with a pulsed-field gradient accessory and a triple resonance probe with an actively shielded z gradient. No water presaturation was used. Figure 2 illustrates an $F_1(^{13}C\alpha/\beta) - F_3(^1H\alpha)$ slice at a C′ shift of 178.1 ppm. The slight amount of residual water does not pose a problem for the observation of correlations to Hα protons that resonate at or very near the water line.

In summary, a pulsed field gradient experiment is presented which correlates $^{13}C\alpha/\beta$, $^{13}C'$, and $^1H\alpha$ chemical shifts with high sensitivity. The field gradient approach described here is equally applicable to other experiments such as the HCACO and HCA(CO)N and should greatly facilitate recording of all of the triple resonance backbone experiments in H_2O.

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Preparation, Catalytic Reactivity, and X-ray Crystal Structure of the First Group 4 Alkyl/Alkene Complexes. The First Structural Models of the Key Ziegler–Natta Catalytic Intermediate

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We herein describe the preparation and reactivity of the first group 4 complexes that contain both an alkyl ligand and a coordinated alkene; these complexes are the first group 4 molecular analogues of the key alkyl/alkene intermediate[1,2] that just precedes the insertion step in the mechanism of the Ziegler–Natta polymerization of alkenes. Interestingly, some of these complexes are active catalysts for the dimerization of alkenes.

Alkylation of $HfCl_4$ with 6 equiv of ethyllithium in diethyl ether at −78 °C, followed by warming to room temperature and addition of *N,N,N′,N′*-tetramethylethylenediamine (tmed), gives colorless crystals of the remarkable species $[Li(tmed)]_2[Hf(C_2H_4)Et_4]$ (**1**), which is formally an ethylene complex of Hf^{II}.[3,4] The ^{13}C NMR

$$HfCl_4 + 6LiEt + 2tmed \rightarrow [Li(tmed)]_2[Hf(C_2H_4)Et_4] + 4LiCl + C_2H_6$$

spectrum of **1** in C_7D_8 at 20 °C contains a triplet at δ 30.5 due to the ethylene ligand; the $^1J_{CH}$ coupling constant of 119 Hz is unprecedentedly low for an ethylene ligand. In comparison, $^1J_{CH}$ coupling constants for all other transition-metal ethylene complexes are 144 Hz or larger and are typically 150–160 Hz.[5-8]

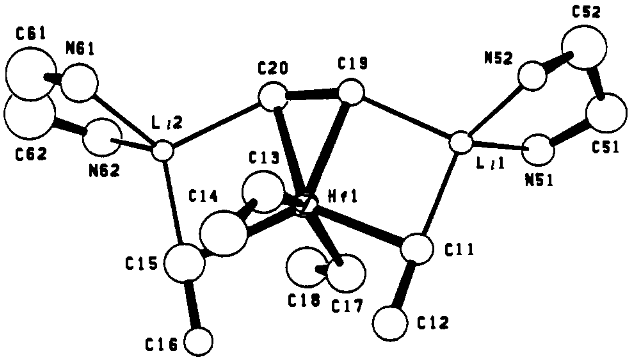

Figure 1. Molecular structure of $[Li(tmed)]_2[Hf(C_2H_4)Et_4\}$. Thermal ellipsoids are represented by the 35% probability surfaces; the methyl groups of the tmed ligands have been omitted for clarity. Important bond distances (Å) and angles (deg) for molecule 1: Hf(1)–C(19) 2.26(4), Hf(1)–C(20) 2.31(4), Hf(1)–C(11) 2.39(5), Hf(1)–C(15) 2.45(4), Hf(1)–C(13) 2.38(4), Hf(1)–C(17) 2.43(6), C(19)–C(20) 1.49(6), Li(1)–C(19) 2.40(9), Li(2)–C(20) 2.37(9), Li(1)–C(11) 2.05(8), Li(2)–C(15) 2.04(9), Hf(1)–C(13)–C(14) 109(3), Hf(1)–C(17)–C(18) 110(4), Hf(1)–C(11)–C(12) 101(3), Hf(1)–C(15)–C(16) 105(3), C(13)–Hf(1)–C(17) 149(2), C(11)–Hf(1)–C(15) 132(1), C(11)–Hf(1)–C(19) 94(2), C(15)–Hf(1)–C(20) 97(2).

The formation of the $[Hf(C_2H_4)Et_4{}^{2-}]$ dianion presumably proceeds via the hexaethylhafnate complex $[HfEt_6{}^{2-}]$, which would be analogous with the known[9] hexamethylhafnate species $[HfMe_6{}^{2-}]$. However, $[HfEt_6{}^{2-}]$ is evidently unstable and spontaneously loses 1 equiv ethane. The gases evolved upon treating $HfCl_4$ with 2,2,2-trideuterioethyllithium ($LiCH_2CD_3$) were analyzed by GC/MS and were found to consist almost exclusively of ethane-d_4. This result clearly shows that the principal pathway for formation of the $[Hf(C_2H_4)Et_4{}^{2-}]$ dianion is β-elimination.

The X-ray crystal structure[10] of $[Li(tmed)]_2[Hf(C_2H_4)Et_4]$ reveals that the complex can best be considered as a square-based pyramid with the ethylene ligand occupying the axial position and the four ethyl groups occupying the basal sites (Figure 1). The $[Li(tmed)^+]$ cations bridge between the ethylene ligand[11] and two

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[3] Anal. Calcd for **1**: C, 46.4; H, 9.94; N, 9.84; Li, 2.24; Hf, 31.4. Found: C, 46.3 H, 9.76; N, 9.83; Li, 2.77; Hf, 30.6. ^1H NMR (C_7D_8, 20 °C): δ 0.31 (s, Hf-C_2H_4); 0.05 (q, J_{HH} = 7.5, Hf-*CH*$_2$Me); 2.06 (t, J_{HH} = 7.5, Hf-CH$_2$*Me*); 2.00 (s, NMe_2); 1.70 (s, NCH_2). ^{13}C NMR (C_7D_8, 20 °C): δ 31.0 (t, J_{CH} = 119, Hf-C_2H_4); 41.9 (t, J_{CH} = 106, Hf-*CH*$_2$Me); 13.8 (q, J_{CH} = 121, Hf-CH$_2$*Me*); 45.9 (q, J_{CH} = 132, NMe_2); 56.5 (t, J_{CH} = 136, NCH_2). $^{13}C\{^1H\}$ NMR (CPMAS, −50 °C): δ 31.7 (s, Hf-C_2H_4); 46.7 (s, Hf-*CH*$_2$Me); 14.8 (s, Hf-CH$_2$*Me*); 48.0 (s, NMe_2); 57.7 (s, NCH_2).

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[10] Crystal data for $C_{22}H_{56}N_4Li_2Hf$ (T = 198 K): orthorhombic, space group *Pbca*, a = 21.513(9) Å, b = 17.443(4) Å, c = 32.100(7) Å, V = 12046(11) Å^3, Z = 16, R_F = 0.077, and R_{wF} = 0.078 for 244 variables and 2216 unique data for which $I > 2.58\sigma(I)$. The hafnium atoms were refined anisotropically, and all other non-hydrogen atoms were refined isotropically. Hydrogen atoms on the tmed ligands were included as fixed contributors in idealized positions, and a group isotropic thermal parameter was refined for them. No other hydrogen atoms were included in the refinement. There are two molecules in the asymmetric unit whose metric parameters are generally similar, and each hafnium atom resides on a general position.

[11] NMR studies show that the $^1J_{CH}$ coupling constants are identical in coordinating *and* noncoordinating solvents. We conclude that the Li···C contacts present in the solid-state structure of $[Li(tmed)]_2[Hf(C_2H_4)Et_4]$ are *not* responsible for the unusually small 119-Hz $^1J_{CH}$ coupling constant of the ethylene ligand.

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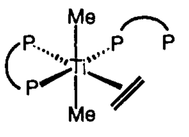
of the ethyl groups in the square base. The C–C distance of 1.49(6) Å between the two carbon atoms of the ethylene ligand must be interpreted cautiously since the standard deviation is large. For comparison, the longest C–C distances reported previously for *any* transition-metal ethylene complex are the 1.438(5)-Å, 1.486(8)-Å, and 1.477(4)-Å bond lengths, respectively, in $(C_5Me_5)_2Ti(C_2H_4)$,[7] $(C_5H_5)_2Zr(C_2H_4)(PMe_3)$,[12] and $(C_5Me_5)Ta(C_2H_4)(CHCMe_3)(PMe_3)_2$.[13]

The orientation of the ethylene ligand with respect to the ethyl groups and its apparent metallacyclopropane character are undoubtedly consequences of strong $d\pi$–$p\pi^*$ overlap with a filled hafnium d_{xz} orbital. The structure of $[Li(tmed)]_2[Hf(C_2H_4)Et_4]$ is further evidence that early transition-metal centers in their lower oxidation states are strong π-donors.[14] The hafnium alkyl/alkene complex **1** does not react with ethylene; in general, hafnium complexes make poor Ziegler–Natta catalysts.

Although the hafnium(II) complex **1** is the first alkyl/alkene derivative of a group 4 metal, it would be of greater interest if such a complex could be prepared for the catalytically most relevant Ziegler–Natta metal, titanium. Treatment of toluene-d_8 solutions of the known[15] titanium(II) alkyl *trans*-$TiMe_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with ethylene (50 equiv) at –40 °C yields two new titanium(II) species, which have been identified as the titanium alkyl/alkene complexes $TiMe_2(C_2H_4)(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$ (**2**) and $[TiMe_2(C_2H_4)(\eta^2\text{-dmpe})]_2(\mu\text{-dmpe})$ (**3**) by a combination of one-dimensional, two-dimensional, and selectively decoupled ^1H, ^{13}C, and ^{31}P NMR experiments.[16] The equilibrium constant $K_{eq} = [\mathbf{3}][dmpe]/[\mathbf{2}]^2$ is approximately 0.3 at –40 °C. The ethylene ligands lie in the plane of the three bound phosphorus atoms in both **2** and **3**, and as a result the two ethylene carbon atoms are chemically inequivalent. Thus, for **2**, the $^{13}C\{^1H\}$ NMR spectrum shows resonances for the ethylene ligand at δ 58.6 and 58.3; the ^{13}C–^{13}C coupling constant is 39.2 Hz as measured for a sample made from $^{13}C_2H_4$, while the $^1J_{CH}$ coupling constant is 146 Hz. The orientation of the ethylene ligand maximizes the π-back-bonding from the filled titanium d_{xy} orbital; no evidence of rotation of the ethylene ligand about the C–C bond is noted up to –10 °C.



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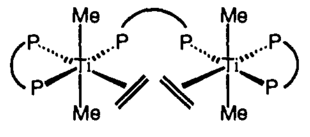

3

Above –40 °C, compounds **2** and **3** become catalytically active. Specifically, ethylene is rapidly dimerized to 1-butene; at 1 atm the rates are ca. 440 turnovers/h at –20 °C.[17,18] If solutions of the catalyst are cooled below -40 °C while the dimerization is taking place, only resonances due to **2**, **3**, free dmpe, ethylene, and 1-butene are seen. No 2-butene was detectable by $^{13}C\{^1H\}$ NMR spectroscopy.

By analogy with the chemistry of other early transition-metal compounds,[17] we propose that substitution of the η^1-dmpe ligands in **2** and **3** with ethylene gives the bis(ethylene) complex $TiMe_2(C_2H_4)_2(dmpe)$, which undergoes an oxidative coupling to form a titanium(IV) metallacyclopentane species. Subsequent β-hydrogen elimination to give a titanium butenyl hydride complex and reductive elimination to give 1-butene completes the catalytic cycle.

The dimerization of propene is much slower but can be accelerated if trimethylaluminum is added to the reaction solutions. Several isomers of hexene are formed: 1-hexene, 4-methyl-1-pentene, 4-methyl-2-pentene, and 2,3-dimethyl-2-butene are generated in a roughly 4:2:2:1 ratio. The distribution of isomers shows that coupling of propene does not occur specifically to give a single metallacyclopentane isomer; instead, most of the catalytic activity is due to head-to-head[19] and head-to-tail coupling. This regiochemistry is different from other early transition-metal alkene dimerization catalysts, in which tail-to-tail coupling predominates.[17b]

Surprisingly, even though **2** is the first alkyl/alkene complex of titanium, it does not undergo Ziegler chemistry. That is, *no insertion of alkenes into the titanium–alkyl bond takes place.* This may be a consequence of the unfavorable relative orientation of the two ligands: insertion of the ethylene molecule into the Ti–alkyl bond probably requires that the ethylene C–C bond and the Ti–alkyl axis be mutually parallel rather than perpendicular. However, even if the proper orientation were established, insertion of the ethylene ligand into the metal–carbon σ-bond may be thermodynamically disfavored due to the loss of the stabilizing π-back-bonding interaction. In contrast, π-back-bonding considerations will favor the formation of metallacyclopentanes from titanium bis(ethylene) intermediates since the two ethylene ligands will be held in a mutually coplanar orientation.[20]

We are continuing to explore the chemistry of these unusual group 4 alkyl/alkene complexes.

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(16) $^{31}P\{^1H\}$ NMR (C_7D_8, –40 °C): compound **2** exhibits an ABCD spin system with $\delta_A = 39.2$, $\delta_B = 13.3$, $\delta_C = 5.1$, $\delta_D = -47.1$, $J_{AB} = 14.3$, $J_{CD} = 20.5$; all other P–P coupling constants are 0; compound **3** exhibits an AA′BB′CC′ spin system with $\delta_A = 38.9$, $\delta_B = 13.2$, $\delta_C = 5.7$, $J_{AB} = 13.6$ Hz, $J_{CC'} = 15$ Hz; all other P-P coupling constants are 0. These complexes are unusual in that the coupling constants between the mutually trans phosphorus atoms are 0. Following are other NMR data for the bound ethylene and methyl ligands of **2**. ^1H NMR (C_7D_8, –40 °C): δ 2.35 (m, Ti-C_2H_4); –2.97 (q, $^3J_{PH} = 4.5$ Hz, Ti-Me). ^{13}C NMR (C_7D_8, –40 °C): δ 58.0 (dd, $^1J_{CH} = 146$ Hz, $^2J_{CP} = 8.8$ Hz, Ti-C_2H_4); 57.1 (dd, $^1J_{CH} = 146$ Hz, $^2J_{CP} = 10.4$ Hz, Ti-C_2H_4); 24.1 (q, $^1J_{CH} = 110$ Hz, Ti-Me). The ^1H and ^{13}C NMR chemical shifts and coupling constants for the ethylene and methyl groups in the dinuclear complex **3** are similar.

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(19) Head-to head coupling puts the methyl groups on the α-carbons of the metallacyclopentane ring. Interestingly, the formation of 1-hexene shows that β-elimination occurs from the hydrogens of the α-methyl groups and not from β-carbon atoms of the metallacyclic ring. See also: Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521–3523.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for $[Li(tmed)][Hf(C_2H_4)Et_4]$; $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra for **2** and **3** (9 pages); table of final observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Rhodium-Catalyzed Silylformylation of Aldehydes: A Mild and Efficient Catalytic Route to α-Silyloxyaldehydes

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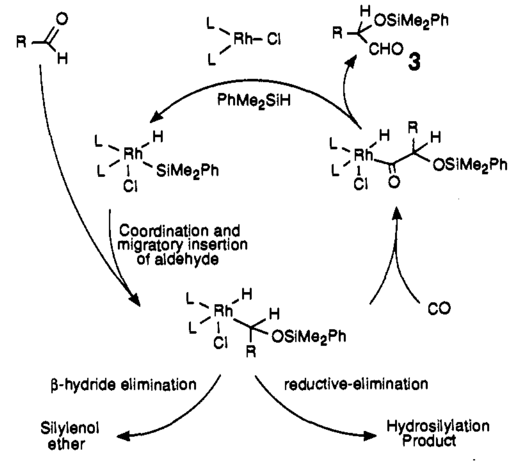
Hydroformylation is a widely used and well understood process catalyzed by a variety of transition metals.[1] The process incorporates an inexpensive source of carbon (i.e., carbon monoxide) and produces the aldehyde functionality, which is one of the most versatile and reactive functional groups in organic chemistry.[2] A variety of alkenes will undergo hydroformylation; however, carbon–oxygen double bonds (e.g., aldehyde) produce a formate ester and *not* the desired α-hydroxyaldehyde.[3] Murai and co-workers[4] in 1979 reported that treatment of aliphatic aldehydes (3-fold excess) with diethylmethylsilane and carbon monoxide (50 kg/cm^2) in the presence of $Co_2(CO)_8/PPh_3$ (100 °C, benzene) afforded α-silyloxyaldehydes in moderate yield.[4] More recently, Ojima and co-workers[5] and Matsuda and co-workers[6] independently reported the transition-metal-catalyzed "silylformylation" of alkynes.[7]

As part of our ongoing research effort to develop new chiral ligands and new reactions catalyzed by rhodium(I),[8] we have discovered that $[(COD)RhCl]_2$ is a very effective catalyst for the silylformylation of aldehydes. The rhodium(I)-catalyzed silylformylation of aldehydes appears very general, affords high yields of the α-silyloxyaldehydes, and does not require the use of excess aldehyde.

Scheme I



Initially our studies focused on the use of diphenylsilane, which is commonly used in rhodium(I)-catalyzed hydrosilylations.[9] Although at early stages in the reaction we could detect a new aldehyde group, at the completion of the reaction no α-silyloxyaldehyde could be isolated. We soon realized that an intramolecular hydrosilylation occurs after silylformylation, thus consuming the α-silyloxyaldehyde and producing the protected diol **1**.[10]

Utilization of the monohydric dimethylphenylsilane is found to work superbly in the rhodium(I)-catalyzed silylformylation of aldehydes (Scheme I, Table I). Since there is no evidence for the production of "diol" products, the relative rate of reaction for the starting aldehyde substrate must be much greater than that of the newly formed α-silyloxyaldehyde. A simple bulb-to-bulb distillation affords analytically pure α-silyloxyaldehydes.[11] Ketone substrates (e.g., acetophenone) yield silylenol ethers as the sole product. This result suggests that β-hydrogen elimination is much faster than migratory insertion of carbon monoxide.[12]

It can be seen from Table I that the reaction is quite general and works well for heterocyclic as well as aliphatic systems. The very mild reaction conditions permit discrimination of the starting aldehyde from the newly formed and more sterically demanding

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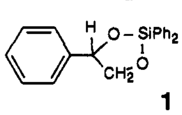
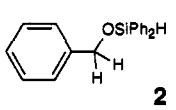
(10) Compound **1** was independently synthesized from phenylethanediol and Ph_2SiCl_2 and found to be identical by GC-MS to the silyloxymethylation product. The hydrosilylation product **2** was unambiguously identified by comparison of ^1H NMR data.



1

"Sila-oxymethylation" product



2

Hydrosilylation product

(11) Full experimental details and spectroscopic and analytical data for the α-silyloxyaldehydes are deposited in the supplemental material. $C_6H_5CH(OSiMe_2Ph)CHO$ (3a) (74%, bp 130–140 °C at 0.1 mmHg): ^1H NMR ($CDCl_3$) δ 9.52 (s, 1 H, C*H*O), 7.55–7.28 (m, 10 H, Ar H), 4.99 (s, 1 H, –C*H*CHO), 0.43, 0.37, 0.33 (ss, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 198.4 (CHO), 139.4 (Ar C), 136.3 (Ar C), 135.9 (Ar C), 133.3 (Ar CH), 132.8 (Ar CH), 132.7 (Ar CH), 130.0 (Ar CH), 129.7 (Ar CH), 129.0 (Ar CH), 128.5 (Ar CH), 128.3 (Ar CH), 128.2 (Ar CH), 128.1 (Ar CH), 128.0 (Ar CH), 127.8 (Ar CH), 127.5 (Ar CH), 126.5 (Ar CH), 126.2 (Ar CH), 79.9 (–*C*HCHO), 0.6, –1.4, –1.6, ($SiCH_3$); IR (CH_2Cl_2) $\nu_{C=O}$ 1736. Anal. Calcd for $C_{16}H_{18}O_2Si$: C, 71.06; H, 6.72. Found: C, 71.12; H, 6.94. It is noteworthy to mention that in each silaformylation reaction studied to date we observe at least two NMR signals for the prodiastereotopic silicon methyl groups. We also believe rotomers about the silicon–oxygen bond exist and have been indirectly supported by molecular mechanics analysis.

(12) Experimental data strongly suggests that the α-silyloxy moiety favors migratory insertion [see: Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766]; however, its influence on the β-hydride elimination pathway has not been established.

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