Table I. Diastereoselectivity in the Reaction in **1–4**[a]

entry	substrate	reagent, RM	reacn condn[d]	syn/anti (**5**/**6**)	total isold yield, %
1	**1**	MeCu	-78 → -20, 1.5	77/23	72
2	**1**	Me_2CuLi	-78 → -20, 1.5	87/13	73
3	**1**	BuCu	-78 → -20, 1.5	77/23	89
4	**1**	Bu_2CuLi	-78 → -20, 1.5	91/9	79
5	**1**	Me_4AlLi	-78 → 0, 2	37/63	75
6	**1**	$CH_2{=}CHCH_2SnBu_3$, $TiCl_4$	-78 → -20, 1.5	29/71	52
7	**1**	$CH_2{=}CHCH_2SnBu_3$, phenanthrene	hν, rt,[e] 1	70/30	4[b]
8	**1**	BuI, Bu_3SnH, AIBN	toluene, 110, 1	18/82	13[c]
9	**2**	MeCu	-78 → -20, 1.5	38/62	92
10	**2**	Me_2CuLi	-78 → -20, 1.5	62/38	91
11	**2**	BuCu	-78 → -20, 1.5	25/75	79
12	**2**	Bu_2CuLi	-78 → -20, 1.5	75/25	68
13	**3**	MeCu	-78 → -20, 1.5	25/75	93
14	**3**	Me_2CuLi	-78 → -20, 1.5	68/32	87
15	**3**	BuCu	-78 → -20, 1.5	31/69	83
16	**3**	Bu_2CuLi	-78 → -20, 1.5	67/33	90
17	**4**	MeCu	-78 → -20, 1.5	16/84	62
18	**4**	$Me_2CuLi{\cdot}MeLi$	-78 → -20, 1.5	60/40	87
19	**4**	BuCu	-78 → -20, 1.5	14/86	91
20	**4**	Bu_2CuLi	-78 → -20, 1.5	78/22	83

[a] All reactions were carried out on 1-mmol scale. The product was isolated through a column of silica gel. The isomer ratio was determined by capillary GLC (SE-30, 25 m) and/or ^1H NMR analyses. Three equivalents of the organocopper reagents were used. In entries 5 and 6, a slight excess of RM was added. In entries 7 and 8, 2 equiv of allyltin and BuI were utilized. [b] The regioisomer of **5a**, $PhCHMeCH_2CRXY$, was obtained as a major product (see ref 7). [c] The reaction was not clean, and many unidentified products were obtained along with the desired adduct. [d] Temperatures are given in °C, and time is measured in hours. [e] Room temperature.

Table II. Diastereoselectivity in the Presence of pDNB[a]

entry	substrate	organocopper	pDNB (equiv)	syn/anti (**5**/**6**)	total yield,[b] %
1	**1**	MeCu	3	33/67	30
2	**1**	Me_2CuLi	3	33/67	99
3	**1**	BuCu	3	28/72	21
4	**1**	Bu_2CuLi	3	32/68	79
5	**2**	Me_2CuLi	1	39/61	99
6	**2**	Bu_2CuLi	1[c]	39/61	99
7	**3**	Me_2CuLi	1	42/58	99
8	**3**	Bu_2CuLi	3	34/66	82

[a] To an ether solution of organocoppers (3 mmol) was added pDNB in THF at -78 °C, and then substrates (1 mmol) were added. [b] By GLC. The starting substrate was recovered when the reaction resulted in low yield. [c] pDNB in ether was used.

an electron transfer to the Michael acceptors and the copper species[11] reacts with **1–3** instead of their anion radicals.

The difference between RCu and R_2CuLi in **2–4** and the similarity between RCu and R_2CuLi in **1** are in good agreement with the E_{red} values. Both reagents must produce the radical anion of **1**, since **1** possesses high ability to accept an electron. When the ability of substrates **2–4** is not so high, only R_2CuLi which possesses higher electron-donating capability must produce the radical anions. Taken together, the syn selectivity can be explained by the intermediacy of the radical anions of Michael acceptors.[12]

The attack angle, θ, of nucleophiles and radicals is greater than 90°,[2] and thus the steric factor of the outside region becomes important in controlling the selectivity. Therefore, the anti isomer is produced via **7** (a modified Felkin model). On the other hand, in the radical anion intermediate the interaction between the HOMO of substrate and R* group dictates the stereoselectivity.[2] The electrophilic attack occurs with acute θ, and the inside region of **8** is stereodetermining. In conclusion, the stereochemical results taken as a whole not only provide the first example of acyclic stereocontrol via an electron-transfer process but also demonstrate a delicate balance of the mechanisms of the organometallic conjugate additions.

Acknowledgment. We thank Professor T. Miyashi of our department for measurement of E_{red} values.

Supplementary Material Available: Experimental details of the structure determination of **5** and **6** (2 pages). Ordering information is given on any current masthead page.

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[12] The syn selectivity of organocopper addition to **1** may be ascribed to participation of the d-orbital.[13] However, the difference in **2–4** and the effect of pDNB cannot be explained by this concept.

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Inorganic Analogues of Langmuir–Blodgett Films: Adsorption of Ordered Zirconium 1,10-Decanebisphosphonate Multilayers on Silicon Surfaces

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The preparation of organized monolayer and multilayer molecular assemblies at interfaces continues to be an area of great current interest.[1-5] Studies of these assemblies have been motivated by their relevance to a variety of heterogeneous phenomena including solid-state microelectronics,[6] electrochemistry,[4,7] and catalysis.[8] One route to the preparation of such structures is via the classical Langmuir–Blodgett monolayer transfer technique;[9] this powerful approach unfortunately suffers from several drawbacks, most notably the requirement for planar substrates and a sensitivity to environmental contaminants. Sagiv and coworkers[10] have demonstrated the feasibilty of multilayer synthesis via sequential adsorption and chemical activation of chlorosilanes. Their synthetic method is conceptually novel because it does not involve monolayer transfer steps; however, it has failed to yield organized surface structures more than two or three layers thick because of imperfect ordering of alkyl chains within the layers.

We report here a multilayer synthesis based on the sequential adsorption of components of zirconium 1,10-decanebisphosphonate (ZDBP), $Zr(O_3PC_{10}H_{20}PO_3)$. This is a water-insoluble salt which contains alternating polar Zr–O–P and nonpolar alkyl layers, with a 17.3-Å crystallographic layer spacing.[11] We selected this compound as a basis for surface multilayer synthesis because it (like many transition-metal phosphonates) spontaneously crystallizes as a layered compound when solutions of the appropriate metal salt and phosphonic acid are mixed. The process of growing ZDBP surface multilayers is shown in Scheme I. In the first step,

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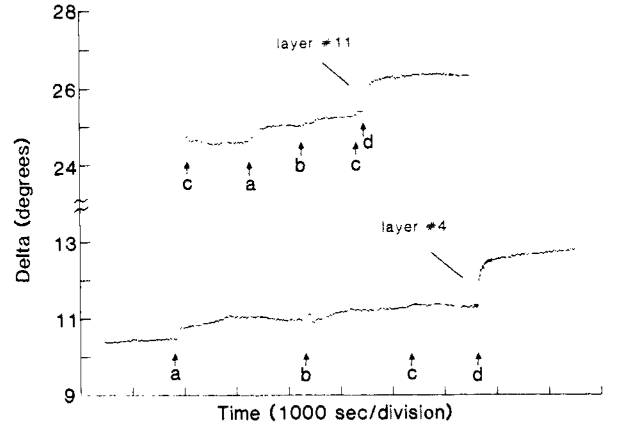
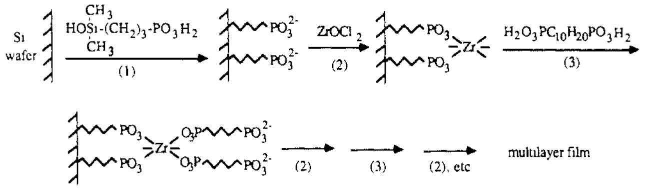


Figure 1. Relative phase shift Δ versus time for ZDBP layers grown on a Si wafer. Arrows marked a, b, c, d correspond, respectively, to addition of $ZrOCl_2$ solution to the cell, beginning of water rinse, end of water rinse, and addition of 1,10-decanebisphosphonic acid solution. Measurements were taken in an ellipsometer flow cell with an angle (Φ_o) of 72° between the incident beam and surface normal.

Scheme I



the Si substrate is exposed to a warm aqueous solution of a silanol,[12] producing a monolayer of covalently anchored phosphonate groups. After copious washing with water, the surface is exposed at ambient temperature to a 5.0 mM aqueous $ZrOCl_2$ solution, washed, and then exposed to 1.25 mM aqueous 1,10-decanebisphosphonic acid. Repetition of the second and third steps leads to a multilayer ZDBP film. The anchoring of phosphonate groups via the silanol (step 1) is crucial to the formation of the ZDBP multilayer. When, 1,10-decanebisphosphonic acid was substituted for the silanol in step 1, no film growth was observed by ellipsometry.

The structure of these films, probed by ellipsometry, is insensitive to the immersion time in either solution; samples were incubated between 1 and 24 h with indistinguishable results. Figure 1 shows the change in Δ[13] versus incubation time for the fourth and eleventh ZDBP layers on a Si wafer. This experiment was carried out in an ellipsometer cell which could be flushed with various solutions in situ, and Δ was monitored continuously. (Of the two observables Δ and Ψ, Δ is most sensitive to changes in film thickness[13]). Δ increases rapidly after injection of either decylbisphosphonic acid or zirconyl chloride and reaches a plateau within 5 min. In this cell these adsorption steps could be repeated to give at least 12 ZDBP layers without obvious degradation of the response in Δ versus time. Injection of water into the cell following either step does not appear to cause loss of material from the surface. A very slight increase in Δ is observed when the $ZrOCl_2$-treated surface is flushed with water; the cause of this apparent thickening of the layer is not known. We speculate that it may arise from hydrolysis of surface Zr–Cl bonds. Washing the 1,10-decanebisphosphonic acid-treated surface with water gives no observable change in Δ, indicating that phosphonic acid multilayers do not form under these conditions on the Zr-terminated surface.

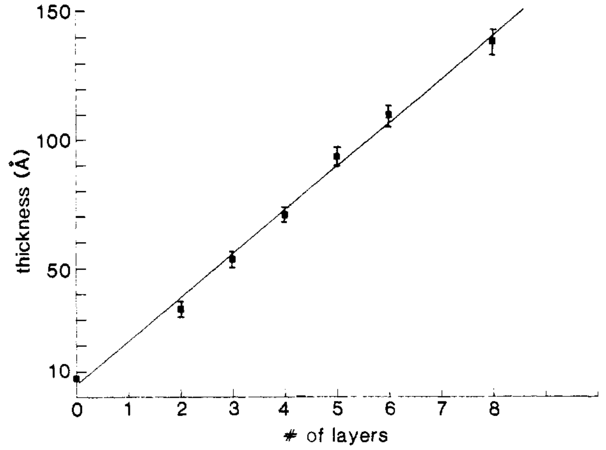


Figure 2. Film thickness[14] versus number of layers for ZDBP films grown on Si; Φ_o = 72°.

Figure 2 shows a plot of film thickness versus number of layers for ZDBP films.[14] The data points were taken from several different silicon wafers which were treated with the silanol anchoring agent, then dipped in $ZrOCl_2$, deionized water, and 1,10-decanebisphosphonic acid solutions, and measured in air. In this plot n layers corresponds to a sequence of adsorption steps (Scheme I) 1-2-$[3\text{-}2]_n$. The data point for zero layers therefore corresponds to a wafer which was exposed to the silanol and $ZrOCl_2$ but not to the 1,10-decanebisphosphonic acid; the zeroth layer has a measured thickness of ca. 7 Å. The slope of the line drawn through the points for n = 0–8 is 17.0 Å/layer which corresponds, within experimental error, to the 17.3-Å spacing between layers in crystalline $Zr(O_3PC_{10}H_{20}PO_3)$. We hestitate (because of uncertainties in oxide layer thickness and refractive index) to assign absolute thicknesses to the ZDBP films solely on the basis of optical ellipsometry. It is nevertheless clear from the slope of the line, which is insensitive to these errors, that the film is growing in an oriented manner and is reasonably compact even after eight layers. Electrochemical and XPS experiments carried out on four-layer films, which will be described in detail elsewhere,[15] show that the multilayers are continuous and pinhole-free.

While full structural characterization of these films awaits diffraction and vibrational spectroscopic measurements, the ellipsometric study clearly shows that organized multilayers can be built up via sequential adsorption of two soluble components of an insoluble layered salt. The success of this method derives from the thermodynamic stability of this layered solid, which crystallizes spontaneously when the two soluble components are mixed.[11] We are currently testing the scope of this approach with other metal phosphonates adsorbed as multilayers on planar and nonplanar surfaces.

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(12) Solutions of the silanol were prepared by alkaline hydrolysis of the corresponding siloxane. The alkaline solution was acidified to pH 3 with HCl immediately before use to give an ca. 1 mM silanol solution. Water from a millipore train, resistivity 18.3 MΩ-cm, was used to prepare this and other solutions and in the washing steps. Silicon wafers with polished (100) faces, obtained from Aurel Corp., were cleaned with trichloroethylene, isopropyl alcohol, and water and were incubated 1–3 days at 50 °C in the silanol solution. Ellipsometric measurements from wafers treated with blank HCl solutions show that under these conditions an oxide layer approximately 20-Å thick remains.

(13) The ellipsometrically measured paıameters Δ and Ψ are related to the film thickness d and indices of refraction n_{film}, n_{air}, and n_{Si} through a complex function f

$$\tan(\Psi)\exp(i\Delta) = f(\lambda, \Phi_o, d, n_{\text{film}}, n_{\text{air}}, n_{\text{Si}})$$

where λ and Φ_o are the wavelength and angle of incidence of the analyzing light (For in situ measurements of film growth, n_{air} is replaced by n_{water}). The explicit form of f is given by Azzam et al. (Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North Holland, 1977; pp 332–340). Ellipsometric measurements were made with a Rudolf 437 ellipsometer equipped with an RR-2000 rotating analyzer detector and 6328 Å (He-Ne laser) analyzing light.

(14) Film thicknesses were calculated from the measured Δ and Ψ values by using a refractive index of 1.54 ± 0.03 for the ZDBP film. This is the refractive index of a bulk $Zr(O_3PC_{10}H_{20}PO_3)$ sample measured by the immersion method; an excellent index match was found with benzaldehyde (n = 1.544), while substantially poorer matches were obtained with carbon disulfide (n = 1.628) and toluene (n = 1.494).

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Competitive α- and β-Elimination in an Iridium Alkyl

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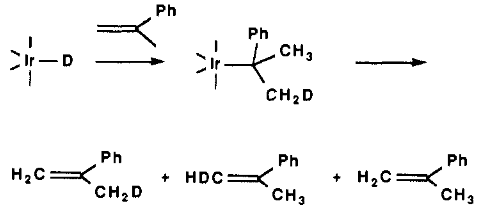
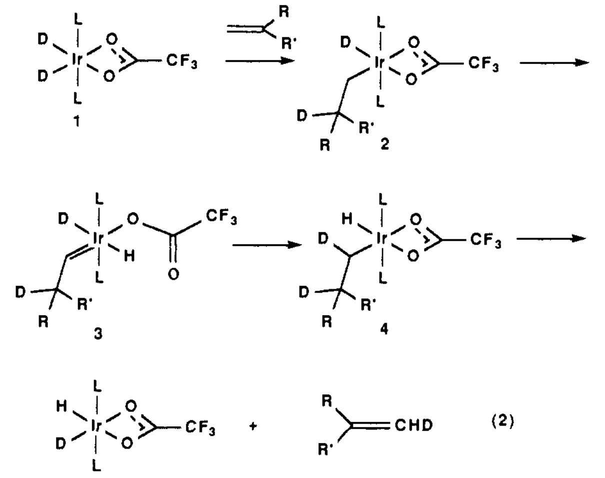
C–H bond activation is an area of great current interest.[1a] We recently described[1b] thermal alkane dehydrogenation by using $[IrH_2(\eta^2\text{-}O_2CCF_3)(PAr_3)_2]$ (**1**, Ar = $p\text{-}C_6H_4F$) as catalyst in the presence of $t\text{-}BuCH{=}CH_2$ (tbe) as hydrogen acceptor. We now find that **1**-d_2 gives selective H/D exchange with the vinyl hydrogens of various alkenes, including tbe. Direct vinylic C–H activation has recently been reported,[2] but this mechanism is not operating here. Instead, an alkene insertion/β-elimination route is involved. Unexpectedly, rapid α-elimination can also be identified as a pathway leading to exchange.

Monitoring the reaction of **1**-d_2 with tbe-d_0 (15 mol equiv) in C_6H_6 at 25 °C by ^2H NMR showed that D incorporation occurs at the same rate (±5%) for all the vinyl positions; no further incorporation is seen after 2 h at 25 °C. The deuteriated product is ca. 85% tbe-d_2 by GC-MS. Similar rates and selectivities are observed for styrene, stilbene, α-methylstyrene, and ethyl vinyl ether. An insertion/β-elimination mechanism could only account for this result if insertion were taking place twice as fast to give the more hindered branched alkyl than to give the linear alkyl, contrary to what is normally found.[4a] Such a mechanism would tend to give tbe-d_1 as the major product because once one D is incorporated the tbe-d_1 should dissociate; this is rapid on the NMR time scale at 25 °C. Finally, for α-methylstyrene, β-elimination should take place in each of the two possible directions from any intermediate tertiary alkyl, assuming free rotation[4b] about the Ir–C bond (eq 1). We observe D incorporation into the methyl groups


(1)

at an insignificant (<2%) relative rate, again inconsistent with insertion/β-elimination. $Me_2C{=}CH_2$ behaves similarly. Alternatively, vinyl activation might be taking place at equal rates at all sites. This should give tbe-d_1 as a major product, should give some tbe-d_3, and should give *trans-t*-BuCH=CHD selectively as observed by Faller and Felkin;[2a] none of these features is seen here. The evidence therefore seems to require insertion to give the 1° alkyl followed by α-elimination to account for the deuteriation of the terminal vinyl groups (eq 2). Radical mechanisms can


(2)

be ruled out because these should give tbe-d_1 as a major product. In addition, the reaction rate is essentially the same in CH_2Cl_2 and toluene, and in no case is D incorporated into the solvents, nor is bibenzyl formed from toluene.

Our results are consistent with insertion and rapid α-elimination followed by β-elimination. The ca. 1:1:1 regiochemistry of D incorporation is, we propose, the result of a balance between equilibrium isotope effects for the α-elimination equilibrium, which should favor **4** over **2**, and the kinetic isotope effect for β-elimination, which should favor H elimination.[5] At each step the trifluoroacetate can open or close to preserve an 18e configuration at Ir.

The formation of deuteriated alkane by reductive elimination from **2** or **4** is much slower. When this happens, the Ir is irreversibly trapped by the solvent to give $[PhIrH(\eta^2\text{-}O_2CCF_3)(PAr_3)_2]\text{-}d_0$ (**5**). Such adducts have been seen before[6] but never from an alkane conversion catalyst as here. Like **1**, **5** is a thermal alkane dehydrogenation catalyst,[1b] and the alkyl hydride **2** must also be involved in the catalytic cycle. Many alkyl hydrides have been observed and isolated,[6] but in only one case[7] has an alkylidene hydride been detected and then only spectroscopically at low temperatures.

Although α-elimination is rarely observed, it may be a common process for unsaturated alkyls but require isotopic labeling to be detected. Our results suggest that α-elimination must proceed at least as fast as β-elimination and faster than reductive elimination in this system. Shilov et al.[8] have proposed rapid α-elimination to explain multiple H/D exchange in their Pt-based alkane activation chemistry. Shapley et al.[9] have reported faster α- and β-elimination in a cluster alkyl. Schrock et al.[10a] have seen competitive α- and β-elimination and Bercaw and Parkin,[10b] faster α- than β-elimination in some tantalum alkyls. Our results suggest that α-elimination may be more facile for the late metals than previously suspected.

Acknowledgment. We thank NSF (M.J.B.) and DOE (R.H.C.) for support.

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