra(*tert*-butoxy)tin with the hydroxylated Al surface in UHV.

2.4. The reaction of **2** with surface hydroxylated Ti in UHV

Aluminum is a somewhat atypical substrate in that it is relatively easy to heavily hydroxylate the oxide layer that forms spontaneously on exposure of the



Scheme 5. Deposition of Sn and Zr alkoxides onto hydroxylated Ti.

clean metal to water or oxygen [9,10]. In contrast, it is difficult to surface hydroxylate the oxide layer that forms on Ti on exposure of that clean metal to water or oxygen [14]. Indeed, thermal treatment of **Ti-3** yields very little, if any, titanium analog of **Al-4**, and simple complex thermolysis dominates [15]. Even for **6**, reactivity with surface OH is slow, and, here, stepwise conversion of **Ti-8** to **Ti-7** was observed (Scheme 5).

The stoichiometry of each of the surface complexes described above was determined by XPS analysis [16–18]. Integration of the signals for carbon and the metals, plus de-convolution of the C 1s spectrum into its component parts (i.e., the two different types of carbons present in a *tert*-butoxy ligand) establishes the speciation of surface-bound materials [15].

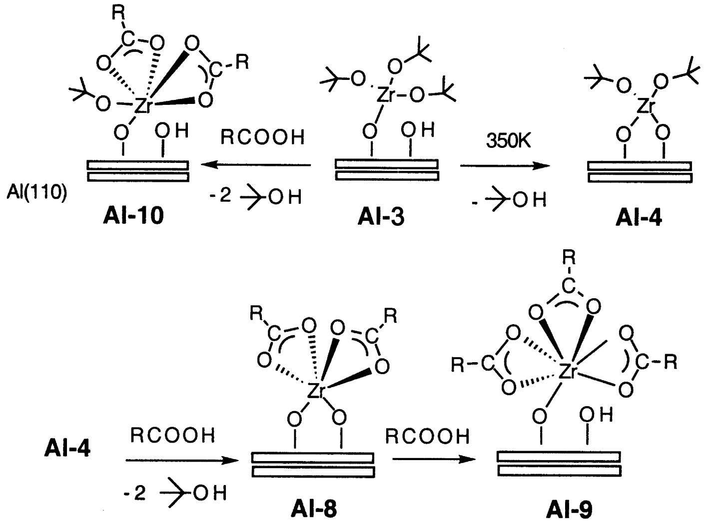
3. Surface complex elaboration through ligand exchange (metathesis)

The second phase of our surface modification protocol involves substitution of *tert*-butoxide ligands in the coordination sphere of our surface complexes. In general, organic species that are more acidic than *tert*-butanol replace these ligands to give ensembles that are held together through strong covalent bonding.

3.1. Metathesis with carboxylic acids

Alkanecarboxylic acids adsorb onto surface-oxidized Al, but this interaction can be reversible. A simple QCM study showed that *n*-octanoic acid adsorbs onto surface-oxidized Al from the vapor phase, but the acid is easily removed by evacuation [19]. A similar experiment showed that irreversible adsorption of the acid onto **Al-4** occurred, apparently by strong covalent bond formation, to give carboxylate complex **Al-8** [19].

Reactions of **Al-3** and **Al-4** with *n*-octanoic acid were also studied in UHV; in each case, stoichiometries and speciation of surface complexes were determined by XPS and FT-RAIRS methods [20]. We found that **Al-4** reacts cleanly with *n*-octanoic acid to give bis-carboxylate **Al-8**. Continued exposure of **Al-8** to the carboxylic acid causes cleavage of first one (**Al-9**), and then the second, surface O–Zr bond. In contrast, reaction of tris-compound **Al-3** with *n*-octanoic acid gave a species in which only two of the three *tert*-butoxide groups were replaced (Scheme 6). It is reasonable to propose that ligand metathesis initially involves coordination of the carboxylic acid to the surface metal alkoxide complex; proton transfer from the coordinated acid to an alkoxide ligand liberates free alcohol and gives the metal carboxylate.



Scheme 6. Ligand metathesis with a carboxylic acid.

It is also reasonable to propose that formation of this adduct occurs by coordination of the carboxylic acid in a sterically accessible region about the metal. Perhaps mixed alkoxide–carboxylate species **Al-10** fails to react further with the carboxylic acid because the last alkoxide unit is in a sterically inaccessible location; in other words, reaction of **Al-10** with additional carboxylic acid may simply give rise to degenerate carboxylate ligand metathesis (Scheme 6).

3.2. Metathesis with co-polymeric carboxylic acids

Simple co-polymers of polyethylene and carboxylic acids, e.g., polyethylene co-acrylic acid (5%), react from solution with surface organometallic compounds to give composites in which the polymer is bound to the metal via its native oxide layer and the surface complex linker [21]. For metals such as copper or iron, in which surface OH content is apparently low, surface metal alkoxide compound “loading” is dilute. Nonetheless, a dramatic improvement in surface adhesion between the co-polymer and the metal surface can be effected if the metal native oxide layer is first treated to give a surface organometallic complex (**Cu-3**). This adhesion enhancement could be demonstrated easily by IR analysis (Fig. 2).

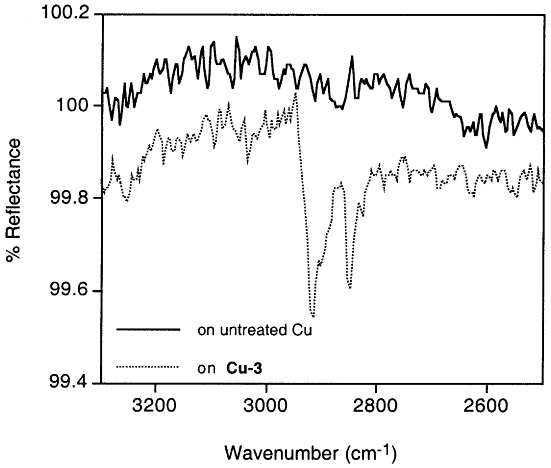


Fig. 2. FT-RAIRS analysis (following solvent wash) of the reaction between polyethylene–co-acrylate with the native oxide of Cu (top) or **Cu-3** (bottom).

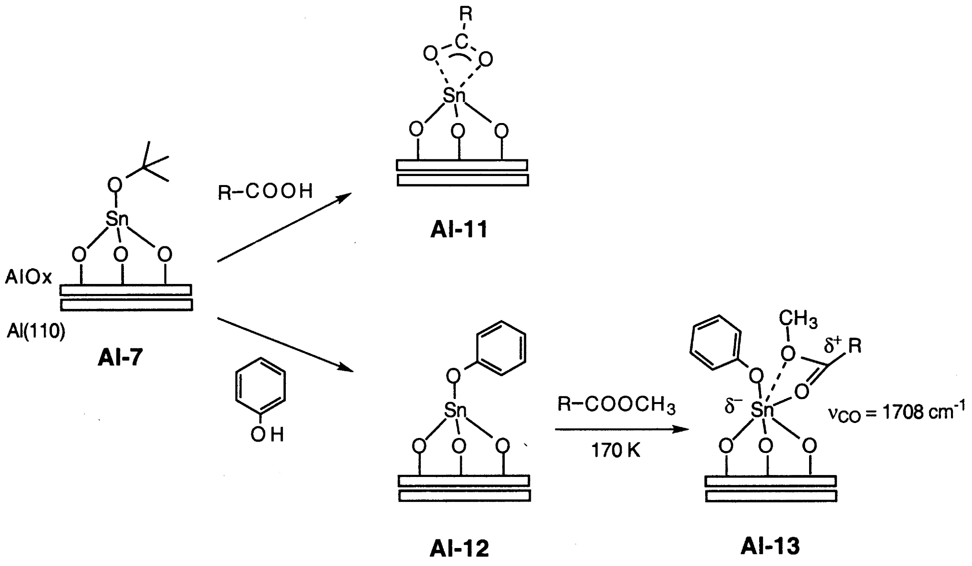
3.3. The development of the simple trans-esterification catalyst

Ligand metathesis reactions which can be accomplished for surface Zr compounds can also occur for Sn analogs. For example, reaction of **Al-7** with an alkanecarboxylic acid first yields tin carboxylate **Al-11**, and continued treatment results in cleavage of surface O–Sn bonds. Phenols are also generally more acidic that *tert*-butanol, so it is not surprising that metathesis of **Al-7** with simple phenols gives **Al-12** [22], which can be monitored under normal laboratory conditions, or in UHV. Metathesis of **Al-7** with a carboxylic acid [23] (or a phenol) likely occurs through formation of an adduct, followed by proton transfer and elimination of *tert*-butanol. The reaction between a simple carboxylic acid ester and **Al-12** was studied to model the reaction with a carboxylic acid: **Al-12** reacted with methyl butanoate at 170 K in UHV to give ester adduct **Al-13**, which could be characterized by FT-RAIRS [23] (Scheme 7).

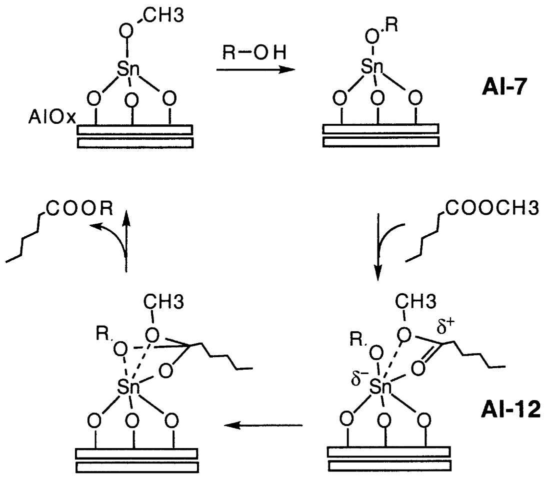
The observations made for metathesis and ester coordination of **Al-7** suggest a simple trans-esterification catalytic cycle. In this representation, **Al-7** would coordinate a carboxylic acid ester, which activates the carbonyl group as an electrophile (**Al-12**). Intramolecular attack of a coordinated alkoxide ligand upon this carbonyl group would give a new carboxylic acid ester–alkoxide ligand arrangement, and ejection of the ester would yield a tin alkoxide. Exchange with free alcohol completes the catalytic cycle. We find, indeed, that simply treating a suspension of **Al-7** with ethyl acetate in the presence of a variety of alcohols gave high yield and efficient trans-esterification. An interesting facet of this catalyst is that it enables trans-esterification using a secondary, and even a tertiary, alcohol [23,24]. In contrast, homogeneous Sn catalyst species are generally effective only with primary alcohols [25,26] (Scheme 8).

3.4. Applications of surface organometallic interfaces to electronics materials

An organometallic complex bound to the surface of an electrode might improve “carrier injection” in the context of a simple device (see Fig. 3). For example, the architecture of many modern light emitting diodes based on organic materials involves a stack



Scheme 7. Ligand metathesis with a phenol, and formation of an ester adduct.



Scheme 8. A catalytic cycle for tin complex-catalyzed trans-esterification.

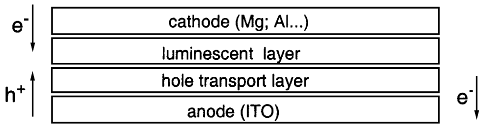
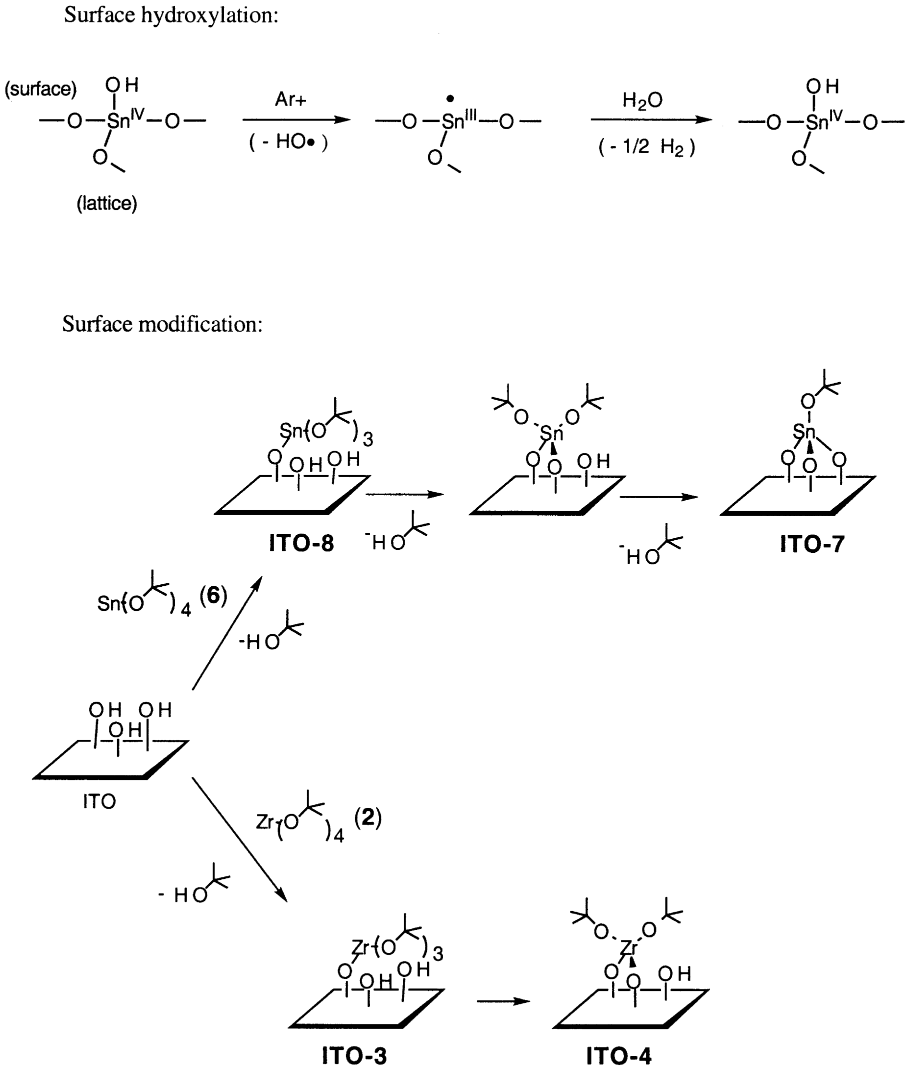


Fig. 3. A layered OLED.

consisting of an anode (often indium tin oxide (ITO) on glass) [27–29] with a “hole (h+)” transport layer material deposited on this anode; the hole transport layer (HTL) material is often an aromatic tertiary amine. A luminescent layer (which acts also as an electron (e^-) transport material) is next deposited, and finally the system is capped with a cathode, usually a low work function metal such as magnesium or a magnesium alloy [30]. In this device, the anode effectively oxidizes the HTL material, and the holes thus generated migrate toward the cathode. Electrons are injected from the cathode into the luminescent material, and migrate toward the anode. An encounter between the hole and a reduced electron transport material species can give rise to an equivalent of a photo-excited state, which emits light, but inefficiency in “hole injection” can result in device failure [30]. Since the ITO anode is an oxide and the hole transport material is an aromatic amine, “wetting” of the ITO by the HTL material may not be good. Attaching an organometallic compound onto the ITO surface in such devices might have a beneficial effect on hole injection. The metal could surface-coordinate the ITO via its hydroxyl and oxide functionality, and organic ligation in the coordination sphere of this surface complex could interact with the organic HTL material.



Scheme 9. Surface hydroxylation and organometallic complex deposition onto ITO.

We studied the surface chemistry of ITO as a first step in the development of functional interfaces for application in optoelectronic devices [31]. Cleaning the ITO surface in UHV was accomplished by bombardment with argon ions. This generates Sn(III) sites [31]; these can be captured with water to give surface Sn(IV)–OH groups [32], which react with **2** or **6** to generate the corresponding surface organometallic complexes, much in the same way that such species are formed on native oxides of single metallic substrates (Scheme 9).

Polyvinylcarbazole, PVK, is a common HTL material used in organic light emitting diodes (OLEDs) [33,34]. We prepared a simple co-polymer of PVK and crotonic acid [35], and we showed that this polyvinylcarbazole–co-crotonate adhered better to ITO in the presence of **ITO-7** than it did to the untreated surface. For example, PVK deposited onto ITO-on-glass from solution did not “stick”, as determined by IR analysis, after solvent washing. The co-polymer, which can interact more strongly with the ITO surface than PVK, either through hydrogen bond-

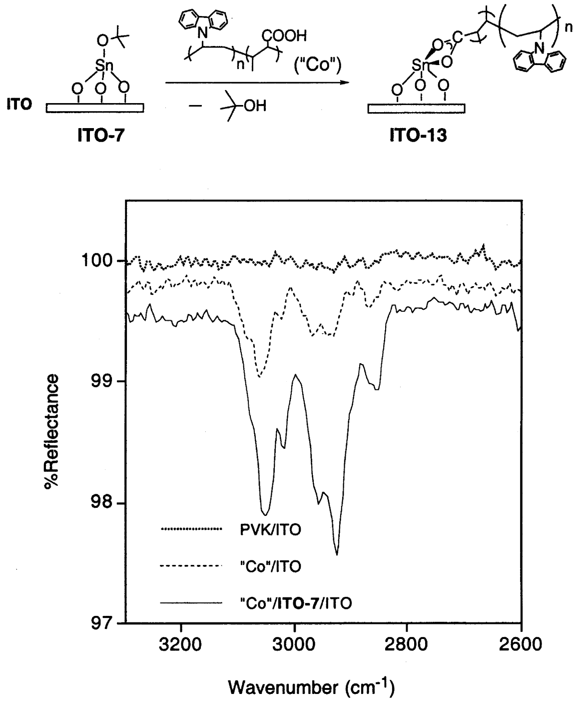


Fig. 4. FT-RAIRS analysis (following solvent wash) of the reaction between polyvinylcarbazole–co-crotonate with untreated ITO (center) or with **ITO-7** (bottom). The top trace is for reaction of ITO with ordinary PVK.

ing or proton transfer, adheres somewhat better than does PVK. However, the co-polymer adheres best by reaction with **ITO-7** (as **ITO-13**), and this interaction is stable to multiple cycles of solvent wash (Fig. 4).

3.5. Surface organometallic chemistry for surface processing for biomedical "implants"

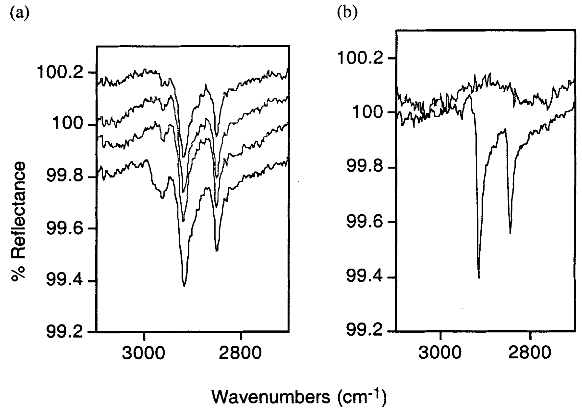
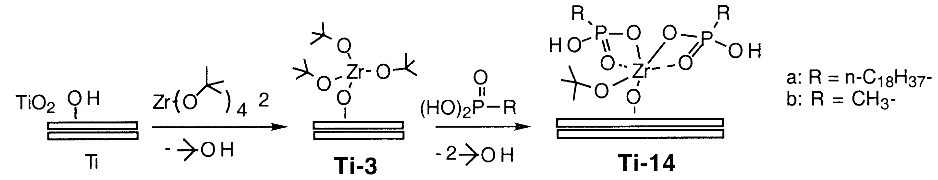


Fig. 5. DRIFT analysis of octadecanephosphonate surface species on oxidized Ti. (a) With Zr alkoxide pretreatment (**Ti-14**): bottom spectrum — as deposited; next — after 1 THF rinse; following — after 2 THF rinses; top — after 2 THF rinses and tape "peel". (b) Without Zr alkoxide pretreatment (control): bottom spectrum — as deposited; top — after 1 THF rinse.

Many modern biomedical implants are made from the titanium alloy, Ti–6Al–4V (which contains 6% Al and 4% V in the bulk) [36–38], and an important area of current research involves surface modification of such alloys to enhance adhesion of incipient bone, which has as its major mineral constituent hydroxyapatite, $Ca_5(PO_4)_{10}(OH)_2$. It has been shown that the surface of Ti–6Al–4V is substantially Ti, with some enrichment of Al and depletion of V compared with the bulk [36]. As noted above, the surface of oxidized Ti (as a model for the alloy) is only lightly hydroxylated [15], and reaction with **2** gives **Ti-3**; warming **Ti-3** gives rise primarily to decomposition.

Alkanephosphonic acids are good surrogates for modeling surface inorganic phosphate binding since they provide for convenient monitoring of adhesion testing by IR analysis of alkyl side chain C–H modes. We find that reaction of surface-oxidized Al with octadecanephosphonic acid enables adhesion strong enough to withstand some washing and tape-based peeling, and that this adhesion is enhanced through reaction with **Al-3** to give **Al-14** [39]. In contrast, essentially no octadecanephosphonic acid remains



Scheme 10. Surface derivatization with phosphonates.

bound to the Ti native oxide surface, following even one rinse with solvent. However, the phosphonic acid sticks strongly to the Ti native oxide surface by reaction with **Ti-3** to give **Ti-14**. Here, binding of the phosphonic acid to Ti via the interface withstands several cycles of "washing" and "peeling" with no apparent degradation. A methanephosphonic analog was characterized in UHV [39], which enabled determination of the stoichiometry of the surface Zr phosphonate adduct (Fig. 5, Scheme 10).

4. Conclusions

We have shown that the preparation of surface organometallic complexes can be accomplished quite readily, especially using Zr or Sn alkoxide precursors, by reaction with surface OH functionality. We have also shown that alkoxide ligands which remain in the coordination sphere of the metal following chemisorption can be easily replaced by other organic groups. Indeed, the sequence of surface complex formation — ligand metathesis enables formation of a variety of surface species, many of which might not be easy to prepare directly due to the unavailability or unfavorable physical properties (such as low solubility or low volatility) of appropriate starting materials. Given the wide variety of surfaces that can be easily processed using our methodology and the range of organics that can be adhered to such surfaces using these interfaces, it seems that the future of surface organometallic chemistry as a focus for interface science is limited only by the ingenuity and skills of the organometallic chemist.

Acknowledgements

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References

[1] Y. Xia, M. Mrksich, E. Kim, G.M. Whitesides, J. Am. Chem. Soc. 117 (1995) 9576.
[2] J.B. Miller, J. Schwartz, Inorg. Chem. 29 (1990) 4579.
[3] J.B. Miller, J. Schwartz, S.L. Bernasek, J. Am. Chem. Soc. 115 (1993) 8239.
[4] J.B. Miller, J. Schwartz, Acta Chem. Scand. 47 (1993) 292.
[5] C. Lu, A.W. Czanderna, Applications of Piezoelectric Quartz Crystal Microbalances, Elsevier, New York, 1984.
[6] G. Sauerbrey, Z. Phys. 155 (1959) 206.
[7] M.D. Ward, J. Phys. Chem. 92 (1988) 2049.
[8] J.B. Miller, S.L. Bernasek, J. Schwartz, J. Am. Chem. Soc. 117 (1995) 4037.
[9] G. Lu, K.L. Purvis, J. Schwartz, S. Bernasek, Langmuir 13 (1997) 5791.
[10] J.B. Miller, S.L. Bernasek, J. Schwartz, Langmuir 10 (1994) 2629.
[11] G. Lu, J. Schwartz, S.L. Bernasek, Langmuir 14 (1998) 1532.
[12] H. Reuter, M. Kremser, Z. Anorg. Allg. Chem. 598/599 (1991) 259.
[13] B.A. Vaartstra, J.C. Huffman, P.S. Gradeff, L.G. Hubert-Pfalzgraf, J.-C. Daran, S. Parraud, K. Yunlu, K.G. Caulton, Inorg. Chem. 29 (1990) 3126.
[14] G. Lu, S.L. Bernasek, J. Schwartz, Surf. Sci. 485 (2000) 80.
[15] K.L. Purvis, G. Lu, J. Schwartz, S.L. Bernasek, Langmuir 15 (1999) 7092.
[16] H. Willemen, D.F. van de Vondel, G.P. van der Kelen, Inorg. Chim. Acta 34 (1979) 175180.
[17] D.T. Clark, D. Kilcast, W.K.R. Musgrave, J. Chem. Soc., Chem. Commun. (1971) 516.
[18] U. Gelius, P.F. Heden, J. Hedman, B.J. Lindberg, R. Manne, R. Nordberg, C. Nordling, K. Siegbahn, Phys. Scripta 2 (1970) 70.
[19] Y.G. Aronoff, B. Chen, G. Lu, C. Seto, J. Schwartz, S.L. Bernasek, J. Am. Chem. Soc. 119 (1997) 259.
[20] K.L. Purvis, G. Lu, J. Schwartz, S.L. Bernasek, Langmuir 14 (1998) 3720.
[21] S.K. Van der Kam, A.B. Bocarsly, J. Schwartz, Chem. Mater. 10 (1998) 685.
[22] S.K. Van der Kam, G. Lu, S.L. Bernasek, J. Schwartz, J. Am. Chem. Soc. 119 (1997) 11639.
[23] J. Schwartz, S.L. Bernasek, G. Lu, J.P. Keegan, K. Purvis, S.K. Van der Kam, J. Mol. Catal. A 146 (1999) 45.
[24] A. Quenot, J. Schwartz, Unpublished results.
[25] R. Imwinkelried, M. Schiess, D. Seebach, E. Vedejs, Org. Syn. 65 (1987) 230.
[26] A. Orita, A. Mitsutome, J. Otera, J. Org. Chem. 63 (1998) 2420.
[27] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.
[28] Z. Shen, P.E. Burrows, V. Bulović, S.R. Forrest, M.E. Thompson, Science 276 (1997) 2009.
[29] P.E. Burrows, S.R. Forrest, Appl. Phys. Lett. 64 (1994) 2285.
[30] S.R. Forrest, P.E. Burrows, M.E. Thompson, Laser Focus World 31 (1995) 99.
[31] D.J. Milliron, I.G. Hill, A. Kahn, J. Schwartz, J. Appl. Phys. 87 (2000) 572.
[32] K.L. Purvis, G. Lu, J. Schwartz, S.L. Bernasek, J. Am. Chem. Soc. 122 (2000) 1808.
[33] J. Kido, H. Shionoya, K. Nagai, Appl. Phys. Lett. 16 (1995) 2281.

[34] S.A. Van Slyke, C.H. Chen, C.W. Tang, Appl. Phys. Lett. 69 (1996) 2160.

[35] S.J. Woodson, S.K. Van der Kam, J. Schwartz, Unpublished results.

[36] C. Sittig, M. Textor, N.D. Spencer, M. Wieland, P.-H. Vallotton, J. Mater. Sci. 10 (1999) 35.

[37] J. Lausmaa, J. Electron. Spectr. Rel. Phen. 81 (1996) 343.

[38] N.L. Hernández de Gatica, G.L. Jones, J.A. Gardella, Appl. Surf. Sci. 68 (1993) 107.

[39] E.S. Gawalt, G. Lu, S.L. Bernasek, J. Schwartz, Langmuir 15 (1999) 8929.