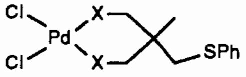
formational change was estimated to be ca. 13.3 kcal/mol.[6]

It would be of interest to compare this fluxional behavior with that of $(P_2S)PdCl_2$ (**12**)[7] and $(S_3)PdCl_2$ (**13**). There is no indication of **12** undergoing such displacement, but all three sulfur donors of **13** have similar exchange behavior. The fluxional behavior in **13** was confirmed similarly by variable-temperature ^{1}H NMR studies. The chemical shifts of all three methylene units attached to sulfur donors of **13** appeared as follows: (i) at 50°C, a broad peak, (ii) at room temperature, two broad overlapped peaks, and (iii) at lower temperature, a complicated splitting pattern.



12, X = PPh_2
13, X = SPh

Acknowledgment. We are grateful for financial support from the National Science Council (ROC), Grant NSC78-0208-M002-15.

Registry No. **2**, 129521-04-6; **4**, 3663-46-5; **5**, 129521-00-2; **6**, 69773-90-6; **7**, 129521-01-3; **9**, 129521-02-4; **10**, 129521-03-5; **11**, 129521-06-8; **13**, 129521-05-7; $(PhCN)_2PdCl_2$, 14220-64-5; PhCOCl, 98-88-4.

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(6) (a) The barrier was estimated from NMR technique, see: Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Company, Philadelphia, PA, 1977; p 252. (b) Cf. Abel, E. W.; Orrell, K. G.; Bhargava, S. K. The Stereodynamics of Metal Complexes of S, Se and Te Containing Ligands. *Prog. Inorg. Chem.* **1987**, *32*, 1.

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Chemical Deposition of an Organozirconium Complex onto an Oxided Aluminum Surface: Using the "Quartz Crystal Microbalance" To Probe Microscopic Surface Acidity

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Surface modification of metal oxides by organometallic complex attachment (often to reactive hydroxyl groups) is well-known, but comparable treatment of metals, themselves, is less well established. An overlayer of a chemically reactive oxide on a metal can provide a "covalent" interface between the bulk metal and a target surface modification reactant. In this context, reproducible production of bound organometallic complexes on such modified metallic surfaces requires reproducible preparation of the reactive overlayer. A readily measured property of an oxided support is its total Brønsted acidity, related to the concentration of surface hydroxyl groups, usually determined by titration.[1] Differently prepared surfaces could have greatly different total acidities. Protolytic organometallic complex deposition procedures[2] on hydroxylated surfaces could depend, however, not on total acidity of the support but on *microscopic* (or local –OH group) considerations.

Table I. Kinetics Data for QCM-Monitored Depositions

deposition medium	hydroxylation method	rate const, 10^3 s^{-1}	areal loading,^{a} ng/cm^2	areal concn,^{a} nM/cm^2
pentane	steam	4.5	4700	20
gas phase	steam	3.7	4800	21
gas phase	D_2O steam	0.44	5000	21
gas phase	water	4.3	2200	10
gas phase	"atmosphere"	4.2	1300	6

^{a} For the surface ligated fragment $Zr(C_5H_{11})_2$.

In principle, studying the stoichiometry of organometallic complex deposition onto an oxided metal surface could involve techniques similar to those for oxide surface modification, but, except for metal powders, low surface areas of metallic substrates and attendant low content, per unit weight, of reactive hydroxyl groups make titrimetric quantification of surface reactive sites difficult. Similarly, deposition kinetics can be difficult to ascertain: depositions could involve very small amounts of the organometallic reagent, the organic products could partition between the gas and solution phases, and spectroscopic probes are difficult to employ in situ.

Piezoelectric quartz can be made to oscillate at a resonant frequency that is determined by the cut and mass of a given crystal, and the "quartz crystal microbalance" (QCM) technique allows accurate determination of mass changes on an electrode deposited on such a crystal. Just as for a classical oscillator, a change in electrode mass results in a change in resonant frequency that can be easily and accurately measured. The QCM is, thus, ideal for monitoring surface reactions of target metals when they are used as electrodes. Furthermore, since time-dependent QCM measurements are readily obtained, reaction kinetics,[3] as well as stoichiometries, can be probed. In an effort to determine whether total surface or local (hydroxyl group specific) acidity determines reactivity of an oxided overlayer toward an organometallic reagent, we adapted a QCM to directly measure deposition rates of tetraneopentylzirconium onto variously oxidized and hydroxylated aluminum electrode surfaces of that device.

Results

The surface of aluminum metal, deposited on a standard gold on chromium electrode on a quartz crystal, was hydrolyzed according to three regimes of increasing vigor. In the first, the surface of the aluminum was simply exposed to ambient conditions of the laboratory; in the second, it was treated with water, and in the third, with steam. In a parallel experiment, bulk aluminum metal powder was treated according to two of these same procedures, and the content of surface hydroxyl groups obtained by each route was determined by methyllithium titration and quantitative measurement of evolved methane. Bulk aluminum powder titrated after atmospheric exposure showed an hydroxyl loading of 0.007 mmol·g^{-1}, and steam-treated Al had a loading of 0.024 mmol·g^{-1}. Quantitative analysis of the reaction of hydroxylated, powdered Al with $Zr(C_5H_{11})_4$ showed evolution of 2.0 equiv of neopentane per Zr. The QCM was used to determine the course of the reaction between the surface of an aluminum electrode and $Zr(C_5H_{11})_4$. In typical procedures, the zirconium reagent was transported to the Al electrode in one of two ways. One was deposition from the gas phase with constant flux of the $Zr(C_5H_{11})_4$; the other was deposition from solution. In all experiments, the resonance frequency of the crystal was measured vs time and related to the mass change at the surface.[4] De-

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(1) Methyllithium titration has been used to determine total hydroxyl concentration for metal oxides: Ward, M. D. Ph.D. Dissertation, Princeton University, 1981. Titrations also often employ substituted pyridines and may be able to differentiate between Brønsted and Lewis acid sites. See for example: Murrekk, L. L.; Dispenziere, N. C. *J. Catal.* **1989**, *117*, 275.

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(4) To interconvert frequency and mass, the following relationship is employed:

$$\Delta m = \frac{\Delta f}{(-2.26 \times 10^{-6})f_0^2}$$

See: Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206. A review of QCM applications is available: Lu, C.; Czanderna, A. W., Eds.; *Applications of Piezoelectric Quartz Crystal Microbalances*; Elsevier: New York, 1984.

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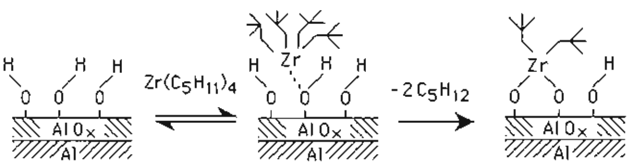
Scheme I



positions were performed with excess organozirconium reagent under pseudo-first-order conditions; mass change data were fitted[5] to a pseudo-first-order function, $\Delta m = A(1 - \exp(-k_{obs}t))$, and the deposition rate constant, k_{obs}, was determined. In control experiments, deposition attempts onto gold electrodes showed no frequency (mass) changes.

As shown in Table I, the areal loading of surface hydroxyl groups increases with greater vigor of the hydroxylation reaction of the Al surface. Thus, comparison of areal loadings of the organozirconium complex deposited on aluminum, obtained by using the QCM, with hydroxyl group contents for aluminum powders, obtained by MeLi titration, suggests that, for both forms of the metal, steam-treated aluminum has ca. 3.5 times the hydroxyl concentration of aluminum simply exposed to the laboratory atmosphere. Surprisingly, deposition reaction rate *constants* were similar for all methods used either for surface preparation or organometallic complex deposition onto the Al electrode. To elucidate details of the protolytic deposition step, a fully deuterated oxidized aluminum surface was prepared, ab initio, by exposing a freshly O_2-oxidized aluminum electrode to D_2O steam. Deposition of $Zr(C_5H_{11})_4$ from the gas phase was performed and was monitored with time, and a large isotope effect, $k_H/k_D \approx 8.5$, was measured. (In a control experiment, neopentane-d_1 (>98% D) was observed from a solution deposition procedure using D_2O steam-hydroxylated bulk aluminum powder.)

Discussion

The insensitivity of observed deposition rate constants to surface hydroxyl group content (total acidity) of the metal and to the transport method employed indicates that these "bulk" phenomena have little effect on the kinetic acidity of individual –OH groups. The large measured isotope effect[6] suggests that proton transfer is rate determining for overall organozirconium complex deposition in a sequence in which (reversible) coordination of the organometallic to the hydroxylated surface preceeds (irreversible) chemical attachment,[7] as shown in Scheme I.

Experimental Section

General Data. Gas analyses were accomplished by using a Hewlett-Packard Model 5840A gas chromatograph (neopentane yields) or a Hewlett-Packard Model 5992B GC/MS (deuterium incorporation). Both instruments were equipped with columns packed with 1% SP-1000 on 60/80 Carbopack B (Supelco) or 0.19% picric acid on 80/100 Carbopack C (Supelco). Manipulation of aluminum powder, freshly deposited aluminum electrodes, and organozirconium reagents was carried out in a nitrogen-filled Vacuum Atmospheres glovebox or under dry argon by using standard Schlenk techniques. Gas manipulations were done on a high-vacuum manifold equipped with oil diffusion and Töpler pumps and a calibrated manometer. Water (HPLC grade) and D_2O (99.9%) were degassed prior to use. Diethyl ether was distilled from sodium benzophenone ketyl. *n*-Pentane was distilled from CaH_2 and degassed before use (GC analysis showed <0.01% neopentane). Tetraneopentylzirconium[8] was sublimed (50 °C, 10^{-3} Torr) prior to use.

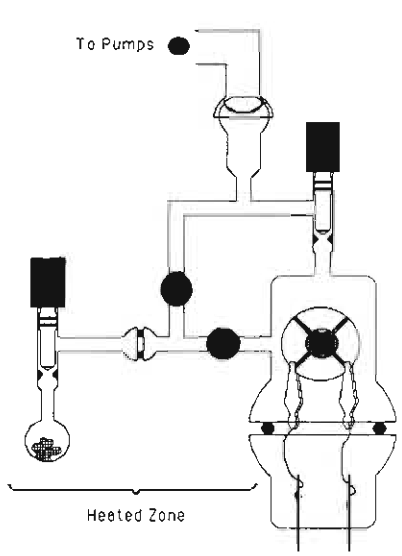


Figure 1. Gas-phase deposition apparatus. (Large circles indicate valves; small circles are O-ring seals.)

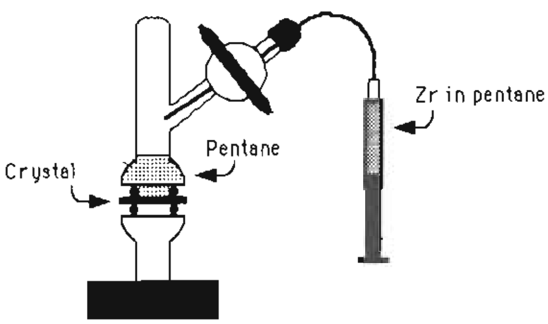


Figure 2. Solution-phase deposition apparatus.

"Quartz Crystal Microbalance". Quartz crystals (5.5MHz, AT-cut, fundamental mode) were obtained from Valpey-Fisher and were cleaned before use by soaking in H_2SO_4, copiously rinsed first with water and then with acetone, and then oven-dried. Electrodes were vapor-deposited onto the crystals by using an Edwards Coating System E306A at $<10^{-6}$ Torr. Electrodes were prepared as a 500-Å aluminum (Aesar, 99.5%) layer on a 1500-Å gold (Aldrich, 99.99%) layer on top of a 150-Å chromium (Aldrich, 99.5%) base. The electrode overlap area was 0.27 cm^2. The QCM was driven with either a home-built Clapp oscillator[9] or an Intellemetrics IL02 single-crystal oscillator. Either circuit was powered by a Hewlett-Packard 6234A dual-output power supply. The Intellemetrics circuit was separated from the supply by a 12.5-mH choke. The crystal frequency was measured by using a Hewlett-Packard 5334B universal counter and recorded on a laboratory computer.

Hydroxylation of Aluminum. Atmospheric oxidation was accomplished by exposure of the aluminum metal (powder or vapor deposited electrodes) to ambient laboratory conditions (relative humidity ca. 60% at 20 °C) for 12–18 h, followed by overnight evacuation with the diffusion pump. Water hydroxylation was accomplished by first exposing the metal to ambient conditions followed by immersion in water for 12 h, air-drying at room temperature, and then evacuation overnight. "Steam" hydroxylation was done as follows. Degassed H_2O (or D_2O) (ca. 2 mL) in a valve-sealed vial was attached to a flask containing the aluminum and the ensemble was evacuated (in an assembly similar to the one shown in Figure 1). The metal was then exposed to dry oxygen (160 Torr) for 1 h followed by evacuation. The valve between the flask and vial was opened, and the assembly was placed in an oven (80 °C) for ca. 18 h. The water vial was then resealed, and the metal was quickly evacuated and maintained in vacuo overnight by using the diffusion pump.

Hydroxyl Group Titration of Oxidized Bulk Aluminum Powder. Methyllithium (ca. 20 mL, Aldrich, 1.4 M in Et_2O) was placed in a vial and degassed. This vial was then attached to a flask containing the atmosphere-exposed aluminum sample (10.0 g, Aldrich, 99.99%) to be titrated and the ensemble was evacuated. The methyllithium solution was introduced to the metal and stirred for 45 min. The slurry was cooled to

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(5) Fitting was accomplished by using a commercially available least-squares routine. For all fits, $R^2 > 0.97$.

(6) The large isotope effect may be rationalized by considering the cleavage of a strong O–H bond and the formation of a weak two-electron, three-center [Zr(R)(H)] unit in the transition state for Zr–R bond breaking. For discussion of analogous protonation of a (η^4-diene)iron tricarbonyl complex, see: Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 907.

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−78 °C and the evolved methane (0.07 mmol) Töpler pumped through a trap (at −196 °C) into the calibrated manometer. Steam-treated aluminum powder (10.0 g) was similarly titrated to yield 0.24 mmol of methane. Measurement of the surface area of the aluminum powder was not attempted.

Gas-Phase Deposition of Tetraneopentylzirconium onto Surface-Activated Aluminum. Tetraneopentylzirconium (ca. 150 mg) was placed in a small vial that was then attached to a cell containing an electrode-deposited quartz crystal held by spring clips (Figure 2). The cell was designed to allow separate evacuation of the reagent vessel and the one containing the crystal. The reagent vial was wrapped with heating tape and covered with glass wool and aluminum foil for insulation. The heated zone was warmed to 50–60 °C under vacuum; the temperature was monitored via a thermocouple or thermometer. After a short time (3–5 min), the vapor of the zirconium reagent was introduced into the crystal-containing chamber while the crystal frequency was monitored (ca. 0.5-Hz sampling rate). The crystal chamber was continuously evacuated by using the diffusion pump during and after exposure. The crystal frequency was periodically monitored, even after exposure, to ensure that mass changes observed were due to the deposition reaction and not to simple sublimation.

Deposition of Tetraneopentylzirconium from Solution onto Surface-Activated Aluminum. The crystal was clamped between two O-ring connectors under dry, oxygen-free N_2, and 1–2 mL dry *n*-pentane was placed on the crystal in order to eliminate mass changes due to solvent effects.[10] A 0.5-mL aliquot of 0.05 M $Zr(C_5H_{11})_4$ in pentane was added via syringe (see Figure 2). For depositions onto hydroxylated aluminum powder, solid $Zr(C_5H_{11})_4$ was mixed with the metal in a flask separated by a valve from a vial containing 5–10 mL of degassed pentane. The assembly was evacuated, and the valve was opened. Upon completion of this procedure, organic materials were distilled and the neopentane yield was measured (2.0 equiv).

Determination of Deuterium Incorporation in Evolved Neopentane. Neopentane-d_1 was collected from the reaction of neopentyllithium[11] (ca. 100 mg) with $D_2O(g)$. GC/MS analysis (for neopentane minus methyl; molecular ion not observed) showed m/z 57:m/z 58 = 0.49:1. Neopentane evolved from deposition of $Zr(C_5H_{11})_4$ onto D_2O-steam-treated aluminum powder was collected and analyzed by GC/MS, which showed m/z 57:m/z 58 = 0.49:1. Thus, deuterium incorporation into evolved neopentane is ca. 100%.

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Supplementary Material Available: Figures showing frequency vs time data for deposition of $Zr(C_5H_{11})_4$ onto surface-oxidized aluminum (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Cyanoiron(II) Complexes Bound to the Bridging Ligand Tetrakis(2-pyridyl)-1,4-diazine (tpd)

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Nitrogen aromatic heterocyclic ligands, such as 2,3-bis(2-pyridyl)pyrazine (dpp),[1–8] 2,3-bis(2-pyridyl)quinoxaline (dpq),[9,10] 2,2′-bipyrimidine (bpm),[10–17] and benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]tripyrazine (hat),[10,18,19] have recently been used to prepare complexes with low-spin d^6 metals including Ru(II), Fe(II), Rh(III), and group 6 carbonyls. These complexes possess highly absorbing MLCT transitions in the visible–near-UV region of the spectrum, and good metal–metal electronic interaction in polymetallic systems has been observed.[20–22] Mono- and bimetallic d^6 complexes coordinated to this type ligand have thus been prepared and studied as models for photoinitiated excited-state energy-transfer reactions, photochemistry and photophysics of polymetallic complexes, and solvatochromic behavior.

Our research group has been interested in the design and characterization of low-spin d^6 transition-metal complexes bound through the bis-tridentate ligand tetrakis(2-pyridyl)-1,4-diazine (tpd), for potential use in photo-capture/excited-state energy-transfer processes. Bimetallic complexes with tpd have only recently prepared with Ru(II)[23,24] and Rh(III)[25] centers. We report the preparation and characterization of the first cyanoiron(II) complexes bound with tpd.

Experimental Section

Materials. Analytical reagent grade solvents and compounds were used for preparations and experiments described in this work. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Instrumentation. Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on a Bio Analytic Systems CV-1B cyclic voltammograph with a Princeton Applied Research Model 0074 X-Y recorder. Cyclic voltammograms were recorded in distilled H_2O with 0.10 M KCl and in DMF with 0.10 M tetrabutylammonium perchlorate as supporting electrolyte. A Pt working electrode (2.0-mm diameter) and an Ag/AgCl (3 M KCl nominally −0.44 V vs SCE) reference electrode were used. All potentials are reported vs SCE and are uncorrected for junction potentials. Infrared spectra were recorded as solid KBr samples on a Nicolet Model 20DX FTIR spectrometer from 4000 to 400 cm^{-1} using 2-cm^{-1} resolution. ^1H NMR spectra were obtained on a Bruker Model AC 300 Fourier Transform NMR instrument operating at 300.1 MHz. Samples were run in a 10.0-mm probe with D_2O as the solvent and internal lock. The reference was $(CH_3)_3SiC_3H_5SO_3^-Na^+$ (δ = 0.015 ppm vs TMS).

Synthesis. The tpd ligand was prepared according to the literature without difficulty.[26] The Na[Fe(CN)$_3$(tpd)] complex was prepared by

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