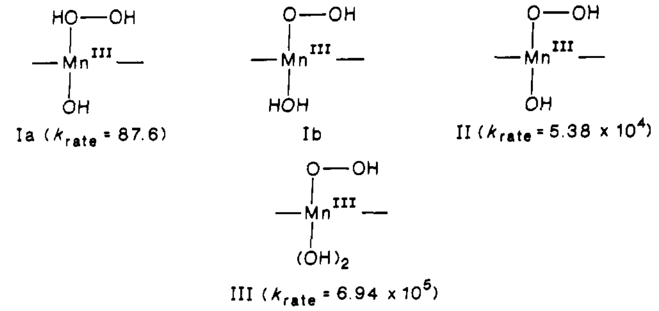
Chart III



Ia (k_{rate} = 87.6)

Ib

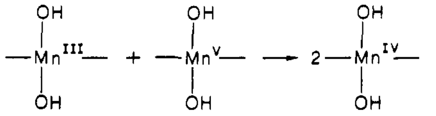
II (k_{rate} = 5.38 x 10^4)

III (k_{rate} = 6.94 x 10^5)

idizes ABTS in preference to H_2O_2. The manganese(III) of structure Ia should be of high spin, and HOO^- need only compete with water for ligation. At the intermediate pH of 10.2, HOO^- is oxidized only two times faster than is ABTS. At this pH, HOO^- need only compete with water for ligation; however, comparison of structures Ia and II suggests that the manganese moiety of the latter should be of lower spin. A decrease in spin state is proposed to result in the preferential oxidation of ABTS over HOO^-. At pH 12.0 there is formed no more than 10% O_2. The change in relative rates of formation of O_2 and ABTS$^{\bullet+}$ in going from pH 10.2 to 12.0 amounts to a $\Delta\Delta G^{\ddagger}$ of but 0.65 kcal·M^{-1}. Such small differences in free energies of activation are most difficult to explain in terms of mechanism. The increase in rate of ABTS$^{\bullet+}$ formation over O_2 on going from pH 10.2 to 12.0 with ImH as an axial ligand or at pH 10.2 by adding ImH as an axial ligand amounts, in both cases, to an even smaller change in $\Delta\Delta G^{\ddagger}$ (0.4 kcal·M^{-1}).

It should be noted that there is a distinct difference in the dependence of yield of O_2 and ABTS$^{\bullet+}$ upon pH for (**1**)Mn^{III}X compared with the (**1**)Fe^{III}X.[10] With the former, preference for ABTS oxidation is seen at high pH, whereas with the latter ABTS oxidation is favored over H_2O_2 oxidation at low pH. This shows that at higher pH higher valent manganese-oxo species prefer to undergo two one-electron reductions (thereby producing two ABTS$^{\bullet+}$ radical species), whereas the iron(IV)-oxo π-cation radical more easily undergoes a single two-electron reduction. In the presence of water the potentials for the iron(III)-oxo porphyrin/iron(IV)-oxo porphyrin and iron(IV)-oxo porphyrin/iron(IV)-oxo porphyrin π-cation radical are superimposable.[28]

Identification of Higher Valent Manganese-Oxo Porphyrin Species by Repetitive Spectral Scanning (350-700 nm) during the Course of the Reaction. In the absence of ABTS and ImH at pH 7.59 a buildup of a higher valent manganese-oxo porphyrin species is not observed, and the catalyst remains at the manganese(III) oxidation state throughout the reaction. Under the same conditions at pH 12.5 the manganese(III) porphyrin is quantitatively converted to a manganese(IV)-oxo species (λ_{max} 422 nm, ϵ 8.6 × 10^4 M^{-1} cm^{-1}). This observation supports the previous finding that high-valent Mn-oxo species (both Mn(IV) and Mn(V)) are stabilized by hydroxide ion ligation.[20,29] Thus, it has been shown by electrochemical methods that the exchange of H_2O for HO^- as axial ligand is accompanied by the conversion of manganese(III) porphyrin π-cation radical to manganese(IV) porphyrin.[30] The formation of manganese(IV)-oxo porphyrin above ~pH 11.5 may be explained by the trapping of manganese(V) by unreacted manganese(III) porphyrin (eq 23). The comproportionation reaction of eq 23 is eminently reasonable. Thus, manganese(V) porphyrin carries out a 1e oxidation of ABTS.



$$-\underset{OH}{\overset{OH}{Mn^{III}}}- \;+\; -\underset{OH}{\overset{OH}{Mn^{V}}}- \;\longrightarrow\; 2\,-\underset{OH}{\overset{OH}{Mn^{IV}}}- \qquad (23)$$

Acknowledgment. This work was supported by the National Institutes of Health and National Science Foundation.

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(28) (a) Lee, W. A.; Calderwood, T. S.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4301. (b) Calderwood, T. S.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8272. (c) Calderwood, T. S.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 3722.

(29) Calvin, M. *Rev. Pure Appl. Chem.* **1965**, *15*, 1.

(30) Spreer, L. O.; Maliyackel, A. C.; Holbrook, S.; Otvos, J. W. Calvin, M. *J. Am. Chem. Soc.* **1986**, *108*, 1949.

Communications to the Editor

The First α-Silicon-Substituted Simple Enol. The Stabilizing Effect of the Silyl Substituent

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There is considerable current interest in both organosilicon chemistry[1] and in simple enols.[2] A combination of our interests[3,4] in these fields led to isolation of the first stable simple α-silyl enol, which shows a remarkable stability relative to the corresponding keto isomer in comparison with the corresponding α-alkyl analogues.

In Jerusalem we had recently studied a group of highly congested enols of the general type **1** (Mes = mesityl) which exhibit an unusually high kinetic and thermodynamic stability.[3] The keto $\rightleftharpoons$ enol equilibrium constants (K_{Enol} = [**1**]/[**2**]) in hexane depend on the α-substituent. For aliphatic R's K_{Enol} decreases with the increased bulk of R from 20 for R = H to 0.64 for R = Me (**1a**) to 0.06 for R = *t*-Bu (**1b**).[3b] For R = meta- and para-substituted α-aryl groups K_{Enol} decreases with electron donation (0.3 for *p*-anisyl) and increases with electron withdrawal (3.6 for R = 3,5-$Br_2C_6H_3$).[3c] For bulky α-aryl groups K_{Enol} is higher (79 for R = Mes).[3a]

Can a "simple" substituent (e.g., not strongly electron withdrawing) be found which will increase K_{Enol} above the values for R = alkyl and ortho-substituted aryl groups? Our studies in Haifa of organosilicon compounds provided an answer. Silicon is less electronegative than carbon,[5] and as expected from the above data,

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(1) (a) Chvalosky, V.; Bellama, J. M. *Carbon-Functional Organosilicon Compounds*; Plenum Press: New York, 1984. (b) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 541.

(2) (a) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1. (b) For a recent reference, see: Chiang, Y.; Hojatti, M.; Keefe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000.

(3) (a) Biali, S. E.; Rappoport Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007. (b) Nugiel, D. A.; Rappoport, Z. *Ibid.* **1985**, *107*, 3369. (c) Nadler, E. B.; Rappoport, Z. *Ibid.* **1987**, *109*, 2112.

(4) (a) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. (b) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462; **1983**, *48*, 5413. (c) Stanger, A. Ph.D. Thesis, Technion, Haifa, Israel, 1985.

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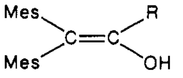
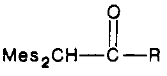
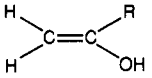
replacing the methyl of **1a** by SiH_3 might decrease K_{Enol}. However, we found theoretically in the gas phase and experimentally in solution that α-silyl substitution destabilizes carbenium ions relative to methyl.[4a] Due to the resonance hybrid $R_2C^+–O^-$ a carbenium ion can be regarded as a model for a carbonyl group. Hence, in analogy to α-silylcarbenium ions,[4a] α-silyl ketones (e.g., **2c**) should be destabilized relatively to analogous alkyl ketones. As the effect of replacing a methyl by a silyl in the enols is relatively small,[4b,c] we hypothesized that K_{Enol} will be significantly larger for α-silyl ketones than for the corresponding α-alkyl ketones.



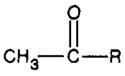
1a, R = CH_3
b, R = *t*-Bu
c, R = $SiMe_3$
d, R = SiH_3



2a, R = CH_3
b, R = *t*-Bu
c, R = $SiMe_3$
d, R = SiH_3



3a, R = CH_3
b, R = SiH_3



4a, R = CH_3
b, R = SiH_3

First we tested these assumptions by carrying out ab initio MO calculations[6] for the model compounds **3** and **4**.[7] Their geometries were fully optimized by using analytical gradient techniques[6] and the polarized 6-31G* basis set[8a] and single point MP2/6-31G*//6-31G* (i.e., including a perturbational treatment of correlation energy)[8b] followed. At 6-31G* and MP2/6-31G* we calculated that acetone **4a** is more stable than enol **3a** by 18.8 and 18.1 kcal mol^{-1}, respectively.[9] This estimate is 4.7 kcal mol^{-1} (including ZPE)[9] higher than the reported gas-phase experimental value of 14.0 kcal mol^{-1}.[10] For the analogous silylated **3b–4b**, the calculated difference is reduced by 6.4 and 6.0 kcal mol^{-1} to 12.4 and 12.1 kcal mol^{-1} at 6-31G* and MP2/6-31G*, respectively. The energy change of 6.0 kcal mol^{-1} amounts to ca. 25 000-fold increase in K_{Enol} at 25 °C.

We have calculated the energies of the isodesmic eq 1 and 2,

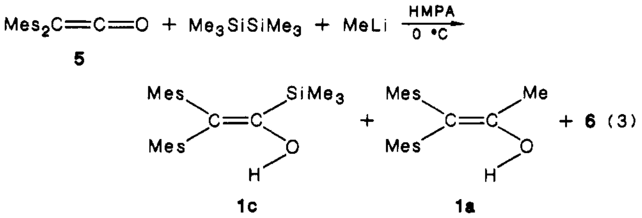
$$CH_3COCH_3 + H_3SiCH_3 \rightarrow H_3SiCOCH_3 + CH_3CH_3 \qquad (1)$$

$$H_2C{=}C(OH)CH_3 + H_2C{=}CHSiH_3 \rightarrow H_2C{=}C(OH)SiH_3 + H_2C{=}CHCH_3 \qquad (2)$$

which denote the effect of replacing α-methyl by α-silyl on the stability of the keto and enol forms, respectively. Positive energies indicate a higher stability of the alkyl compared with the silyl derivative (relative to the corresponding alkanes and silanes). In agreement with the above qualitative arguments we find that the change $CH_3 \rightarrow SiH_3$ destabilizes the carbonyl group by 12.0 kcal mol^{-1} (eq 1, MP2/6-31G*) and the enol by only 2.3 kcal mol^{-1} (eq 2, MP2/6-31G*).[11] Thus, the larger silyl destabilizing effect in the ketone than in the enol reduces the keto–enol energy difference.

From the linear log K_{Enol} (**3**/**4**) vs log K_{Enol} (**1**/**2**) relationship (slope 1.33)[12] it is reasonable that the substituent effect calculated for **3b–4b** also operates in the sterically congested **1** and **2**. Hence, the calculations predict that K_{Enol} for the α-silyl pair **1d–2d** would be >100-fold higher than for **1a**. For synthetic convenience the synthesis of the $SiMe_3$ derivatives **1c** and **2c** was attempted.

Addition of MeLi to hexamethyl disilane in hexamethylphosphoramide (HMPA) at ca. 0 °C under argon, followed by addition of dimesitylketene (**5**)[13] and workup with 5% HCl gave several products whose ratios depended on the temperature and the time lapse before addition of **5**. Chromatography gave the desired **1c** (mp 123 °C,[14] highest yield 49%), enol **1a**, and **6** (resulting from reaction of **5** with HMPA)[15] (eq 3). The sharp absorption of **1c** at 3480 cm^{-1} is indicative of a OH–π(cis-Mes) hydrogen bonding and hence a syn conformation around the C–O bond.[16] A syn conformation was also calculated for **3b** although hydrogen bonding and severe steric effects are absent. The ^1H NMR of **1c** (δ −0.07 ($SiMe_3$), 4.80 (sharp OH), 2.13, 2.16, 2.22, 2.25 (br Me s), 6.75, 6.85 (Mes–H) in $CDCl_3$) indicates the occurrence of rotational processes around the C–Mes bonds.[17] The much lower field ^{13}C C_β signal of **1c** than in **1b** parallels the calculated C_β charges of **3a** and **3b**. The base peak is at *m/z* 73 (Si^+Me_3).



Enol **1c** is stable as a solid at room temperature but in CH_2Cl_2 or acetone solution it slowly decomposes.[18] When heated in hexane/0.2% CF_3COOH (TFA) for 21 h at 94.5 °C or in hexane/1% TFA for 6 days at 67 °C **1c** remained unchanged, whereas the alkyl analogues **1a** and **1b** isomerize almost completely to the **1a–2a** and **1b–2b** equilibrium mixtures within 1 h. Heating of **1c** in hexane/0.2% TFA at 94.5 °C for 40–90 h or in $(MeOCH_2CH_2)_2O$ saturated with HCl at 120 °C for 48 h resulted in decomposition, detected by appearance of additional NMR signals and new TLC spots (but not one corresponding to the expected position of **2c**).[19] In hexane/0.2% Et_3N **1a** and **1b**, but not **1c**, isomerize appreciably after 15 h at 94.5 °C.

In hexane, the keto–enol equilibration of several α-alkyl-substituted enols, e.g., **1a** and **1b**, is complete in ≤14 h at 80.6 °C. Since **2c** was not observed under more drastic conditions, we assume that it is formed in <5%, and hence K_{Enol} for **1c** is >20, i.e., higher than for either **1a** or **1b**. The experiments with **1c** therefore corroborate the calculations on models **3b** and **4b**. A better estimate of K_{Enol} might be obtained if the keto–enol equilibrium could be achieved starting from **2c**. Unfortunately, our attempts to prepare **2c** have failed.[20] Further studies on **1c**

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(5) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

(6) An IBM version of the GAUSSIAN 82 series of programs was used: Binkely, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A. Carnegie-Mellon University, 1982.

(7) For previous theoretical studies on substituent effects on keto ⇌ enol equilibria, see: Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593 and ref 3 and 4 therein.

(8) (a) First row: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Second row: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (b) Frisch, M. J.; Krishnan, R.; Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66 and references therein.

(9) Addition of zero-point energies (ZPE) increases the keto ⇌ enol difference by 0.6 kcal mol^{-1} for **3a–4a** and by 0.4 kcal mol^{-1} for **3b–4b**.

(10) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648. For an earlier estimated value of 13.9 ± 2, see: Pollack, S. K.; Hehre, W. J. *Ibid.* **1977**, *99*, 4845. In water at 25 °C the corresponding $\Delta G°$ as calculated from pK_{Enol} is 11.1 kcal mol^{-1} (Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460).

(11) The large absolute destabilization energy of eq 1 includes also the energy of methyl and silyl transfer between sp^2 and sp^3 centers. Thus, silyl destabilization is larger also for the enol (6.0 kcal mol^{-1} at MP2/6-31G*) if one uses eq 1a, which is analogous to eq 1. Substraction of eq 1a and eq 1 gives 6.0 kcal mol^{-1} (at MP2/6-31G*) as the keto–enol energy difference between the alkyl and silyl systems.

$$H_2C{=}C(OH)CH_3 + H_3SiCH_3 \rightarrow H_2C{=}C(OH)SiH_3 + CH_3CH_3 \qquad (1a)$$

(12) Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 4730.

(13) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

(14) Microanalysis, NMR, and MS cleavage are consistent with structure **1c**. Crystals for X-ray diffraction could not be obtained.

(15) The structure of **6** which does not contain silicon is under investigation.

(16) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

(17) The mechanism of the analogous rotational processes in **1a** and **1b** was reported: Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 3357.

(18) This may be due to air oxidation of the double bond as suggested for MesC(Me)=C(OH)Mes: Fuson, R. C.; Byers, D. J.; Rabjohn, N. *J. Am. Chem. Soc.* **1941**, *63*, 2639. We observed similar decomposition for other β,β-dimesityl-α-alkyl (or aryl) ethenols.

(19) Based on analogy with R_f values of other **1**/**2** pairs. One fraction from chromatography of the mixture obtained when **1c** in hexane was kept for 90 h at 94.5 °C showed ν_{max} at 1730 cm^{-1}, a base peak at *m/z* 73 (Si^+Me_3), and a small peak at *m/z* 352, but no NMR signal in the expected region for the CH of **2c**.

and related α-silicon-substituted enols are now in progress.

Acknowledgment. This work was supported in Jerusalem and in Haifa by grants from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel and in Haifa by the Israel Commission for Basic Research, The Israel Academy for Sciences and Humanities, to which we are indebted.

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(20) E.g., $Mes_2CHCOCl$ + $LiSiMe_3$ in HMPA gave mostly **1c** and **6**. Mes_2CHCHO + $LiSiMe_3$ gave mainly isomerization to $Mes_2C{=}CHOH$ and not the alcohol which may be a precursor to **2c**. Other methods are under study.

Isolation, and Partial Characterization by XPS, of Two Distinct Catalysts in the Ziegler-Natta Polymerization of Ethylene

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Although Ziegler-Natta polymerization has been known for over 25 years and is widely used for the production of high-density polyethylene and isotactic polypropylene, the reactive catalytic intermediate(s) involved have not been characterized.[2-4] As part of our continuing studies of the use of X-ray photoelectron spectroscopy (XPS) in the characterization of the electronic properties of transition-metal complexes,[5] we have studied the homogeneous zirconocene-based[6] Ziegler-Natta polymerization of ethylene. We now report the first isolation and direct characterization of highly active Ziegler-Natta polymerization catalysts. This was accomplished through the use of our technique for the isolation and purification of reactive organometallic intermediates bearing macromolecular ligands.[8]

As shown in Table I, treatment of dichlorozirconocene (**1**), methylchlorozirconocene (**2**), or dimethylzirconocene (**3**) with methylaluminoxanes in toluene gave solutions of catalyst in which **1**, **2**, and **3** were all converted into new zirconium derivatives, which had the same zirconium(IV) binding energy.[9] This increase in binding energy relative to **1**, **2**, and **3** indicates that this catalyst is electron deficient (oxidized) in comparison to the three zirconocenes used as starting materials. This catalyst was very long-lived since, in the absence of oxygen and moisture, no change in the binding energy of this species could be detected after 10 days.[10] Exposure of this catalyst solution to an atmosphere of ethylene led to the immediate formation of polyethylene. After the initially formed catalyst had reacted with ethylene, no trace of material with a binding energy of 182.4 eV could be detected. Instead a new zirconium species with a binding energy of 182.1 eV was observed. This new material was also a catalyst for the polymerization of ethylene.

Table I. Binding Energies of Two Distinct Catalytic Species Obtained from **1**, **2**, and **3** Methylaluminoxanes and Ethylene in Toluene

	$Zr(3d_{5/2})$ binding energies (±0.1 eV)		
compd	zirconocene (eV)	catalyst before ethylene addn (eV)	catalyst after ethylene addn (eV)
1	181.7	182.4	182.1
2	181.2	182.4	182.1
3	180.7	182.4	182.1

Table II. XPS Binding Energies of Substituted Zirconocenes

compd	compd no.	$Zr(3d_{5/2})$ binding energy[a] (±0.1 eV)	Δ eV relative to **1**
Cp_2ZrCl_2	**1**	181.7	0.0
$Cp_2Zr(Cl)(CH_3)$	**2**	181.2	-0.5
$Cp_2Zr(Cl)[CH_2CH_2C(CH_3)_3]$	**4**	181.3	-0.4
$Cp_2Zr(Cl)[CH{=}CHC(CH_3)_3]$	**5**	181.3	-0.4
$Cp_2Zr(CH_3)_2$	**3**	180.7	-1.0
$Cp_2Zr(Cl)[OCH(CH_3)_2]$	**6**	181.6	-0.1
$Cp_2Zr[OCH(CH_3)_2]_2$	**7**	181.5	-0.2
$[Cp_2ZrCl]O$	**8**	181.5	-0.2
$Cp_2Zr(Cl)(H)$	**9**	181.3	-0.4
Cp_2ZrH_2	**10**	180.0	-1.7

[a] Measured in eV.

In order to evaluate the significance of the binding energy values of 182.4 and 182.1 eV obtained for the two catalytic materials, it is necessary to understand the effect of a wide variety of substituents on the $Zr(3d_{5/2})$ binding energy of zirconocenes. Table II provides data which illustrate that replacement of the chloride of **1** by alkyl, alkoxyl, or hydride results in greater electron donation to the zirconium and, as a result, in a net reduction in binding energy relative to **1**. Since both active catalysts have binding energies which show that the zirconium is electron deficient relative to **1**, any simple exchange of one or more of these three ligands for the chlorides of **1** could not provide an intermediate which would be an active catalyst.

In order to ascertain whether one or more of the cyclopentadienide ligands might have been lost or replaced, the initial catalyst was also formed from either (η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)zirconium(IV) dichloride (**11**) or bis(η^5-pentamethylcyclopentadienyl)zirconium(IV) dichloride (**12**) and methylaluminoxanes. Both **11** and **12** gave catalysts which readily polymerized ethylene. In forming the active catalyst from **11** [$Zr(3d_{5/2})$ binding energy = 181.4 eV], a change in binding energy to 181.9 eV before exposure to ethylene occurred (Δ eV = 0.5). In forming the active catalyst from **12** [$Zr(3d_{5/2})$ binding energy = 181.0 eV], a change in binding energy to 181.7 eV before ethylene addition occurred (Δ eV = 0.7). These numbers can be compared to a change of 0.7 eV observed for the formation of active catalyst from **1**. These data provide convincing evidence that the cyclopentadienyl derived ligands are not lost in the formation of active catalyst.[11]

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(1) Division of Organic Chemistry of the American Chemical Society Fellow sponsored by the Rohm & Haas Company, 1986-1987. General Electric Co. Fellow, 1985-1986.

(2) For detailed reviews of Ziegler-Natta polymerization, see: (a) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (b) Quirk, R. P. *Transition Metal Catalyzed Polymerization, Alkenes and Dienes*; Harwood Academic Publishers: New York, 1983.

(3) For selected references, see: (a) Cossee, P. *Tetrahedron Lett.* **1960**, 12. Cossee, P. *J. Catal.* **1964**, *3*, 80. Arlman, E. J.; Cossee, P. *Ibid.* **1964**, *3*, 99. (b) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857. (c) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(4) Fink, G.; Rottler, R.; Schnell, D.; Zoller, W. *J. Appl. Polym. Sci.* **1976**, *20*, 2779.

(5) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470. Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Ibid.* **1984**, *3*, 385. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

(6) We chose to study a system recently developed by Kaminsky and co-workers[3c] which is based on variously substituted zirconocene halide and alkyl complexes as the catalyst and methylaluminoxanes as the cocatalyst. This catalytic system was chosen because it exhibits prolonged stability in solution, high activity for polymerization of ethylene and α-olefins, and extremely high overall yields of active catalytic centers.[7]

(7) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

(8) Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380.

(9) The fact that **1**, **2**, and **3** were all converted into a material with the same binding energy, while providing very strong evidence for the formation of the same catalyst from all three precursors, does not *prove* the existence of a single species. The identity of the binding energies establishes that in all three examples the zirconium resides in the same electronic environment.

(10) After this same time period, no change was noted in the activity of the catalyst on the addition of ethylene. In addition, formation of this first catalyst followed by addition of ethylene for 1.0 h after the initially formed catalyst had stood for 0.0, 0.5, and 1.0 h gave similar yields of polyethylene (41, 40, and 43 kg per h per g of starting zirconium).

(11) This suggestion is consistent with the results obtained through the use of chiral catalysts: Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. See, also: ref 7.

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