a single transient absorption was formed within the response time of the detection system, in the 1750–1880-cm⁻¹ region of the IR spectrum. We assign these IR bands to the acyl radicals indicated in Table I on the basis of their carbonyl stretching frequencies,[6–9] their kinetic behavior, and the identification of the expected reaction products which grow in at the same rate as the radicals decay.

Under our experimental conditions, the acyl radical IR absorptions decayed within microseconds with kinetics that were first order for pivaloyl but were predominantly second order for the other three acyl radicals (which presumably decay largely by radical–radical recombination). The pivaloyl radical is known to undergo a relatively rapid decarbonylation, reaction 2.[5,13] By

$$(CH_3)_3CC^{\bullet}{=}O \rightarrow (CH_3)_3C^{\bullet} + CO \qquad (2)$$
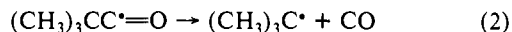
using a static system from which all traces of oxygen (vide infra) were removed by several freeze–pump–thaw cycles, we found the rate constant for decay of the pivaloyl radical to be $7 \times 10^5$ s⁻¹, independent of the laser dose. We equate this rate constant with $k_2$ (see footnote 14) and note that it is in satisfactory agreement with an indirectly determined value of $4.4 \times 10^5$ s⁻¹ at 25 °C which was obtained by Fischer and co-workers[5,15] using an EPR method.

The rates of decay of the transient IR signals can be increased by the addition of compounds (quenchers) which might be expected to react with acyl radicals, e.g., CCl₄, CCl₃Br, C₆H₅SH, and O₂. By a careful analysis of the decay traces found with different concentrations of added quenchers (including fitting the experimental data with mixed (pseudo) first- and second-order kinetics), kinetic data were obtained as illustrated for the benzoyl radical in Table II. The loss of the 1828-cm⁻¹ band of benzoyl was matched for CCl₄ and CCl₃Br (see Figure 1) by the growth of new carbonyl absorptions which occurred at the known frequencies for the expected products, viz., C₆H₅C(O)Cl and C₆H₅C(O)Br, respectively. However, the rate constant for reaction with C₆H₅SH[16] could only be determined from the decay of the benzoyl radical since absorption from the expected product, C₆H₅CHO, was masked by absorption of the starting ketone. With oxygen as the quencher, a new absorption grows in at 1820 cm⁻¹, which we assign to the benzoylperoxyl radical.[17]

From the known extinction coefficient of C₆H₅C(O)Br we estimate that the extinction coefficient for the benzoyl radical at 1828 cm⁻¹ has a value of ca. 1300 M⁻¹ cm⁻¹.

(12) For details of our instrumentation, see: Rayner, D. M.; Nazran, A. S.; Drouin, M.; Hackett, P. A. *J. Phys. Chem.* **1986**, *90*, 2882–2888. Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 6644–6650.

(13) (a) Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194–2200. (b) Schuh, H.; Hamilton, E. J., Jr.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 2011–2024. (c) Vollenweider, J.-K.; Fischer, H.; Hennig, J.; Leuschner, R. *Chem. Phys.* **1985**, *97*, 217–234.

(14) We rule out any significant contribution to the measured first-order rate constant from an attack on the *n*-hexane solvent because the other three acyl radicals decay with second-order kinetics. We estimate that at room temperature the reaction RC�•=O + C₆H₁₄ → RCHO + C₆H₁₃• must have $k \leq 5 \times 10^3$ M⁻¹ s⁻¹.

(15) An earlier value[13b] of $1.2 \times 10^5$ s⁻¹ at 25 °C in methylcyclopentane would appear to have been in error. A third value of $3.5 \times 10^5$ s⁻¹ derived from indirect CIDNP measurements[13c] is in fair agreement with the latest result.[5]

(16) The large magnitude of this rate constant is somewhat surprising since thiyl radicals are believed to abstract hydrogen from aldehydes rather efficiently. See: Walling, C. *Free Radicals in Solution*; Wiley and Sons Inc.: New York, 1957; pp 325–326.

(17) For the matrix-trapped (and possibly "perturbed") HC(O)OO• radical, $\nu_{C=O}$ has been reported to be 1790 cm⁻¹.[18]

(18) Tso, T.-L.; Diem, M.; Lee, E. K. C. *Chem. Phys. Lett.* **1982**, *91*, 339–342.

## η²-Silanimine Complexes of Zirconocene: Synthesis, Structure, and Reactivity of Cp₂Zr(η²-SiMe₂=NᵗBu)(PMe₃)

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Silanimines (R₂Si=NR′) are one of several classes of very reactive species exhibiting unsaturation at silicon.[2] Several examples of stable silanimines in which the Si=N bond is protected by bulky substituents have been isolated.[3] Recently, there has been interest in stabilizing unsaturated silicon species such as silylenes (:SiR₂),[4] silenes (R₂Si=CR′₂),[5] and disilenes (R₂Si=SiR′₂)[6] by coordination to transition metals. We now report the synthesis, structure, and reactivity of Cp₂Zr(η²-SiMe₂=NᵗBu)(PMe₃) (Cp ≡ η⁵-C₅H₅), the first example of a metal silanimine complex.

The synthetic strategy employed (Scheme I) involves formation of the unsaturated fragment by β-hydrogen abstraction and loss of alkane, in analogy to previously reported syntheses of organic imine complexes.[7] The amido complex Cp₂Zr(H)(NᵗBuSiMe₂H) (1) is prepared by metathesis of [Cp₂ZrHCl]ₙ with LiNᵗBuSiMe₂H·THF.[8] Treatment of 1 with MeI yields the iodide Cp₂Zr(I)(NᵗBuSiMe₂H) (2) and methane. Alkylation of 2 with LiCH₂SiMe₃ in benzene solution generates the (trimethylsilyl)methyl derivative, Cp₂Zr(CH₂SiMe₃)(NᵗBuSiMe₂H) (3), which is observed as an unstable intermediate by ¹H NMR. Compound 3 decomposes in solution ($t_{1/2} < 30$ min at 25 °C) with elimination of SiMe₄, presumably via the reactive intermediate Cp₂Zr(η²-SiMe₂=NᵗBu). However, generation of this 16e⁻ intermediate in the presence of trimethylphosphine as a trapping ligand yields the stable η²-silanimine complex Cp₂Zr(η²-SiMe₂=NᵗBu)(PMe₃) (4, 73% isolated).

As depicted in Scheme I, and in analogy to metal–olefin complexes, the bonding of the silanimine fragment to the metal is expected to fall between the two extreme resonance forms of a metallacycle (sp³ hybridization at Si) and a π-donor complex (sp² hybridization at Si). The molecular structure of 4 as determined by a single-crystal X-ray diffraction study is shown in Figure 1.[9]

(1) Alfred P. Sloan Fellow, 1990–1992.

(2) (a) Parker, D. R.; Sommer, L. H. *J. Organomet. Chem.* **1976**, *110*, C1. (b) Zigler, S.; Johnson, L. M.; West, R. *J. Organomet. Chem.* **1988**, *341*, 187. (c) Wiberg, N.; Schurz, K. *J. Organomet. Chem.* **1988**, *341*, 145. (d) For a recent review, see: Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons, Ltd.: New York, 1989; Chapter 17.

(3) (a) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591. (b) Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649.

(4) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (c) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (d) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (e) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

(5) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079. (c) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405. (d) Koloski, T. S.; Carroll, P. J.; Berry, D. H., manuscript in preparation.

(6) (a) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (b) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (c) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452. (d) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *Polyhedron*, in press.

(7) See, for example: (a) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

(8) Full details on the preparation and characterization of new compounds are included in the supplementary material.
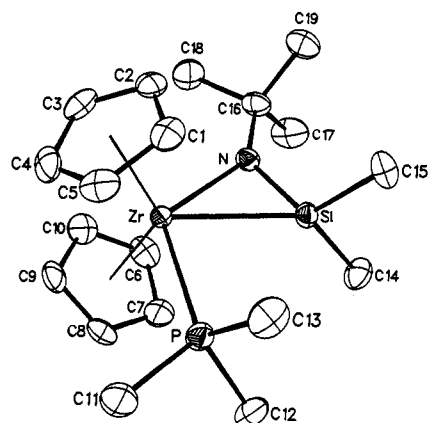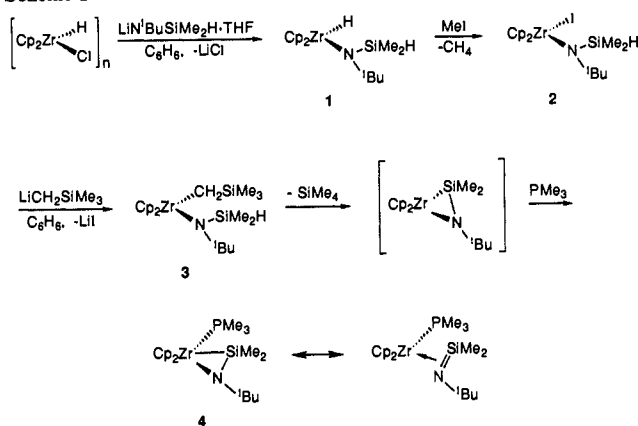
Communications to the Editor

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**Figure 1.** ORTEP drawing of **4**. Selected bond distances (Å) and angles (deg): Zr–Si, 2.654 (1); Zr–N, 2.167 (3); Zr–P, 2.7082 (9); Si–N, 1.687 (3); Si–C(14), 1.904 (5); Si–C(15), 1.894 (5); N–C(16), 1.473 (4); Si–Zr–N, 39.36 (7); Zr–N–Si, 86.1 (1); Zr–Si–N, 54.5 (1); Si–Zr–P, 77.66 (3); Si–N–C(16), 133.8 (3); Zr–N–C(16), 140.1 (3); N–Si–C(14), 115.9 (2); N–Si–C(15), 116.4(2); Zr–Si–C(14), 126.7 (2); Zr–Si–C(15), 127.7 (2); C(14)–Si–C(15), 104.2 (2).

**Scheme I**



The Zr–Si distance of 2.654 (1) Å is significantly shorter (ca. 0.1–0.16 Å) than the three other Zr–Si bond lengths reported.[10] Furthermore, the Si–N distance of 1.687 (3) Å falls within the range observed for Si–N single bonds in a wide variety of compounds (1.64–1.80 Å).[11] The only structurally characterized free silanimine, $^tBu_2Si=NSi^tBu_3$, has a much shorter $Si=N$ double bond length of 1.568 (3) Å,[3a] and a Lewis base adduct of a related silanimine, $THF \cdot Me_2Si=NSi^tBu_3$, also displays short $Si=N$ distances of 1.588 (9) and 1.574 (10) Å in two crystallographically independent molecules.[3a] The short Zr–Si and long Si–N bond distances in **4** suggest that the bonding between the metal and silanimine fragments is best described by the metallacyclic (Zr-(IV)) resonance form shown in Scheme I.
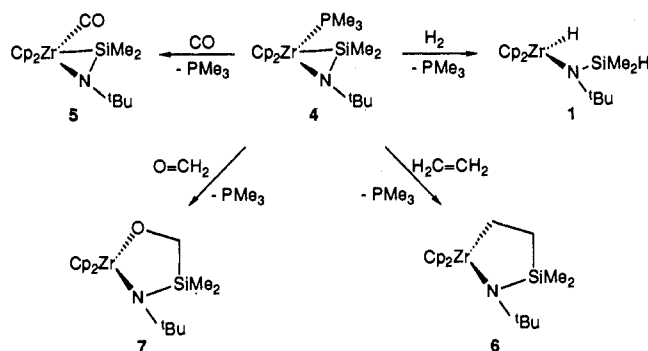
Addition of trimethylphosphine (ca. 0.5 equiv) to solutions of **4** results in the broadening of resonances due to free and coordinated $PMe_3$ in both the $^1H$ and $^{31}P\{^1H\}$ NMR spectra. It

**Scheme II**



therefore appears that the phosphine ligand in **4** is quite labile and exchanges with free $PMe_3$ on the NMR time scale at room temperature. Consistent with this lability, **4** reacts immediately with carbon monoxide (1 atm, 25 °C) to yield $PMe_3$ and a compound corresponding to the ligand substitution product, $Cp_2Zr$-$(\eta^2$-$Me_2Si=N^tBu)(CO)$ (**5**) (Scheme II).[12] Although the insertion of CO into early-metal silicon bonds to generate silaacyl complexes has been demonstrated by Tilley and co-workers,[13] spectroscopic data are most consistent with characterization of **5** as a simple carbonyl adduct rather than as the insertion product $Cp_2Zr(C(=O)SiMe_2N^tBu)$. In particular, the small value of $J_{Si–C}$ (24 Hz) observed in the $^{29}Si$ NMR spectrum of **5**-$^{13}CO$ is not consistent with a direct bonding interaction between the silicon and the carbonyl carbon.[14] Furthermore, the carbonyl exhibits a stretch at 1797 cm$^{-1}$ in the infrared, more than 300 cm$^{-1}$ higher than would be expected for a silaacyl.[15]

Compound **4** also reacts readily with a variety of other substrates (Scheme II). Cleavage of the Zr–Si bond of **4** with hydrogen (ca. 3 atm) in benzene-$d_6$ generates **1** and $PMe_3$ within minutes at 25 °C. In addition, insertion of ethylene into the Zr–Si bond also occurs at 25 °C, leading to $Cp_2Zr(CH_2$-$CH_2SiMe_2N^tBu)$ (**6**). Similar cleavage and insertion processes have been observed in the reactions of simple zirconium silyls with $H_2$ and ethylene.[13a,16] Metallacycle **6** is also formed in the reaction of **1** with ethylene at 50 °C, in which ethane is a byproduct. Initial hydrozirconation of ethylene, generating the ethyl derivative $Cp_2Zr(CH_2CH_3)(N^tBuSiMe_2H)$, is most likely the first step. Analogous to **3**, ethane elimination would generate the intermediate $Cp_2Zr(\eta^2$-$SiMe_2=N^tBu)$, which could then couple with another ethylene molecule to yield **6**.

Ring expansion also results from the treatment of **4** with formaldehyde at 25 °C in benzene-$d_6$. The insertion product, $Cp_2Zr(OCH_2SiMe_2N^tBu)$ (**7**), is also formed in the reaction of **1** with excess CO at 50 °C.[17] The $^{29}Si$ NMR spectrum of **7**-$^{13}CH_2$, which displays a doublet with $^1J_{Si–C} = 62$ Hz, establishes the presence of a Si–C bond and confirms the regiochemistry of the insertion. The reactivity of **4** toward unsaturated organic

(9) A crystal of **4** ($C_{19}H_{34}NPSiZr$, fw 426.77) measuring 0.50 × 0.38 × 0.30 mm and enclosed in a glass capillary was mounted on an Enraf-Nonius CAD-4 diffractometer, and cell parameters were determined: monoclinic space group $P2_1/c$ ($Z = 4$), with $\beta = 105.56$ (2)°, $a = 9.849$ (2) Å, $b = 13.441$ (3) Å, $c = 17.011$ (4) Å, and $V = 2169$ (2) Å$^3$. A total of 4966 unique reflections were measured (2.0° ≤ $\theta$ ≤ 27.5°), of which 3361 with $I > 3\sigma$ were used in the refinement (208 variables). Final agreement factors: $R_1 = 0.032$, $R_2 = 0.046$, and goodness of fit = 1.412. Full details of data collection and refinement are included in the supplementary material.

(10) (a) $Cp_2Zr(SiPh_3)Cl$, $d(Zr–Si) = 2.813$ (2) Å: Muir, K. W. J. Chem. Soc. A **1971**, 2663. (b) $Cp_2Zr(SiMe_3)(S_2CNEt_2)$, $d(Zr–Si) = 2.815$ (1) Å: Tilley, T. D. Organometallics **1985**, 4, 1452. (c) $(^tBuO)_3ZrSi(SiMe_3)_3$, $d$-(Zr–Si) = 2.753 (4) Å: Heyn, R. H.; Tilley, T. D. Inorg. Chem. **1989**, 28, 1768.

(11) Lukevics, E.; Pudova, O.; Sturkovich, R. Molecular Structure of Organosilicon Compounds; Ellis-Horwood: Chichester, 1989.

(12) Selected data for **5**: $^{13}C\{^1H\}$ NMR $\delta$ 290.68 (CO); $^{29}Si$ NMR (DEPT) $\delta$ −69.88 ($^2J_{SiC} = 24.1$ Hz); IR ($C_6H_6$) 1797 cm$^{-1}$ ($\nu_{CO}$).

(13) (a) Campion, B. K.; Falk, J.; Tilley, T. D. J. Am. Chem. Soc. **1987**, 109, 2049. (b) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. J. Am. Chem. Soc. **1989**, 111, 149.

(14) Typical values of $^1J_{SiC}$ are 50–60 Hz for sp$^3$-hybridized carbon. Larger $^1J_{SiC}$ would be expected for sp$^2$-hybridized carbon. For example, silyl-substituted acetylenes have $^1J_{SiC} = 70$–90 Hz and $^2J_{SiC} = 12$–18 Hz: Liepins, E.; Birgele, I.; Lukevics, E.; Bogoradovsky, E. T.; Zavgorodny, V. S. J. Organomet. Chem. **1990**, 393, 11.

(15) fac-$Re(CO)_3(diphos)(\eta^1$-$COSiPh_3)$, the only known $\eta^1$-silaacyl, exhibits an acyl stretch at 1490 cm$^{-1}$: Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. Inorg. Chem. **1977**, 16, 2281. $\eta^2$-Silaacyls exhibit stretches at comparable energies (<1500 cm$^{-1}$).[13]

(16) (a) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. Organometallics **1989**, 8, 324. (b) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. Organometallics **1989**, 8, 2284.

(17) This reaction involves the reduction of carbon monoxide by **1** to yield $Cp_2Zr(OCH_2SiMe_2N^tBu)$ (**7**). Studies to further elucidate the mechanism of this reaction are currently in progress.

molecules parallels that observed for $\pi$-complexes of group 4 metallocenes (e.g., $\eta^2$-olefin, alkyne, and imine complexes), which also yield five-membered metallacycles.[7b,18] Further investigations of the reactivity of **4** with organic and inorganic reagents are currently in progress and will be described in future publications.

**Supplementary Material Available:** Description of synthetic procedures and spectroscopic data for all new compounds, details of X-ray data collection and refinement for **4**, and tables of positional parameters, anisotropic thermal parameters, and intramolecular bond distances and angles for **4** (17 pages); listings of final structure factor amplitudes for **4** (17 pages). Ordering information is given on any current masthead page.

(18) For example, see: (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (c) Alt, H. G.; Herrmann, G. S. *J. Organomet. Chem.* **1990**, *390*, 159.

# Book Reviews

**Proceedings of General Physics of the Academy of Sciences of the USSR. Volume 11. Resonant Heterogeneous Processes in a Laser Field.** By V. A. Kravchenko, A. N. Orlov, Yu. N. Petrov, and A. M. Prokhorov (Institute of General Physics of the Academy of Sciences of the USSR), translated by S. A. Stewart. Nova Science Publishers: New York and Budapest. 1989. viii + 253 pp. $72.00. ISBN 0-941743-70-5.

This book is a translation of a monograph originally published in 1988. It presents a compendium of the results of experimental and theoretical research performed at the Institute of General Physics by the authors and co-workers. It is the first systematic treatment of laser-induced perturbations of molecular diffusion through porous membranes, regular pores and capillaries, and photosorption and surface photodiffusion of molecules.

This field of research is not widely investigated and is little known in the US. The authors make a convincing case that lasers can have strong effects on separation processes under certain circumstances. That is because separation processes often rely on small differences of weak molecular–surface interactions. The separation of one component of a mixture which is resonant with the laser field can be appreciably perturbed by even relatively weak fields of a few watts per $cm^2$. Often the influence of laser light is opposite to that of heat. For example, the diffusion of bromine through a silica porous glass can be dramatically slowed by an argon-ion laser because the molecule–surface adsorption interaction is increased by the field. In other cases using visible and infrared lasers, it is shown that the permeability of finely porous membranes may be controlled by illumination with laser light.

It is still difficult to assess whether laser-assisted separation processes can compete on an industrial scale. The overwhelming problem has always been the relative expense of laser photons as a reagent. However, the relatively weak fields required to alter separation coefficients and new advances in low-cost diode-pumped tunable solid-state lasers suggest that this largely unknown field is worthy of increased attention.

In seven chapters, the authors discuss general physical principles, interactions between pairs of molecules when one is excited, selective diffusion, photosorption and photodiffusion at a surface, and photoprocesses in pores and capillaries. Finally a theoretical model is presented for the effective absorption potential of a molecule in a resonant laser field, which the authors believe is the dominant mechanism for laser-influence of surface diffusion. The theoretical treatments of these processes are detailed and complete. The limited amount of experimental data reflect the nature of this field, but nevertheless these experiments are insightful and carefully performed to rule out trivial thermal effects. This book is thought-provoking and it provides a systematic treatment of the theoretical aspects which cannot be found elsewhere in a single source. It would be of particular interest to workers on the cutting edge of separation science.

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**Fluoride Glasses: Critical Reports on Applied Chemistry. Volume 27.** Edited by Alan E. Comyns. John Wiley & Sons for the Society of Chemical Industry: New York and Chichester. 1989. ix + 219 pp. $89.95. ISBN 0-471-92352-4.

This first monograph on fluoride glasses presents a thorough review of a highly empirical field of fundamental and applied research, with each chapter prepared by a major contributor to the research and/or technology being discussed. Each topic is presented authoritatively, and the organization and presentations are largely appropriate for a field that is advancing without clear guidance from fundamental principles. A brief overview of the field by the editor, which includes a useful nomenclature key, is followed by chapters by eight different (sets of) authors. Though some overlap and repetition is unavoidable, these chapters focus on well-defined subsections of the problems and advances in the development and application of fluoride glasses.

Following the Introduction, M. Poulain places the fluoride glasses in context with what is known about glasses in general (Chapter 2), while also describing the particular problems of synthesis of fluoride glasses, including recognition and control of the composition of the glasses produced. Chapter 3, by D. R. MacFarlane and L. J. Moore, dwells on the nature and control of the nucleation of crystal phases that tend to spoil the optical properties of the fluoride glasses. In Chapter 4, which seems a bit out of position, B. E. Kinsman considers one aspect of the basics of fluoride glass preparation, namely the chemical and physical properties of raw materials, such as zirconium fluoride, and the preparation/availability of these materials for production of fluoride glasses having desirable properties. The description of the optical properties and the factors that limit the desirable characteristics of fluoride glasses, by P. W. France, S. F. Carter, C. R. Day, and M. W. Moore in Chapter 5, will be the highlight of the monograph for many readers. The transparency properties of fluoride glasses, particularly in the near-infrared spectral region, have been the driving interest for a large fraction of the research and development devoted to these materials, so the degree to which their promise as optical materials is being realized, through advances in the technology, is of particular concern. More general physical and chemical properties of fluoride glasses are considered in Chapter 6 (J. M. Parker) and Chapter 7 (A. B. Seddon) while the monograph is completed by discussions of the techniques of fluoride-glass fibre drawing (H. W. Schneider: Chapter 8) and applications of fluoride-glass optics (G. Maze: Chapter 9).

Though it does not appear that new unifying principles have emerged through the development of this monograph, this book should be of particular value to researchers with a casual or emerging interest in fluoride glass research/technology, while also providing a compendium of useful information to those individuals thoroughly involved in the advancement of this important, but quite specialized, field of study.

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