*Inorg. Chem.* **1981**, *20*, 2889-2894

Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506

# Preparation and Structural Characterization of Early-Transition-Metal Hydrides. $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, a Binuclear Zirconium Hydride Complex[1]

S. BART JONES and JEFFREY L. PETERSEN*

*Received January 6, 1981*

The binuclear zirconocene hydride complex $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ was prepared by the stoichiometric addition of 2 equiv of $LiAlH(O\text{-}t\text{-}Bu)_3$ to 1 equiv of $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$ and was characterized by elemental analysis, IR, $^1H$ NMR, hydrolysis, and X-ray diffraction methods. The molecular structure of this binuclear complex consists of two $(\eta^5\text{-}C_5H_4CH_3)_2ZrH$ molecular units linked by two three-center, two-electron Zr–H–Zr bonds. Its molecular geometry is constrained by a crystallographic center of inversion, which requires a trans orientation for the two terminal hydrides. The important bond angles within the $Zr_2H_4$ core are $H_t\text{–}Zr\text{–}H_b = 70\ (1)°$, $H_t\text{–}Zr\text{–}H_b' = 130\ (1)°$, $H_b\text{–}Zr\text{–}H_b' = 60\ (1)°$, and $Zr\text{–}H_b\text{–}Zr' = 120\ (1)°$, and the metal–hydrogen bond distances are $Zr\text{–}H_t = 1.78\ (2)$ Å, $Zr\text{–}H_b = 2.05\ (3)$ Å, and $Zr\text{–}H_b' = 1.94\ (2)$ Å. So that inter-ring repulsions introduced during dimer formation might be relieved, the methylcyclopentadienyl rings have been rotated so that the methyl substituents on opposite sides of the molecule are directed away from one another. The compound crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with refined lattice parameters of $a = 6.390\ (2)$ Å, $b = 8.291\ (3)$ Å, $c = 11.308\ (4)$ Å, $\alpha = 85.39\ (3)°$, $\beta = 74.36\ (3)°$, $\gamma = 68.87\ (2)°$, $V = 538.0\ (3)$ Å$^3$, $Z = 1$ dimer of fw 502.9 per cell, and $\rho_{calcd} = 1.552$ g/cm$^3$. Full-matrix least-squares refinement (based on $F_o^2$) of 2489 diffractometry data converged with final discrepancy indices of $R(F_o) = 0.0197$, $R(F_o^2) = 0.0357$, and $R_w(F_o^2) = 0.0463$ with $\sigma_1 = 1.30$.

## Introduction

Transition-metal hydrides have demonstrated an increasingly important role in contemporary organometallic chemistry.[2,3] Although most of the interest during the past decade was focused on hydride complexes of group 6–8 metals, recent developments have indicated that early-transition-metal hydrides may represent potentially valuable reagents for organic synthesis and for CO reduction. For example, studies by Schwartz and co-workers[4] have shown that $[(\eta^5\text{-}C_5H_5)_2ZrCl(H)]_x$ reacts with olefins and acetylenes in a highly regioselective manner. Insertion of the unsaturated hydrocarbon into the Zr–H bond followed by carbonylation or halogenation ultimately leads to functionalization of the least-hindered carbon position. Bercaw and co-workers[5] have also explored in detail the unusual chemical reactivity of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ toward CO and olefins. Of particular significance is the demonstrated ability of this dihydride to absorb CO (at −80 °C), which subsequently undergoes migratory insertion into a Zr–H bond.

Despite the interest in these zirconium hydrides, little is known about the structural properties of either $[(\eta^5\text{-}C_5H_5)_2ZrCl(H)]_x$ or its dihydride counterpart $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$. Both are presumed to be polymeric on the basis of their characteristic insolubility. Since replacement of $C_5H_5$ by $C_5H_4Me$ (as well as $C_5Me_5$) is known to enhance the solubility and crystallizability of other $(\eta^5\text{-}C_5H_5)_2ML_2$-type complexes, we have undertaken an effort to prepare the corresponding methylcyclopentadienyl derivatives and examine their stereochemistry and chemical reactivity. We wish to report the preparation and structural characterization via X-ray diffraction methods of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, which provides the first structural evidence for binuclear hydrides of zirconium with bridging hydride ligands.

## Experimental Section

**Materials.** All manipulations were performed under a dry nitrogen or Ar atmosphere with the aid of a double-manifold vacuum line. Solvents were purified by standard methods and freshly distilled under Ar prior to use. The $ZrCl_4$ was purchased from Alfa Ventron and sublimed under a dry nitrogen stream. Bis(methylcyclopentadienyl)zirconium dichloride and $LiAlH(O\text{-}t\text{-}Bu)_3$ were prepared by published methods[6,7] and purified by sublimation. $LiAlD(O\text{-}t\text{-}Bu)_3$ was purchased from Alfa Ventron.

**Physical Measurements.** $^1H$ NMR spectra were measured on a Varian CFT-20 NMR spectrometer operating in the FT mode. $Me_4Si$ was used as the internal standard. The infrared spectra were recorded on an Beckman IR-8 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Preparation of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$.** The synthesis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ was accomplished by the addition of 75.1 mL of 0.665 M $LiAlH(O\text{-}t\text{-}Bu)_3$ in THF (49.94 mmol) to a suspension of 8.0 g of $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$ (24.97 mmol) in 40 mL of THF. The reaction mixture was stirred under an Ar atmosphere overnight and filtered at −10 °C. The white product was washed three times with 10-mL portions of cold THF and dried under vacuum to give 5.61 g (11.15 mmol, 89.3% yield) of the dihydride. Although $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ exhibits a limited degree of solubility in THF, suitable parallelepiped-shaped crystals for the structural and chemical analyses were obtained by cooling of a saturated THF solution. The deuterated analogue, $[(\eta^5\text{-}C_5H_4CH_3)_2ZrD(\mu\text{-}D)]_2$, was prepared in a similar manner from $LiAlD(O\text{-}t\text{-}Bu)_3$.[8,9]

Anal. Calcd for $C_{12}H_{16}Zr$ (empirical formula): C, 57.31; H, 6.41; Zr, 36.28. Found: C, 57.06; H, 6.38; Zr, 36.41. Infrared spectrum (KBr disks): $\nu_{Zr\text{-}H(D)}$ 1565 (1125), 1330 (962) cm$^{-1}$.[10] $^1H$ NMR spectrum (THF-$d_8$): $\delta$ −2.98 ($Zr\text{–}H_b$, triplet, $J_{H\text{-}H} = 7.5$ Hz), 3.75 ($Zr\text{–}H_t$, triplet, $J_{H\text{-}H} = 7.5$ Hz), 2.13 ($CH_3$), 5.76 (complex multiplet, $C_5H_4$–); ratio of peak areas, 1:1:6:8. The $^1H$ NMR spectrum of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is illustrated in Figure 1 and confirms that the dimer's structure remains intact in solution at 25 °C. The complex resonance pattern for the ring protons arises from the fact that the virtual mirror symmetry of the $Zr_2H_4$ unit coupled with the center of symmetry leaves only one $C_5H_4CH_3$ ring as unique for NMR purposes. The chirality of each Zr center (as found in the solid-state structure) requires that the four ring protons remain nonequivalent even in the presence of rapid rotation about the Zr–ring centroid axis. Thus, the 2, 5 and 3, 4 protons form diastereotopic pairs and produce a complex ABCD pattern rather than an $A_2B_2$ pattern such as observed for $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$. The assignments given for the bridging and terminal hydrido groups are based upon spectral data reported for

---

[1] Presented in part at the 12th Central Regional Meeting of the American Chemical Society, Pittsburgh, PA, Nov 1980.

[2] Saillant, R. B.; Kaesz, H. D. *Chem. Rev.* **1972**, *72*, 231.

[3] Bau, R. *Adv. Chem. Ser.* **1978**, *No. 167*.

[4] Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521 and references cited therein.

[5] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121 and references cited therein.

[6] Eisch, J. J.; King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1.

[7] Brown, H. C.; McFarlin, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 5372.

[8] An alternative method for the preparation of $[(\eta^5\text{-}C_5H_4R)_2ZrH_2]_2$ (R = Me, $Me_2CH$, $Me_3C$) has been reported by Couturier and Gautheron[9] and involves the hydrogenation of $(\eta^5\text{-}C_5H_4R)_2Zr(Me)_2$ at 60 atm and 80 °C.

[9] Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, *157*, C61.

[10] $\nu_{Zr\text{-}H(D)}$ for $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ (KBr disk): 1520 (1100), 1300 (960) cm$^{-1}$ [Kautzner, B.; Wailes, P. C.; Weigold, H. *J. Chem. Soc. D* **1969**, 1105].

0020-1669/81/1320-2889$01.25/0 © 1981 American Chemical Society

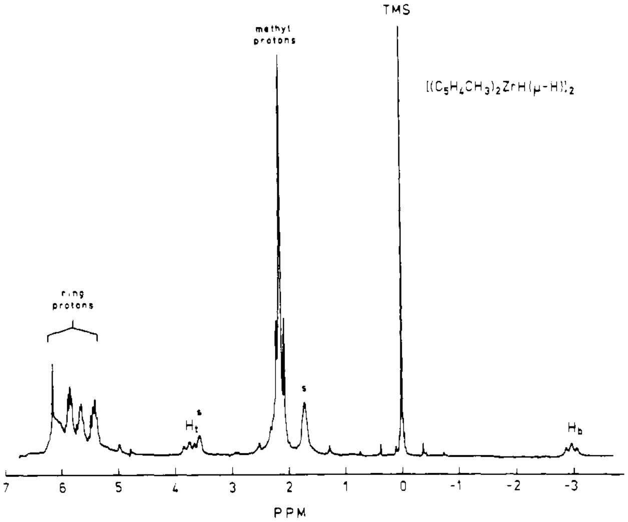


**Figure 1.** Proton NMR spectrum of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ in THF-$d_8$. The s denotes resonance lines due to solvent impurities.

$[(\eta^5\text{-}C_9H_{11})_2ZrH(\mu\text{-}H)]_2$[11] and $[(\eta^5\text{-}C_5H_5)_2Zr(H\text{-}AlMe_3)(\mu\text{-}H)]_2$.[12] Weigold et al.[11] observed similar spectral features in the $^1H$ NMR spectrum (below −10 °C) of a related zirconium hydride species prepared by the hydrogenation of bis($\eta^5$-indenyl)dimethylzirconium (IV). They proposed a dimeric structure for this hydride complex with the high-field triplet centered at $\delta$ −1.56 assigned to a pair of $\mu$-hydrido groups and the low-field triplet at $\delta$ 4.59 to a pair of terminal hydrides. Wailes et al.[12] observed a similar high-field triplet at $\delta$ −2.92 for $[(\eta^5\text{-}C_5H_5)_2Zr(H\text{-}AlMe_3)(\mu\text{-}H)]_2$ and subsequently assigned it to a pair of zirconium bridging hydrides.

The hydride:zirconium ratio was determined quantitatively by acid hydrolysis of the complex with a 2 N $H_2SO_4$–THF solution. The evolved $H_2$ gas was passed through two liquid-nitrogen traps and collected in a calibrated volume by means of a Toepler pump. Three different analyses on hydride samples of varying weight indicated the hydride to zirconium ratio to be 1.99 ± 0.02.

**Collection of X-ray Diffraction Data.** A crystal of dimensions 0.175 × 0.25 × 0.60 mm was wedged into a glass capillary tube, which was subsequently sealed to protect the sample from prolonged exposure to moisture. Although the compound is not noticeably air sensitive, crystals left out in the laboratory slowly become clouded due to hydrolysis. The crystal was mounted with the *a* axis nearly parallel to the spindle axis of the goniometer. Preliminary oscillation and Weissenberg photographs were measured with Cu K$\alpha$ radiation and revealed the Laue symmetry to be $C_i$-$\bar{1}$. The sample was transferred to a Picker goniostat under computer control by a Krisel control diffractometer automation system. The angular coordinates ($\omega$, $\chi$, $2\theta$) for 20 diffraction peaks with a $2\theta$ range of $30° < 2\theta < 35°$ were optimized by the automatic-centering routine and least-squares refined to provide the unit cell parameters with $a = 6.390$ (2) Å, $b = 8.291$ (3) Å, $c = 11.308$ (4) Å, $\alpha = 85.39$ (3)°, $\beta = 74.36$ (3)°, $\gamma = 68.87$ (2)°, $V = 538.0$ (3) Å$^3$, $Z = 1$ dimer of fw 502.9 per cell, and $\rho_{calcd} = 1.552$ g/cm$^3$.

Due to the high quality of the crystal, intensity data ($h{\pm}k{\pm}l$) were measured with Zr-filtered Mo K$\alpha$ radiation within the detector range of $3° \leq 2\theta \leq 55°$. Coupled $\theta$ (crystal)–$2\theta$(counter) scans were employed with a fixed scan rate of 2°/min and variable scan widths of $(1.2 + 0.7 \tan \theta)°$. Ten-second background counts were measured at the extremes of each scan. The settings of the pulse-height analyzer of the scintillation detector were adjusted to accept 90% of the diffraction peak. The intensities of three standard reflections were measured after every 90 min of sample exposure, and their combined counts decreased by 2.5% during the data collection period. The intensities of the strongest low-angle reflections were remeasured after insertion of a precalibrated attenuator in order to correct for possible counter saturation effects. The integrated intensity, *I*, and the standard deviation, $\sigma_c(I)$, for each of the 2727 measured reflections were calculated from the respective expressions $I = w(S/t_s - B/t_b)$ and $\sigma_c(I) = w(S/t_s^2 + B/t_b^2)^{1/2}$. In these expressions *S* represents the total scan count in time $t_s$ and *B* is the combined background count in time $t_b$. The intensity data were corrected for absorption and Lorentz–polarization effects. The range of transmission coefficients was 0.79–0.85 with $\mu = 9.55$ cm$^{-1}$ for Mo K$\alpha$ radiation. The standard deviation of the square of each structure factor, $F_o^2 = I/Lp$, was calculated from $\sigma(F_o^2) = [(\sigma_c(F_o^2))^2 + (0.03F_o^2)^2]^{1/2}$ where $\sigma_c(F_o^2)$ is based upon counting statistics. Duplicate reflections were then averaged to provide 2489 unique reflections with $F_o^2 \geq 0$ for the structural analysis.

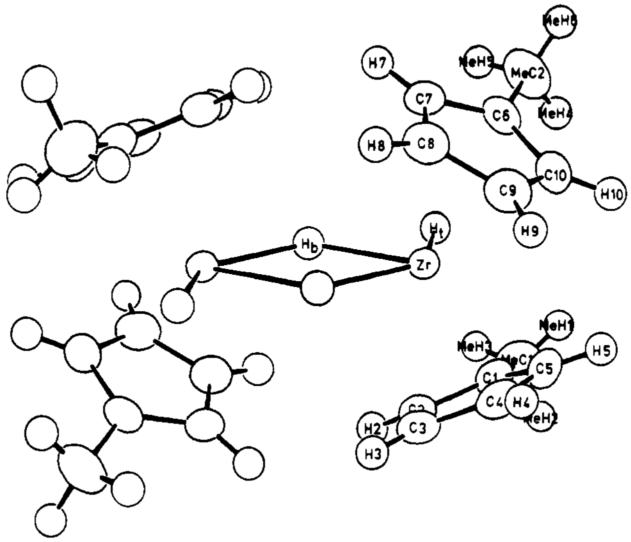


**Figure 2.** Perspective view of the molecular configuration of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ with the atom numbering scheme. The thermal ellipsoids are scaled to enclose 50% probability. For purposes of clarity the radii of the spheres for the hydrogen atoms were arbitrarily reduced.

**Structural Analysis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$.** The initial coordinates of the one independent zirconium atom were interpolated from an analysis of a three-dimensional Patterson map. Subsequent Fourier syntheses provided the approximate coordinates for the 12 independent carbon atoms and confirmed the dimeric structure of this hydride complex. Following an anisotropic refinement of the positional and thermal parameters of the nonhydrogen atoms, a difference Fourier map was calculated and used to obtain initial coordinates for *all* of the hydrogen atoms. The largest peak corresponded to the bridging hydrido ligand. Prior to the final refinement an examination of the agreement between $F_0$ and $F_c$ indicated a small systematic variation due to extinction, and an isotropic secondary extinction parameter, $g$,[13-15] was introduced. Full-matrix least-squares refinement (based on $F_o^2$) with anisotropic temperature factors for the 13 nonhydrogen atoms and isotropic temperature factors for the 16 hydrogen atoms converged with final discrepancy indices[16-20] of

---

(11) Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23.

(12) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C29.

(13) The Zachariasen approximation[14] was used for the overall isotropic extinction parameter, *g*, as defined and scaled by Coppens and Hamilton.[15]

(14) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(15) Coppens, P.; Hamilton, W. C. *Acta Crystallogr., Sect. A*, **1970**, *A26*, 71.

(16) The least-squares refinement[17] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|$, where $w_i$ is the individual weighting factor and *S* is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|/\sum w_iF_o^4]^{1/2}$. The standard deviation of an observation of unit weight, $\sigma_1$, equals $[\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where *n* is the number of observations and *p* is the number of parameters varied (viz., 183) during the last refinement cycle. The corresponding data to parameter ratio for 2489 data with $F_o^2 \geq 0$ is 13.6:1.

(17) The scattering factors employed in all of the structure factor calculations were those of Cromer and Mann[18] for the nonhydrogen atoms and those of Stewart et al.[19] for the hydrogen atoms with corrections included for anomalous dispersion.[20]

(18) Cromer, D. T.; Mann, J. *Acta Crystallogr., Sect. A* **1968**, *A24*, 231.

(19) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(20) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

**Table I.** Positional Parameters and Temperature Factors for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$[a,b]

A. Positional Parameters and Isotropic Temperature Factors

| atom | x | y | z | U, Å$^2$ |
|---|---|---|---|---|
| Zr | 0.02582 (2) | 0.01980 (1) | 0.14608 (1) | |
| C1 | −0.1918 (3) | 0.3146 (2) | 0.2559 (2) | |
| C2 | −0.1510 (3) | 0.3440 (2) | 0.1287 (2) | |
| C3 | 0.0905 (3) | 0.2963 (2) | 0.0769 (2) | |
| C4 | 0.2011 (3) | 0.2330 (2) | 0.1707 (2) | |
| C5 | 0.0267 (4) | 0.2443 (2) | 0.2811 (2) | |
| MeC1 | −0.4257 (5) | 0.3679 (3) | 0.3468 (2) | |
| C6 | 0.0470 (3) | −0.2342 (2) | 0.2935 (2) | |
| C7 | 0.1357 (3) | −0.3043 (2) | 0.1735 (2) | |
| C8 | 0.3419 (3) | −0.2721 (2) | 0.1184 (2) | |
| C9 | 0.3796 (3) | −0.1782 (2) | 0.2029 (2) | |
| C10 | 0.1978 (3) | −0.1546 (2) | 0.3111 (2) | |
| MeC2 | −0.1527 (5) | −0.2596 (4) | 0.3887 (2) | |
| $H_b$ | −0.162 (4) | 0.001 (3) | 0.030 (2) | 0.052 (6) |
| $H_t$ | −0.258 (4) | 0.032 (3) | 0.232 (2) | 0.058 (6) |
| H2 | −0.267 (3) | 0.398 (2) | 0.082 (2) | 0.040 (5) |
| H3 | 0.160 (4) | 0.306 (3) | −0.005 (2) | 0.046 (5) |
| H4 | 0.357 (4) | 0.193 (3) | 0.165 (2) | 0.058 (6) |
| H5 | 0.055 (4) | 0.216 (3) | 0.356 (2) | 0.063 (7) |
| MeH1 | −0.414 (6) | 0.300 (4) | 0.416 (3) | 0.098 (10) |
| MeH2 | −0.471 (6) | 0.493 (5) | 0.373 (3) | 0.112 (11) |
| MeH3 | −0.555 (7) | 0.360 (5) | 0.317 (4) | 0.128 (14) |
| H7 | 0.072 (3) | −0.367 (2) | 0.134 (2) | 0.043 (5) |
| H8 | 0.439 (4) | −0.305 (2) | 0.034 (2) | 0.043 (5) |
| H9 | 0.508 (5) | −0.141 (3) | 0.190 (2) | 0.063 (6) |
| H10 | 0.192 (4) | −0.101 (3) | 0.382 (2) | 0.054 (6) |
| MeH4 | −0.247 (5) | −0.157 (4) | 0.440 (3) | 0.084 (9) |
| MeH5 | −0.261 (6) | −0.272 (4) | 0.349 (3) | 0.098 (10) |
| MeH6 | −0.092 (5) | −0.361 (4) | 0.438 (3) | 0.086 (9) |

B. Anisotropic Temperature Factors

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Zr | 238 (1) | 236 (1) | 283 (1) | −95 (1) | −103 (1) | 19 (0) |
| C1 | 468 (9) | 317 (7) | 403 (8) | −125 (7) | −91 (7) | −71 (6) |
| C2 | 383 (8) | 248 (6) | 436 (8) | −93 (6) | −142 (7) | 5 (6) |
| C3 | 405 (8) | 289 (7) | 480 (9) | −178 (6) | −93 (7) | 37 (6) |
| C4 | 418 (9) | 367 (8) | 668 (11) | −201 (7) | −241 (8) | 15 (7) |
| C5 | 648 (12) | 370 (8) | 456 (9) | −201 (8) | −287 (8) | −14 (7) |
| MeC1 | 635 (14) | 544 (12) | 522 (12) | −143 (10) | 76 (10) | −159 (10) |
| C6 | 479 (9) | 389 (8) | 409 (8) | −191 (7) | −210 (7) | 153 (6) |
| C7 | 456 (9) | 266 (7) | 483 (9) | −133 (6) | −222 (7) | 63 (6) |
| C8 | 345 (8) | 319 (7) | 521 (9) | −29 (6) | −150 (7) | 37 (6) |
| C9 | 345 (8) | 392 (8) | 655 (11) | −115 (7) | −273 (8) | 107 (7) |
| C10 | 544 (10) | 401 (8) | 449 (9) | −179 (7) | −304 (8) | 105 (7) |
| MeC2 | 680 (14) | 750 (15) | 499 (11) | −393 (13) | −165 (11) | 253 (11) |

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures. [b] The form of the anisotropic temperature factors (×10$^4$) is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. The isotropic temperature factor is given by $[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

$R(F_o) = 0.0197$, $R(F_o^2) = 0.0357$, and $R_w(F_o^2) = 0.0463$ with $\sigma_1 = 1.30$ and $g = (1.4\ (2)) \times 10^{-5}$. During the last refinement cycle the maximum parameter shift to error ratio for any of the varied parameters did not exceed 0.01. A final difference Fourier summation was virtually featureless (except for two small residuals of electron density located *ca.* 0.9 Å from the Zr atom) and thereby verified the completeness and correctness of the structural analysis.

The values of the positional parameters and the temperature factors obtained from the last least-squares cycle are provided in Table I for all of the atoms. Interatomic distances and bond angles with their corresponding estimated standard errors calculated from the variance–covariance matrix are given in Table II.[21] Least-squares planes of interest have been calculated and are available with a table of the calculated and observed structure factors.[22]

## Results and Discussion

**Description of the Molecular Configuration in $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$.** The outcome of our X-ray structural analysis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ has provided detailed structural information about the molecular configuration of this binuclear zirconium hydride complex. As depicted in Figure 2 with the appropriate atom labeling scheme, the molecular structure of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ consists of two $(\eta^5\text{-}C_5H_4CH_3)_2ZrH$ molecular units bridged by two three-centered, two-electron Zr–H–Zr bonds. The dimer's geometry, which is depicted stereographically in Figure 3, is constrained by a crystallographic center of symmetry situated at the midpoint of the Zr–Zr line. The crystallographic asymmetric unit therefore consists of 1 Zr atom, 12 C atoms, and 16 H atoms. This crystallographically imposed constraint places the two terminal hydrides of the central $Zr_2H_4$ moiety trans to each other in constrast to the cis arrangement observed by Marks, Williams, and co-workers for $[(\eta^5\text{-}C_5Me_5)_2ThH(\mu\text{-}H)]_2$.[23]

The ligand arrangement about each d$^0$ Zr(IV) atom is similar to that observed by Bau and co-workers[24] for the

---

(21) The computer programs used to perform the necessary calculations are described in: Petersen, J. L. *J. Organomet. Chem.* **1979**, *155*, 179.

(22) Supplementary material.

(23) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* (*Washington, D.C.*) **1979**, *203*, 172.

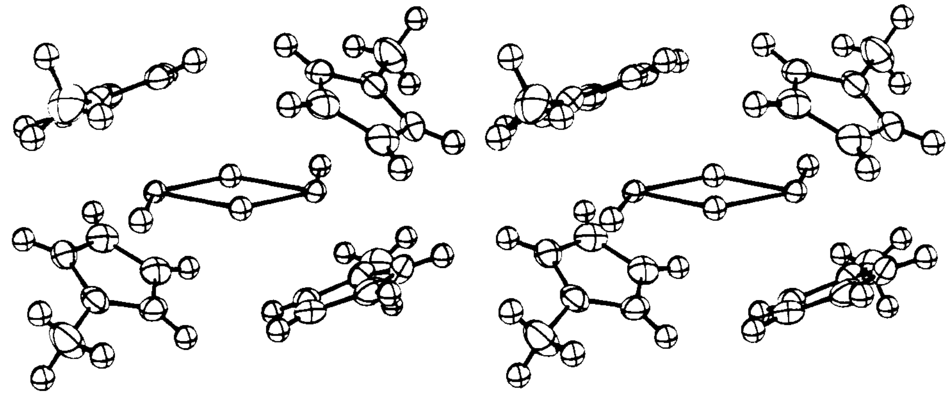


**Figure 3.** Stereographic drawing of the molecular structure of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. The geometry is constrained by a crystallographic center of inversion at the midpoint of the Zr–Zr line.

**Table II.** Interatomic Distances (Å) and Bond Angles (Deg) for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$[a]

A. Interatomic Distances

| | | | |
|---|---|---|---|
| Zr-H$_t$ | 1.78 (2) | Zr···Zr | 3.4599 (2) |
| Zr-H$_b$ | 2.05 (3) | Zr-H$_b$′ | 1.94 (2) |
| Zr–C1 | 2.560 (2) | Zr–C6 | 2.566 (2) |
| Zr–C2 | 2.527 (1) | Zr–C7 | 2.536 (2) |
| Zr–C3 | 2.502 (2) | Zr–C8 | 2.508 (1) |
| Zr–C4 | 2.476 (2) | Zr–C9 | 2.481 (2) |
| Zr–C5 | 2.503 (2) | Zr–C10 | 2.511 (2) |
| C1-MeC1 | 1.502 (3) | C6-MeC2 | 1.499 (3) |
| C1–C2 | 1.408 (2) | C6–C7 | 1.405 (2) |
| C2–C3 | 1.411 (2) | C7–C8 | 1.407 (3) |
| C3–C4 | 1.396 (3) | C8–C9 | 1.399 (3) |
| C4–C5 | 1.415 (3) | C9–C10 | 1.412 (2) |
| C5–C1 | 1.404 (3) | C10–C6 | 1.409 (3) |
| C2-H2 | 0.98 (2) | C7-H7 | 0.96 (3) |
| C3-H3 | 0.92 (2) | C8-H8 | 0.98 (2) |
| C4-H4 | 0.92 (3) | C9-H9 | 0.95 (3) |
| C5-H5 | 0.91 (3) | C10-H10 | 0.93 (3) |
| MeC1-MeH1 | 0.93 (3) | MeC2-MeH4 | 0.97 (3) |
| MeC1-MeH2 | 1.02 (4) | MeC2-MeH5 | 0.96 (4) |
| MeC1-MeH3 | 1.00 (5) | MeC2-MeH6 | 0.98 (3) |

B. Bond Angles

| | | | |
|---|---|---|---|
| H$_t$-Zr-H$_b$ | 70 (1) | H$_b$-Zr-H$_b$ | 60 (1) |
| H$_t$-Zr-H$_b$′ | 130 (1) | Zr′-H$_b$-Zr | 120 (1) |
| MeC1–C1–C2 | 125.6 (2) | MeC2–C6–C7 | 125.8 (2) |
| MeC1–C1–C5 | 127.4 (2) | MeC2–C6–C10 | 126.8 (2) |
| C2–C1–C5 | 106.7 (1) | C7–C6–C10 | 107.0 (2) |
| C1–C2–C3 | 108.8 (2) | C6–C7–C8 | 108.8 (2) |
| C2–C3–C4 | 107.9 (1) | C7–C8–C9 | 107.8 (2) |
| C3–C4–C5 | 107.6 (2) | C8–C9–C10 | 107.8 (2) |
| C4–C5–C1 | 109.0 (2) | C9–C10–C6 | 108.5 (2) |
| H2–C2–C1 | 128 (1) | H7–C7–C6 | 127 (1) |
| H2–C2–C3 | 123 (1) | H7–C7–C8 | 124 (1) |
| H3–C3–C2 | 125 (1) | H8–C8–C7 | 126 (2) |
| H3–C3–C4 | 127 (1) | H8–C8–C9 | 126 (2) |
| H4–C4–C3 | 128 (1) | H9–C9–C8 | 126 (1) |
| H4–C4–C5 | 124 (1) | H9–C9–C10 | 126 (1) |
| H5–C5–C4 | 124 (2) | H10–C10–C9 | 123 (2) |
| H5–C5–C1 | 127 (2) | H10–C10–C6 | 128 (2) |
| C1-MeC1-MeH1 | 108 (2) | C6-MeC2-MeH4 | 113 (2) |
| C1-MeC1-MeH2 | 109 (2) | C6-MeC2-MeH5 | 109 (2) |
| C1-MeC1-MeH3 | 116 (2) | C6-MeC2-MeH6 | 109 (2) |
| MeH1-MeC1-MeH2 | 108 (3) | MeH4-MeC2-MeH5 | 102 (3) |
| MeH1-MeC1-MeH3 | 108 (3) | MeH4-MeC2-MeH6 | 111 (2) |
| MeH2-MeC1-MeH3 | 107 (3) | MeH5-MeC2-MeH6 | 113 (3) |

[a] The esd's given in parentheses for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

trihydride complexes $(\eta^5\text{-}C_5H_5)_2MH_3$ (M = Nb, Ta). In these hydride complexes, six of the nine metal hybridized orbitals are involved in bonding with the two canted cyclopentadienyl rings while the three remaining orbitals interact with three hydridic hydrogens. For $(\eta^5\text{-}C_5H_5)_2MH_3$ these orbitals are used to form three terminal M–H bonds, whereas for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ they are used to form one terminal Zr–H bond and two bridging Zr–H–Zr bonds.

The Zr–Cp(c) distances, where Cp(c) is the centroid of a cyclopentadienyl ring, of 2.211 (2) and 2.219 (2) Å and the Cp(c)–Zr–Cp(c) angle of 129.8 (3) Å are analogous to the values reported for other dicyclopentadienylzirconium(IV) complexes.[25,26] The systematic variation of the Zr–C(ring) distances within the range of 2.48–2.57 Å around each ring indicates that the normal from each ring to the Zr atom is displaced from the ring centroid. The remaining structural parameters within the methylcyclopentadienyl rings do not deviate substantially from their expected values and thereby suggest the presence of only a minimal amount of librational motion for the methylcyclopentadienyl rings in the crystal lattice. The methyl carbon atom attached to each planar cyclopentadienyl ring is similarly displaced 0.17 Å (average) out of the plane in the direction away from the zirconium atom.[27]

A particularly interesting aspect of this structure is the orientation of the methyl groups of the methylcyclopentadienyl rings. So that inter-ring repulsions introduced during dimer formation could be relieved, the methylcyclopentadienyl rings have been rotated so that the methyl groups on opposite sides of the molecule are directed away from one another. Stucky and co-workers[28] have observed a similar orientation effect for the methyl substituents on the cyclopentadienyl rings in $[(\eta^5\text{-}C_5H_4CH_3)_2Ti(\mu\text{-}X)]_2$, where X = Cl or Br. If one now considers replacement of the methylcyclopentadienyl ring with the fully substituted pentamethylcyclopentadienyl ring, the corresponding inter-ring repulsions cannot be similarly reduced by a simple rotation of the rings. The additional steric bulk of the $C_5Me_5$ ring prohibits two $(C_5Me_5)_2Zr$ units from coming close enough to permit dimer formation and thereby provides a reasonable rationalization for the mononuclear structure associated with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$.

**Nature of the Zirconium–Hydride Interactions.** The presence of two distinctly different hydrides in $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is reflected by the corresponding Zr–H bond lengths and H–Zr–H bond angles within the molecule. Although the inherent limitations of the X-ray

---

(24) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Krick, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(25) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290 and references cited therein.

(26) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812 and references cited therein.

(27) Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709.

(28) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, 16, 1645.

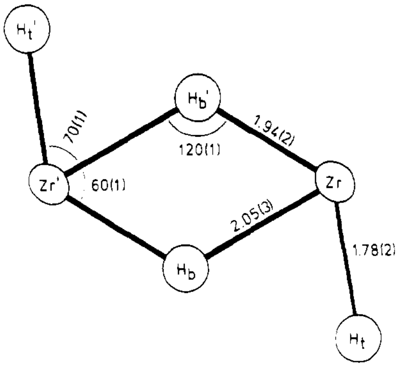


**Figure 4.** The planar, central $Zr_2H_4$ unit with appropriate bond distances and angles provided.

diffraction method prevent a precise determination of the actual atomic positions of the hydride ligands, the X-ray-determined structural parameters within the planar $Zr_2H_4$ moiety are sufficiently well determined to evaluate the nature of the metal-hydrogen interactions in this binuclear complex. For purposes of clarification, the independent terminal and bridging hydrides are designated $H_t$ and $H_b$, respectively, and the prime notation is used to represent the corresponding symmetry-related atoms. The important bond angles within the $Zr_2H_4$ core, as depicted in Figure 4, are $H_t$–Zr–$H_b$ = 70 (1)°, $H_t$–Zr–$H_b'$ = 130 (1)°, $H_b$–Zr–$H_b'$ = 60 (1)°, and Zr–$H_b$–Zr′ = 120 (1)°, and the corresponding metal-hydride distances are Zr–$H_t$ = 1.78 (2) Å, Zr–$H_b$ = 2.05 (3) Å, and Zr–$H_b'$ = 1.94 (2) Å.

The observed 10° difference in the acute H–Zr–H bond angles of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is consistent with the different bonding representations associated with a terminal M–H bond and a bridging, three-center M–H–M bond. For a terminal M–H bond the region of maximum orbital overlap between the hybrid metal orbital and the hydrogen 1s orbital is located along the M–H bond vector but displaced toward the metal atom due to covalency. Thus, the M–H bond direction is generally well-defined despite the fact that the X-ray-determined M–H bond distance is inherently short. In contrast, an entirely different bonding description has emerged for the M–H–M bond as a result of recent neutron diffraction studies of numerous transition-metal hydride complexes containing either supported or unsupported M–H–M bonds.[29] Typically, one finds, upon comparison of X-ray and neutron diffraction data available on the same complex, that the former method gives shorter average M–H distances and larger M–H–M bond angles than the latter.[30] This difference is consistent with a "closed" representation for the M–H–M bond, in which the region of maxiumum orbital overlap is not coincident with the nuclear position of the bridging hydride but is displaced ca. 0.2–0.3 Å toward the centroid of the M–H–M triangle. For binuclear hydrides containing two or more M–H–M bonds, insufficient X-ray and neutron structural evidence is currently available to assume that the X-ray-determined M–H–M bond angle will *always* be larger than the neutron-determined value. However, if one extends this premise to $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, then the X-ray-determined positions for the bridging hydrides should be displaced toward the midpoint of the Zr–Zr line. Consequently, the X-ray-determined $H_t$–Zr–$H_b$ bond angle should be appreciably larger than the $H_b$–Zr–$H_b'$ bond angle. The observed variation for these two acute bond angles for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ is in accord with this description and thereby reflects the covalent nature of the metal–hydrogen interaction in this complex.

The obtuse Zr–$H_b$–Zr′ bond angle of 120 (1)° is comparable to the Th–H–Th bond angle of 122 (4)° reported for $[(\eta^5\text{-}C_5Me_5)_2ThH(\mu\text{-}H)]_2$[23] but significantly larger than the acute Re–H–Re bond angle of 85.0 (3)° for $Re_2(PEt_2Ph)_4H_4(\mu\text{-}H)_4$.[31] For binuclear hydrides that are solely linked by hydrido groups, the magnitude of the M–H–M bond angle depends on the M–M bond order and the number of bridging hydrides, *n*. Whereas the M···M separations of 3.4599 (2) and 4.007 (8) Å for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ and $[(\eta^5\text{-}C_5Me_5)_2ThH(\mu\text{-}H)]_2$, respectively, do not suggest any appreciable metal–metal interactions in these complexes, the much shorter Re···Re separation of 2.538 (4) Å for $Re_2(PEt_2Ph)_4H_4(\mu\text{-}H)_4$ is consistent with the presence of a formal Re–Re triple bond, which accounts for the appreciably smaller M–H–M bond angles in this system. In addition, for binuclear hydrides containing comparable metal–metal interactions, one might expect that as *n* increases, the corresponding M–H–M bond angles decrease to maintain a minimal separation between the hydrogen atoms in the M–$(\mu\text{-}H)_n$–M unit. On the basis of structural data obtained by neutron diffraction, Bau[32] has estimated that the minimal nonbonding H···H contact is ca. 1.85 Å. The corresponding X-ray-determined H···H contacts within the $Zr_2H_4$ core of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ are 1.99 (5) Å for $H_b$···$H_b'$ and 2.21 (3) Å for $H_t$···$H_b$. The average Zr–$H_b$ bond distance of 2.00 Å is noticeably longer than the Zr–$H_t$ bond distance of 1.78 (2) Å. Although structural data of comparable quality on other zirconium hydride complexes are not available, this ca. 0.2 Å difference between the M–H (terminal) and M–H (bridging) distances has been observed in other transition-metal complexes containing bridging hydrogen atoms.[33] In general, as the hydrogen atom becomes coordinated to more metal centers, the resultant metal–hydrogen distances increase. This remark is clearly supported by the neutron diffraction analysis of $[(\eta^5\text{-}C_5Me_5)_2ThH(\mu\text{-}H)]_2$.[23] The mean Th–$H_t$ and Th–$H_b$ distances in this dimer are 2.03 (1) and 2.29 (3) Å, respectively. The terminal Th–H distance is comparable to the sum of the covalent radii for hydrogen and thorium of 2.09 Å, whereas the bridging Th–H distance is ca 0.2 Å longer.

The outcome of our structural analysis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ has verified the binuclear structure of this complex and in doing so has provided structural evidence to establish unequivocally the existence of the Zr–$(\mu\text{-}H)_2$–Zr linkage in binuclear zirconium hydride complexes. By analogy, the molecular structures for the corresponding derivatives $[(\eta^5\text{-}C_5H_5)_2ZrL(H)]_2$, where L = alkyl or $Cl^-$, are presumably similar with a pair of bridging hydrido groups. Although direct structural data for these hydrides are not available, Gell and Schwartz[34] have proposed the analogous structure for the zirconocene alkyl hydrides on the basis of their NMR spectral measurements. The NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2ZrR(H)]_2$ contains a broad proton resonance at $\delta \sim -2$, consistent with the presence of a bridging hydride in the complex. Work is currently in progress to prepare the corresponding methylcyclopentadienyl analogues of $[(\eta^5\text{-}C_5H_5)_2Zr(L)H]_2$ for structural analysis and to investigate the remarkable chemical reactivity of these binuclear zirconocene hydrides toward CO and unsaturated hydrocarbons.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. for support of this work. The

---

(29) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 1976 and references cited therein.

(30) Petersen, J. L.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 1308.

(31) Bau, R.; Carroll, W. R.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(32) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(33) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

(34) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

authors also express their appreciation to Professor K. Caulton (Indiana University) for comments regarding the NMR data. Computer time for the X-ray diffraction data analysis was provided by the West Virginia Network for Educational Telecomputing.

**Registry No.** $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, 77965-67-4; $(\eta^5\text{-}C_5H_4CH_3)_2ZrCl_2$, 12109-71-6.

**Supplementary Material Available:** Listings of least-squares planes and calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

---

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

# (*F*-Tetramethylene)sulfimide and (*F*-Tetramethylene)sulfoxyimide. Some *N*-Alkyl, *N*-(*F*-Alkyl), and *N*-Halo Derivatives

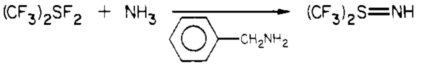
TAKASHI ABE[1] and JEAN'NE M. SHREEVE*

*Received March 10, 1981*

A new *F*-cyclic sulfimide, (*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}{=}NH$, was formed when (*F*-tetramethylene)sulfur difluoride, $\overline{CF_2CF_2CF_2CF_2S}F_2$, and $LiNH_2$ were reacted in the presence of an excess of $NH_3$. With primary amines, $\overline{CF_2CF_2CF_2CF_2S}F_2$ gave the corresponding *N*-alkyl(*F*-tetramethylene)sulfimide, $\overline{CF_2CF_2CF_2CF_2S}{=}NR$ (R = $CH_3$, $C_2H_5$). With $LiN{=}C(CF_3)_2$, $\overline{CF_2CF_2CF_2CF_2S}F_2$ results primarily in the formation of $\overline{CF_2CF_2CF_2CF_2S}{=}NCF(CF_3)_2$ and small amounts of $\overline{CF_2CF_2CF_2CF_2S}{=}NC(CF_3)N{=}C(CF_3)_2$. At reduced temperature, with the exception of *N*-(*F*-alkyl)-substituted *F*-cyclic sulfimides, the cyclic sulfimides $\overline{CF_2CF_2CF_2CF_2S}{=}NR$ (R = H, $CH_3$, $C_2H_5$) are oxidized with *m*-chloroperbenzoic acid to the corresponding cyclic sulfoxyimides $\overline{CF_2CF_2CF_2CF_2S}(O){=}NR$ in high yields. *N*-Halo (Cl and Br) sulfimides were also synthesized by the reaction of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$ with $Cl_2$ or $Br_2$ in the presence of an alkali-metal fluoride (CsF or KF).

## Introduction

Recently, there has been considerable interest in the chemistry of S(IV) compounds, $>SF_2$. For example, it has been shown that bis(*F*-methyl)sulfur difluoride, $(CF_3)_2SF_2$, will undergo metathesis reactions with primary amines to produce a series of new *N*-alkylbis(*F*-methyl)sulfimides, $(CF_3)_2S{=}NR$ (R = $CH_3$, $C_2H_5$, *i*-$C_3H_7$).[2] The bis(*F*-methyl)sulfimide $(CF_3)_2S{=}NH$ has also been shown to result from the reaction of $(CF_3)_2SF_2$ and $NH_3$ in the presence of a primary amine such as benzylamine[2] (eq 1). However, to date, no *F*-cyclic sulfimide nor its derivatives have been reported.



(1)

We have now synthesized (*F*-tetramethylene)sulfimide, *N*-alkyl(*F*-tetramethylene)sulfimides, and (*N*-*F*-alkyltetramethylene)sulfimides by the reaction of $\overline{CF_2CF_2CF_2CF_2S}F_2$ with $LiNH_2$, $RNH_2$ (R = $CH_3$, $C_2H_5$), and $LiN{=}C(CF_3)_2$, respectively, and also (*F*-tetramethylene)sulfoxyimide and *N*-alkyl(*F*-tetramethylene)sulfoxyimides by the oxidation of the corresponding cyclic sulfimides. The halogenation of $\overline{CF_2CF_2CF_2CF_2S}{=}NH$ with $Cl_2$ and $Br_2$ in the presence of CsF or KF affords the corresponding *N*-chloro and *N*-bromo compounds which will be described also in this paper.

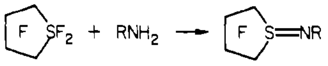
## Results and Discussion

It has been shown that $(CF_3)_2SF_2$ and $\overline{CF_2CF_2CF_2CF_2S}F_2$ do not react with such weak nucleophiles as $H_2O$ and $NH_3$ at ambient temperature.[3,4] In fact, $\overline{CF_2CF_2CF_2CF_2S}F_2$ does not react with $NH_3$ even at 100 °C for 5 h.[4] However, with excess amounts of primary amines, $(CF_3)_2SF_2$ has been shown to give *N*-alkylbis(*F*-methyl)sulfimide in reasonable yields[2] (eq 2). Furthermore, in the presence of primary amines,

$$(CF_3)_2SF_2 + 3RNH_2 \rightarrow (CF_3)_2S{=}NR + 2RNH_2HF \qquad R = CH_3,\ C_2H_5,\ CH(CH_3)_2 \tag{2}$$

$(CF_3)_2SF_2$ has been found to react with $NH_3$ yielding bis(*F*-methyl)sulfimide, $(CF_3)_2S{=}NH$ successfully.[2]

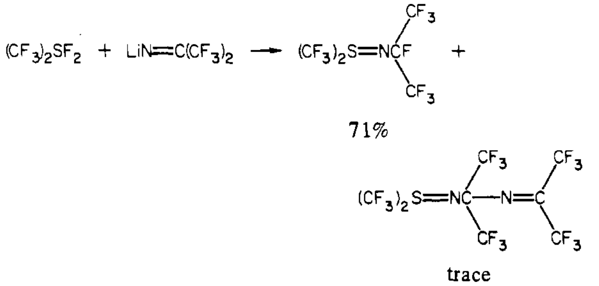
Similarly, we have found that when (*F*-tetramethylene)sulfur difluoride, $\overline{CF_2CF_2CF_2CF_2S}F_2$, was treated with primary amines, new *N*-alkyl(*F*-tetramethylene)sulfimides were formed (eq 3). These compounds are transparent liquids which are moderately stable at 25 °C.



(3)

R = $CH_3$ (70%), $C_2H_5$ (37%)

Lithium *F*-isopropylidenimine, $(CF_3)_2C{=}NLi$, has been used as a reactive nucleophile by workers here and elsewhere.[5,6] With $(CF_3)_2SF_2$, (*F*-isopropyl)bis(*F*-methyl)sulfimide was formed mainly together with small quantities of *N*-(*F*-isopropylidenimino)-*N*-(*F*-isopropyl)bis(*F*-methyl)sulfimide, viz eq 4.



(4)

Similarly, $\overline{CF_2CF_2CF_2CF_2S}F_2$ reacted smoothly with $LiN{=}C(CF_3)_2$, giving mainly *N*-(*F*-isopropyl)(*F*-tetra-

---

(1) Visiting Research Scholar, Government Industrial Research Institute, Nagoya, Japan, 1979-1980.
(2) Morse, S. D.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 33.
(3) Sauer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971**, *1*, 1.
(4) Abe, T.; Shreeve, J. M. *J. Fluorine Chem.* **1973**, *3*, 17.
(5) Swindell, R. F.; Shreeve, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 5713.
(6) Swindell, R. F.; Babb, D. P.; Ouellette, T. J.; Shreeve, J. M. *Inorg. Chem.* **1972**, *11*, 242.

0020-1669/81/1320-2894$01.25/0 © 1981 American Chemical Society