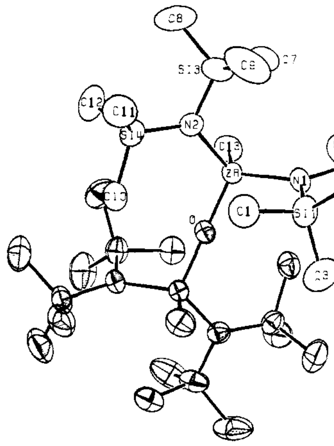
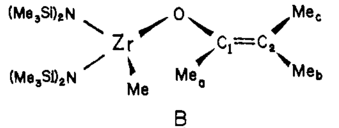


Figure 1. An ORTEP drawing of $\{[(Me_2Si)_2N]_2ZrMe\}_2O$.

metry requiring a Zr–O–Zr bond angle of 180°. The O–Zr–C bond angle of 99.74 (8)° and the Zr–O bond distance of 1.950 (1) Å, are similar to those found in $(Cp_2HfMe)_2O$,[10a] $(Cp_2ZrCl)_2O$,[10b] and $(Cp_2ZrMe)_2O$.[10c] The Zr–C bond length of 2.225 (3) Å and the averaged Zr–N bond length of 2.081 ± 0.001 Å are similar to those found in related compounds.[10d]

The other product, B, was shown to be an enolate complex,[11]



B

since the spectroscopic properties are similar to those described for enolates of lithium, magnesium, zirconium, and tantalum.[4,12] Hydrolysis of B with H_2O or D_2O gives $Me_2CHCOMe$ or $Me_2CDCOMe$, respectively, identified by ^1H MNR spectroscopy. Further, when a sample of $[(Me_3Si)_2N]_2ZrMe_2$ is treated with carbon monoxide (1 atm, PhH-d_6) in an NMR tube, only resonances due A and B are observed by ^1H NMR spectroscopy. Thus, the stoichiometry for the quantitative reaction of $[(Me_3Si)_2N]_2ZrMe_2$ with carbon monoxide is shown in eq 1.

$$3[(Me_3Si)_2N]_2ZrMe_2 + 2CO \rightarrow A + B \qquad (1)$$

Reaction of $[(Me_3Si)_2N]_2ZrMe_2$ with $C^{18}O$ (99.5% ^{18}O) gives A-^{18}O, as shown by mass spectroscopy since the parent ion and fragment ions appear two mass units higher than those found in A-^{16}O.[13] In addition, reaction of $[(Me_3Si)_2N]_2ZrMe_2$ with ^{13}CO (99% ^{13}C) gives B where C(1) and C(2) are derived from the labeled carbon monoxide as shown by ^{13}C NMR spectroscopy.[14]

The reaction of carbon monoxide with $[(Me_3Si)_2N]_2ZrMe_2$, under very mild conditions, causes rupture of the carbon–oxygen triple bond giving an oxodialkyl and an enolate. Thus, this reaction may be viewed as a homogeneous model system for the initial event in Fischer–Tropsch chemistry even though zirconium metal is a poor Fischer–Tropsch catalyst.[15] Surprisingly, the hafnium dimethyl $[(Me_3Si)_2N]_2HfMe_2$ is recovered unchanged from reaction of CO (75 atm, 20 °C, pentane). The reaction of related zirconium alkyls, which give rather different products, as well as mechanistic speculation will be described in future.

Acknowledgment. This work was supported by a grant from the Gas Research Institute. We thank Dr. F. J. Hollander of the UCB X-ray facility (CHEXRAY), which was established by a departmental equipment grant from the N.S.F., for his help with the crystal structure.

Registry No. CO, 630-08-0; $[(Me_3Si)_2N]_2ZrMe_2$, 70969-30-1; $\{[(Me_3Si)_2N]_2ZrMe\}_2O$, 87738-97-4; $[(Me_3Si)_2N]_2Zr[OC(Me)CMe_2][Me]$, 87738-98-5.

Supplementary Material Available: A complete listing of bond lengths, bond angles, positional and thermal parameters, and observed and calculated structure factors for A and the mass spectra of A-^{16}O and A-^{18}O (20 pages). Ordering information is given on any current masthead page.

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(9) The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions $a = 9.1731$ (7) Å, $b = 11.9426$ (11) Å, $c = 21.9768$ (18) Å, $\beta = 96.972$ (7)°, $V = 2389.86$ Å^3, with $Z = 2$ and d(calcd) = 1.21 g cm^{-3}. The data were collected on a Nonius CAD-4 automated diffractometer with Mo Kα X-rays ($\lambda = 0.71073$ Å). The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R- factor of 0.025 ($R_w = 0.034$ and GOF = 1.58) by using 2440 data, where $F^2 > 3\sigma(F^2)$, against 187 variables. The R value for all 3114 unique reflections was 0.047.

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(11) Anal. Calcd for $C_{18}H_{48}N_2OSi_4Zr$: C, 42.3; H, 9.39, N, 5.48. Found: C, 41.8; H, 8.99; N, 5.48. MS $(M-15)^+$, 496; mp 57–61 °C; IR (Nujol) νC=C, 1668 cm^{-1}; NMR (PhH-d_6, 25 °C) ^1H δ 1.97 and 1.90 (s, 3 H each, diastereotopic $\mathit{Me}_2C{=}CMe$); 1.58 (s, 3 H, $Me_2C{=}C\mathit{Me}$); 0.80 (s, 3 H, ZrMe); and 0.39 (s, 36H, Me_3Si); ^{13}C δ 149 (s, $Me_2C{=}\mathit{CMe}$); 107 (s, $Me_2\mathit{C}{=}CMe$); 44.6 (q, $^1J_{CH} = 118$ Hz, ZrMe); 19.8, 19.3, 19.0 (q, $^1J_{CH} =$ 118 Hz, due to the three methyl groups of the enolate) and 4.7 (q, $^1J_{CH} = 118$ Hz, Me_3Si).

(12) (a) Jackman, L. M.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 3687–3692. (b) Jackman, L. M.; Szeverenyi, N. M. *Ibid.* **1977**, *99*, 4954–4962. (c) House, H. O.; Prabhu, A. V.; Phillips, W. V. *J. Org. Chem.* **1976**, *41*, 1209–1214. (d) Fellmann, R.; DuBois, J. E. *Tetrahedron Lett.* 247–250. (e) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370. (f) Stille, J. R.; Grubbs, R. H. *Ibid.* **1983**, *105*, 1664–1665.

(13) The mass spectra of A-^{16}O and A-^{18}O are shown in the supplementary material.

(14) $\delta(C(1)) = 149$; $\delta(C(2)) = 107$; $^1J_{C(1)C(2)} = 88$ Hz; $^1J_{C(1)C(a)} \simeq {}^1J_{C(2)C(b)} \simeq {}^2J_{C(2)C(c)} = 18$ Hz; $^2J_{C(2)H(b)} = 5.8$ Hz; $^2J_{C(1)H(a)} = 5.4$ Hz. $^2J_{C(2)H(c)}$ was not resolved.

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Photoisomerization of Trimesitylvinyl Alcohol. Indirect Evidence for the Keto Form

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Received July 28, 1983
Revised Manuscript Received October 24, 1983

Trimesitylvinyl alcohol (**1e**) has long been known as a stable, crystalline enol.[1-4] All attempts either to synthesize the corresponding keto form (**1k**) directly or to isomerize **1e** to **1k** by acid or base catalysis have thus far been unsuccessful. We describe here the first evidence for the existence for the keto form of this highly hindered molecule.

$(Mes)_2C{=}C(OH)R$	$(Mes)_2CH{-}C({=}O)R$
1e, R = Mes[7]	**1k**, R = Mes
2e, R = Ph	**2k**, R = Ph

We irradiated **1e** with the hope that the photochemically allowed 1,3-hydrogen migration would give **1k** or a photoproduct derived therefrom.[5] We also irradiated the closely related enol **2e**, where the corresponding keto form **2k** is known and could be

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(1) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *J. Am. Chem. Soc.* **1946**, *68*, 389.

(2) For recent reviews of "simple enols", see: Hart, H. *Chem. Rev.* **1979**, *79*, 515. Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685.

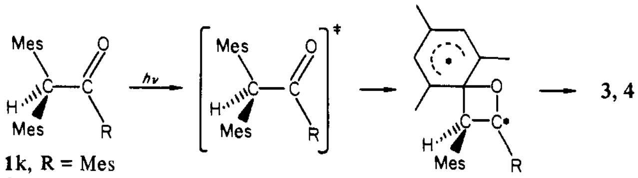
(3) Recent studies on the preparation or detection of simple enols include the following: Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761. Chiang, Y.; Kresge, A. J.; Walsh, P. A. *Ibid.* **1982**, *104*, 6122.

(4) For interesting conformational studies on **1e** and related enols, see: Biali, S. E.; Lifschitz, C.; Rappoport, Z.; Karni, M.; Mandelbaum, A. *J. Am. Chem. Soc.* **1981**, *103*, 2896. Biali, S. E.; Rappoport, Z. *Ibid.* **1981**, *103*, 7350.

(5) Whereas the reverse reaction, i.e., photoenolization, is well-known (for a review, see: Sammes, P. G. *Tetrahedron* **1976**, *32*, 405), photoketonization is either rare or unknown.

0002-7863/83/1505-7775$01.50/0

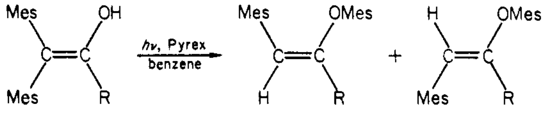
Scheme I



1k, R = Mes
2k, R = Ph

irradiated separately. Enols **1e** and **2e** and ketone **2k** were prepared by the methods of Fuson.[1,6]

Irradiation[8] of benzene solutions of **1e** and **2e** through Pyrex gave, in a very slow reaction but in good chemical yield, the aryl vinyl ethers **3** and **4**, respectively.[9] The structures of **3** and **4** were



1e, R = Mes 3z (96) 3e (4)
2e, R = Ph 4z (80) 4e (20)

secured by their spectra[10] and by other means. For example, treatment of **3z** with sodium amide in liquid ammonia at −78 °C followed by warming to room temperature eliminated mesitol to give the known dimesitylacetylene.[11] An X-ray structure[12] on the major photolysis product of **1e** showed that it was the *Z* isomer **3z**. The vinyl proton appears at lower field in **3z** (δ 5.74) than in **3e** (δ 5.48). Assuming that this relationship would also apply to the isomers of **4**, we assign structure **4z** to the major photoproduct (vinyl proton at δ 5.94) and structure **4e** to the minor product (vinyl proton at δ 5.22) of **2e**. Other features of the spectra are consistent with this conclusion.

Enols ethers **3** and **4** presumably arise from a 1,3-aryl migration involving the ketones **1k** and **2k** (Scheme I). Although rare in ketone photochemistry, precedent for such an aryl migration exists. For example, irradiation of phenyl trityl ketone **5** gave the enol ether **6**:[13]

$$\underset{\mathbf{5}}{Ph_3CC(=O)Ph} \xrightarrow[\text{benzene, 40 h}]{h\nu,\ \text{Pyrex}} \underset{\mathbf{6}\ (65\%)}{Ph_2C=C(OPh)Ph}$$

Consistent with our postulate that the keto forms are intermediates in the photoisomerization of **1e** and **2e**, we observed that separate irradiation of **2k** under similar conditions gave **4z** and **4e** in the same ratio as obtained from **2e**.

The formation of **4** from **2k** is unusual in view of the observation that phenyl benzyhydryl ketone, in contrast to **5**, gives only α-cleavage products.[14] We attribute the aryl migration observed with **5** and **2k** (and presumably **1k**) to ground-state conformations of the hindered aryl groups which favor *ipso* attack by the excited carbonyl oxygen and disfavor the coplanarity needed to stabilize the radical that would be formed by α-cleavage.

It seems likely that ketones (**1k**, **2k**) are the intermediates in photoinduced isomerization of enols (**1e**, **2e**) to enol ethers (**3**,**4**). It is not yet clear, however, whether the reactions are due to undetected traces of ketone present in equilibrium with the enols[15] or whether the ketones are formed via a photoinduced 1,3-hydrogen migration.[16] Further studies to elucidate these details are in progress.

Acknowledgment. We are indebted to the National Science Foundation (CHE 80-17746), the National Institutes of Health (GM 15997), and to the United States–Israel Binational Science Foundation (2696/82) for financial support. We are also indebted to Professor Zvi Rappoport and Silvio Biali for discussions and to Dr. D. L. Ward for the X-ray structure of **3z**.

Registry No. **1e**, 26905-20-4; **1k**, 87902-64-5; **2e**, 77787-80-5; **2k**, 77787-78-1; **3e**, 87902-65-6; **3z**, 87902-66-7; **4e**, 87902-67-8; **4z**, 87902-68-9.

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(7) Mes = mesityl = 2,4,6-trimethylphenyl.

(8) Irradiations were run on a 2.5-mmol scale, using 0.5% degassed (Ar) solutions, a 450-W Hanovia mercury vapor lamp, and Pyrex filter. The longest wavelength absorptions for these enols: **1e**, 282 nm (ϵ 2050); **2e**, 312 nm (ϵ 1550). Products were isolated by flash chromatography on silica gel, using 5% CH_2Cl_2 in hexane as eluent. Irradiation times and isolated yields: **1e**, 125 h, 70% of **3**; **2e**, 30 h, 87% of **4**. The *z*/*e* ratios are shown in the equation.

(9) Separate irradiation of pure **3z** for 72 h under similar conditions gave no detectable **3e** (NMR). However, irradiation of **4z** for 72 h gave what seemed to be the photostationary state, with a ratio **4z**/**4e** of approximately 2.

(10) **3z**: mp 118–120 °C; ^1H (250 MHz, $CDCl_3$) δ 1.68 (s, 6 H), 2.11 (s, 3 H), 2.24 (s, 6 H), 2.26 (s, 3 H), 2.32 (s, 3 H), 2.44 (s, 6 H), 5.74 (s, 1 H), 6.55 (s, 2 H), 6.77 (s, 2 H), 6.88 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.4, 20.5, 20.7, 21.0, 21.4 (one methyl signal in the 20.5–21.4 region is overlapped), 113.5, 127.9, 128.2, 129.0, 131.4, 132.0, 133.4, 134.2, 136.0, 137.1, 137.8, 138.4, 149.7, 149.9; IR (CCl_4) 3090–2880 (vs), 1480–1430 (s), 1200 (s), 1040–1010 (s), 910 cm^{-1} (s); UV (CH_2Cl_2) 244 nm (ϵ 2900); mass spectrum (70 eV), *m*/*e* (relative intensity) 398 (M^+, 9), 264 (13), 263 (M^+ − OMes, 100), 262 (M^+ − MesOH, 44), 248 (6), 233 (8), 143 (13), 119 (23), 117 (6), 91 (10); mass spectrum (high resolution) calcd 398.26097, found 398.26286. **3e**: ^1H NMR (250 MHz, $CDCl_3$) δ 1.55 (s, 3 H), 1.85 (s, 6 H), 2.16 (s, 3 H), 2.24 (s, 6 H), 2.30 (s, 3 H), 2.34 (s, 6 H), 5.48 (s, 1 H), 6.65 (s, 2 H), 6.80 (s, 2 H), 6.92 (s, 2 H); mass spectrum (70 eV), *m*/*e* (relative intensity) 398 (M^+, 12), 264 (18), 263 (100), 248 (13), 143 (34), 91 (25). **4z**: mp 106–108 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 2.07 (s, 3 H), 2.17 (s, 6 H), 2.27 (s, 3 H), 2.43 (s, 6 H), 5.94 (s, 1 H), 6.55 (s, 2 H), 6.88 (s, 2 H), 7.19–7.26 (m, 3 H), 7.37–7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 20.5, 20.6, 20.8, 109.2, 127.3, 127.9, 128.0, 128.1, 128.3, 128.8, 129.4, 129.5, 131.0, 131.4, 132.4, 134.2, 153.4; IR (KBr) 3020–2840 (m), 1480 (s), 1215 (vs), 1150 (s), 1020 (s); mass spectrum (70 eV), *m*/*e* (relative intensity) 356 (M^+, 76), 221 (76), 220 (M^+ − MesOH, 100), 206 (32), 205 (26), 191 (29), 143 (43), 91 (69); mass spectrum (high resolution) calcd 356.21402, found 356.21209. **4e**: This enol ether could not be obtained free of **4z** (TLC, HPLC); ^1H NMR (250 MHz, $CDCl_3$, from mixture with **4z**) δ 2.00 (s, 6 H), 2.21 (s, 3 H), 2.29 (s, 3 H), 2.32 (s, 6 H), 5.22 (s, 1 H), 6.73 (s, 2 H), 6.92 (s, 2 H), 7.19–7.26 (m, 3 H), 7.37–7.45 (m, 2 H).

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(12) Details will be published elsewhere.

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(15) We could not observe any **1k** or **2k** in the solutions of **1e** and **2e** which were being irradiated (NMR, IR, UV).

(16) Irradiation of **2e**-OD gave **4** with >90% retention of D at the vinyl carbon. While this result proves that the vinyl proton originated from the hydroxyl group, it does not distinguish between the two paths to the ketone.

1,1,2,2-Tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane

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Received July 27, 1983

Disilenes are extraordinarily reactive, but have been isolated recently in the form of the tetramesityl and tetrakis(2,6-dimethylphenyl) derivatives.[1,2] Of many reactions one can conceive with this silicon–silicon double bond,[1-3] the addition of a carbene or carbene equivalent attracts special interest, as it leads in a formal sense to the construction of the disilacyclopropane system. Our knowledge of this system is quite limited[4] despite the fact

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(2) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

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