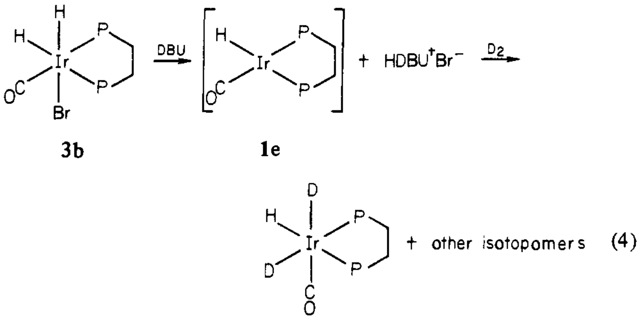
3.[3a] An alternative route to generating **1e**, which in the presence of D_2 makes possible stereochemical analysis of dihydrogen oxidative addition, involves dehydrohalogenation of compound **3b** using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The reaction sequence is shown in eq 4 and leads to stereoselective



3b **1e**

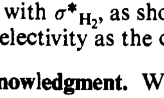
2e-d_2

(4)

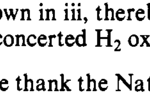
formation of **2e-d$_2$** with one D trans to CO.[11] A slower and subsequent scrambling reaction randomizes the deuterium label among the three hydride positions of **2e** while the total deuterium content (2D/Ir) remains constant. No evidence for the formation of the *mer* isomer **3e** is obtained at any point in the reaction sequence.

In every case we have studied, oxidative addition of H_2 to IrX(CO)(dppe) (X = Cl, Br, I, CN, H) proceeds stereoselectively, giving isomer **2** exclusively. In addition, it has been reported that the carborane complex IrX(CO)(dppe) where X = 7-C_6H_5-1,7-$B_{10}C_2H_{10}$ adds H_2 in the same way giving isomer **2**.[12] Since CO and X are both trans to a phosphine donor of dppe in IrX(CO)(dppe), the orientation of H_2 addition that leads to the observed stereoselectivity must be determined by differences between the CO and X ligands. Steric effects alone cannot account for the observed stereoselectivity since two of the ligands (X = H, CN) are sterically similar to or smaller than CO.[13] Product stability (i.e., thermodynamic control) can also be discounted as the controlling factor since only isomer **2** is formed by H_2 oxidative addition, even when isomer **3** is more stable (X = Cl, Br, I). The orientation of H_2 approach thus appears to be determined by subtle electronic effects exerted early in the course of the exothermic H_2 oxidative addition reaction.

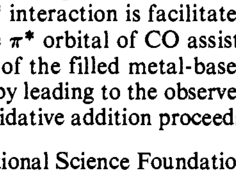
For IrX(CO)(dppe), the approach of H_2 with its molecular axis parallel to P-Ir-CO, i, is clearly preferred over a corresponding one with H_2 parallel to P-Ir-X, ii. If the key interaction in H_2 activation and oxidative addition involves donation from a filled metal d_π orbital to the H_2 antibonding σ^* orbital, as recent theoretical studies indicate,[14] then the experimental results presented here show that this $d_\pi \rightarrow \sigma^*$ interaction is facilitated in i over ii. We propose that for i, the π^* orbital of CO assists this interaction by increasing *overlap* of the filled metal-based orbital with $\sigma^*_{H_2}$, as shown in iii, thereby leading to the observed stereoselectivity as the concerted H_2 oxidative addition proceeds.



i



ii



iii

Acknowledgment. We thank the National Science Foundation (CHE80-11974 and CHE83-08064) for support of this research and the Johnson Matthey Co., Inc., for a generous loan of iridium salts. We also acknowledge helpful discussions with Professor William D. Jones.

Registry No. 1a, 87985-29-3; **1b**, 29638-05-9; **1c**, 85421-68-7; **1d**, 87985-30-6; **1e**, 87985-31-7; **2a**, 87985-32-8; **2b**, 87985-33-9; **2c**, 87985-34-0; **2d**, 87985-35-1; **2e**, 85421-67-6; **3a**, 88035-03-4; **3b**, 88035-04-5; **3c**, 88035-05-6; **3d**, 88035-06-7; **4**, 88035-07-8; Ir(CN)$(CO)_2$(dppe), 87985-36-2; [n-Bu_4N][$IrCl_2(CO)_2$], 73191-02-3; [n-Bu_4N][$IrBr_2(CO)_2$], 73190-78-0; PPN(CN), 65300-07-4.

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(11) The predominance of the isotopomer of **2e** shown in eq 4 is indicated by relative integration of the two different hydride resonances.

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(13) Ligand cone angles for H, CO, CN, Cl, Br, and I are 75°, ~95°, ~95°, 102°, 105°, and 107°, respectively. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

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Cleavage of Carbon Monoxide by Mononuclear Zirconium Dialkyls: Formation of a (μ-Oxo)dialkyl and an Enolate

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The insertion of carbon monoxide into transition-metal–alkyl bonds has been studied extensively since this elementary reaction is involved in the hydroformylation[1] and Fischer–Tropsch reaction.[2] The initial event in heterogeneous Fischer–Tropsch catalysis is thought to be dissociative chemisorption of carbon monoxide giving surface carbides and oxides, i.e., the triple bond of carbon monoxide is cleaved on the metal surface.[3] Only one example of cleavage of carbon monoxide by a mononuclear metal alkyl in homogeneous solution, in which both of the metal–oxygen and metal–carbon fragments were identified as originating from carbon monoxide, has been described.[4-6] In this communication we describe the cleavage of carbon monoxide under mild conditions by the mononuclear dialkyl $[(Me_3Si)_2N]_2ZrMe_2$.[7]

Reaction of $[(Me_3Si)_2N]_2ZrMe_2$ with carbon monoxide (1-2 atm, 20 °C, pentane) gives $\{[(Me_3Si)_2N]_2ZrMe\}_2O$ (A) and $[(Me_3Si)_2N]_2Zr(OC(Me){=}CMe_2)(Me)$ (B). The two compounds were isolated in ca. 80% yield, based upon eq 1, by fractional crystallization from pentane since A is much less soluble in that solvent than B. The (μ-oxo)dialkyl A was identified by spectroscopy[8] and X-ray crystallography (Figure 1).[9] The crystal structure of A has a crystallographically imposed center of sym-

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(1) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 88–145. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311. (c) Wender, I.; Pino, P. "Organic Synthesis with Metal Carbonyls"; Wiley: New York, 1977; Vol. 2. (d) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1–60. (e) Davidson, P. J.; Hignett, P. J.; Thompson, D. J. *Catalysis* **1977**, *1*, 369–411.

(2) (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Rofer-DePoorter, C. K. *Ibid.* **1981**, *81*, 447–474. (d) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117–130. (e) Denny, P. J.; Whan, D. A. *Catalysis* **1978**, *2*, 46–86. (f) Ponec, V. *Ibid.* **1982**, *5*, 48–79. (g) "New Synthesis with Carbon Monoxide"; Falbe, G., Ed.; Springer-Verlag; New York, 1980.

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(5) Many examples of oxide or carbide clusters derived from carbon monoxide are known. Some recent references are: (a) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829–5831. (b) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *Ibid.* **1979**, *101*, 7417–7419. (c) Whitmire, K.; Shriver, D. F. *Ibid.* **1981**, *103*, 6754–6755. (d) Hayward, C. M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816–3820. (e) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203–238.

(6) The dihydride Cp_2ZrH_2 reacts with carbon monoxide (100 atm, 1 week) to give small amounts of $(Cp_2ZrO)_3$, derived by methylene elimination from $(Cp_2ZrCH_2O)_3$. Kroop, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353–3354.

(7) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928–2932.

(8) Anal. Calcd for $C_{26}H_{78}N_4OSi_8Zr_2$: C, 35.7; H, 8.99; N, 6.45. Found: C, 35.8; H, 9.18; N, 6.16. Mp 119–121 °C(dec). The mass spectrum (chemical ionization, CH_5^+) shows an envelope of peaks centered around 868 amu, see supplementary material for the actual spectrum. NMR (PhH-d_6, 25 °C): ^1H δ 0.90 (s, 6 H, MeZr) and 0.42 (s, 72 H, $(Me_3Si)_2N$); ^{13}C δ 43.9 (q, $^1J_{CH}$ = 116 Hz, ZrMe) and 5.70 (q, $^1J_{CH}$ = 118 Hz, $(Me_3Si)_2N$).

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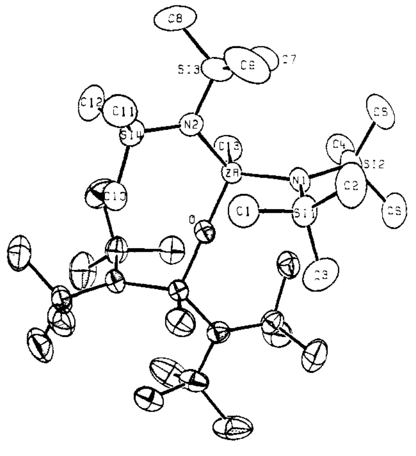
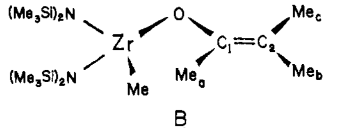


Figure 1. An ORTEP drawing of $\{[(Me_2Si)_2N]_2ZrMe\}_2O$.

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, β = 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 (λ = 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 Me_2C═CMe); 1.58 (s, 3 H, Me_2C═C*Me*); 0.80 (s, 3 H, ZrMe); and 0.39 (s, 36H, Me_3Si); ^{13}C δ 149 (s, Me_2C═*CMe*); 107 (s, Me_2*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.

[15] Benziger, J. B. *Appl. Surf. Sci.* **1980**, *6*, 105-121.

Photoisomerization of Trimesitylvinyl Alcohol. Indirect Evidence for the Keto Form

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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

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

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.

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.