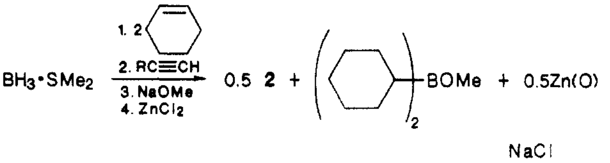
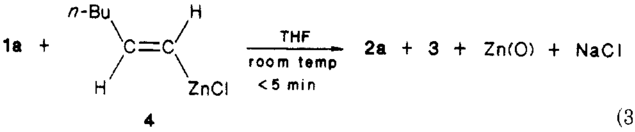
to a slurry of dry, methanol-free NaOMe in THF generates the corresponding sodium methoxy-(*E*)-1-alkenyldicyclohexylborates(1−). Transfer of this resulting solution to zinc chloride in THF affords dienes in excellent overall yield (Table I).[7] Unfortunately, the zinc-promoted reaction is



(2)

not nearly as general as the copper-promoted version of the reaction.[3] For example, stereochemical integrity of the alkenyl unit is not retained in the present case, as sodium methoxy-(*Z*)-1-alkenyldialkylborates(1−) provide nearly pure (*E*,*E*)-conjugated dienes on reaction with $ZnCl_2$.

Perhaps the most intriguing aspect of this process is the mechanism by which coupling occurs. Believing that initial transmetalation from alkenyl boron "ate" complex to the alkenylzinc reagents had occurred, we attempted to couple **1a** with an alkenylzinc chloride derived by transmetalation with $ZnCl_2$ from the corresponding alkenyllithium reagent.[8] In fact, reductive coupling proceeded instantaneously, providing a quantitative yield of diene as in previous reactions with $ZnCl_2$. Curiously, alkenylboron "ate" complexes derived ultimately from internally substituted alkynes (e.g., 4-octyne) do not undergo reductive coupling with either the corresponding alkenylzinc chloride or $ZnCl_2$. Protonolysis of reaction mixtures with glacial acetic acid in these instances revealed quantitative recovery of *cis*-4-octene. Efforts to achieve cross-coupling also failed, as reaction of **1b** with **4** provided a nearly statistical mixture of three dienes.



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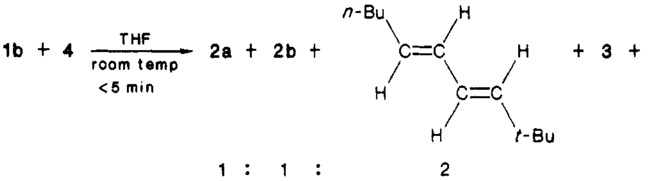

Zn(O) + NaCl (4)

In instances where silver salts or copper salts promote dimerization reactions of boron "ate" complexes, the actual reductive coupling is believed to arise through thermal decomposition of corresponding organosilver or organocopper reagents, produced as intermediates in these reactions.[3,4] As mentioned above, there is little precedence for this process in organozinc chemistry. Indeed, we have prepared distyrylzinc reagents by addition of 2 equiv of alkenyllithium to 1 equiv of $ZnCl_2$. As expected, no reductive coupling occurs over a period of 24 h. However, when methyl dialkylborinates (e.g., *B*-methoxy-9-BBN) are added to the reaction mixture, a slow reaction occurs (72 h), providing 54% of coupled product. Stronger Lewis acids (e.g., $BF_3·Et_2O$) were ineffective in promoting reductive coupling. Neither sodium methoxytrialkylborates(1−) nor corresponding sodium methoxyaryldialkyl- or methoxyalkynyldialkylborates(1−) undergo reaction with $ZnCl_2$. Finally, a variety of Cd(II) and Hg(II) salts are clearly less effective than Zn(II) salts in promoting the desired reaction with sodium methoxyalkenyldialkylborates(1−).[9]

It is tempting to suggest that electron transfer from the electron-rich, readily oxidizable alkenylboron "ate" complex[10] to the alkenylzinc halide[11] somehow initiates reductive coupling. Similar processes have previously been reported for other organometallic pairs of reagents involved in reductive coupling reactions.[12] However, detailed mechanistic postulates for this unique reaction must await further studies.

Acknowledgment. We thank the National Institutes of Health (GM 31013), the Research Corp., and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(7) A simple workup procedure allowed isolation of pure dienes. Thus, THF removed *in vacuo* was replaced by pentane. Ethanolamine (1 equiv) was added to the reaction mixture, precipitating the ethanolamine dicyclohexylborinate ester. The resulting slurry was filtered through a thin pad of Celite to remove the borinate esters, along with the Zn and NaCl. Removal of pentane and simple distillation or recrystallization provided pure dienes.

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(9) Less than 50% yields of symmetrical 1,3-dienes were realized upon addition of a variety of cadmium(II) and mercury(II) salts to the sodium methoxyalkenyldialkylborates(1−).

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Isolation and Characterization of the First Simple Tantalacyclobutane Complexes[1]

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Summary: *cis*,*mer*-$Ta(CHCMe_3)Cl_3(THF)_2$ reacts with $LiO\text{-}2,6\text{-}C_6H_3(CHMe_2)_2·Et_2O$(LiDIPP·$Et_2O$) to give $Ta(CHCMe_3)(DIPP)_3(THF)$. $Ta(CHCMe_3)(DIPP)_3(THF)$ reacts with ethylene to give colorless $\overline{TaCH_2CH_2CH_2}(DIPP)_3$ and with styrene to give orange $\overline{TaCHPhCH(CMe_3)CH_2}(DIPP)_3$. $\overline{TaCHPhCH(CMe_3)CH_2}(DIPP)_3$ crystallizes in the space group $P2_1/n$ with a = 21.338 (11) Å, b = 11.699 (5) Å, c = 37.198 (23) Å, β = 102.66 (5)°, Z = 8, and V = 9060.1 Å^3. $\overline{TaCHPhCH(CMe_3)CH_2}(DIPP)_3$ reacts with THF to give solely $Ta(CHPh)(DIPP)_3(THF)$. Addition of *cis*-2-pentene to $Ta(CHCMe_3)(DIPP)_3(THF)$ leads to rapid, but relatively short-lived metathesis. Tantalacyclobutane complexes react with ketones and aldehydes to give a Wittig-like reaction of an incipient alkylidene complex and/or oxytantalacyclohexane complexes, the products of insertion of the carbonyl bond into the Ta–C_α bond.

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(1) Multiple Metal–Carbon Bonds. Part 44. For part 43 see ref 3.

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Only two types of d^0 metallacyclobutane complexes have been reported. The best known is that containing the bis(cyclopentadienyl) group 4 metal unit (M = Ti[2a,b] or Hf[2c]).[2d] A rather different recent example contains tungsten, two alkoxide ligands, and an imido ligand.[3] Here we report the first observable[4] tantalacyclobutane complexes, examples that contain 2,6-diisopropylphenoxide (DIPP) ligands. The DIPP ligands were chosen on the basis of their ability to stabilize tungstenacyclobutadiene complexes.[6]

cis,mer-$Ta(CHCMe_3)Cl_3(THF)_2$ can be prepared from $TaCl_5$ in two steps.[7] Three equivalents of solid Li-DIPP·Et_2O were added to a solution of $Ta(CHCMe_3)Cl_3(THF)_2$ in a 9:1 mixture of diethyl ether and THF at −20 °C. After the solution was warmed to 25°C, lithium chloride was filtered off. The ether was removed stepwise from the solution in vacuo, and yellow-orange crystals were collected periodically. The product (~85% yield on a scale of ~20 g) has been identified as $Ta(CHCMe_3)(DIPP)_3(THF)$ on the basis of elemental analysis[8] and ^{1}H and ^{13}C NMR spectra.[9] The yield of $Ta(CHCMe_3)(DIPP)_3(THF)$ on a 20-g scale is 60–70% if $Ta(CHCMe_3)Cl_3(THF)_2$ is prepared in situ from $Ta(CH_2CMe_3)_2Cl_3$ in a 3:1 mixture of ether and THF. We assume $Ta(CHCMe_3)(DIPP)_3(THF)$ has a trigonal-bipyramidal geometry in which the DIPP ligands are equatorial. The low value for $J_{CH\alpha}$[9] suggests that the neopentylidene ligand is highly distorted toward a species in which the $Ta{=}C_\alpha{-}C_\beta$ angle approaches 180°.[5a] $Ta(CHCMe_3)(DIPP)_3(THF)$ reacts with acetone (1 h, 25 °C, 95% by GLC), benzaldehyde (4 h, 40 °C, 96% by GLC, trans/cis = 1.9), benzophenone (8 h, 40 °C, 88% by NMR), and *N,N*-dimethylformamide (10 h, 40 °C, 95% by NMR, all trans) to give the expected products of a Wittig-like reaction[10] in the yields quoted.

A solution of $Ta(CHCMe_3)(DIPP)_3(THF)$ in ether reacts rapidly at 25 °C with 30 psi of ethylene to give a colorless solution that contains 0.90 equiv of *tert*-butylethylene (by GLC). The oil that was left behind when all solvents were removed was dissolved in pentane and that solution was stored at −35 °C to give colorless crystals of $TaCH_2CH_2CH_2(DIPP)_3$ in ~70% yield.[11] The ^{1}H NMR spectrum of $TaCH_2CH_2CH_2(DIPP)_3$ shows a multiplet of area 4 for H_α at 3.86 ppm and a multiplet for H_β of area 2 at 0.48 ppm, while the ^{13}C NMR spectrum shows a signal for C_α at 96.1 ppm (J_{CH} = 147 Hz) and one for C_β at −0.68 ppm (J_{CH} = 150 Hz). These NMR parameters are similar to those found for unsubstituted titanacyclobutane[2a] and tungstenacyclobutane complexes.[3] $TaCH_2CH_2CH_2(DIPP)_3$ will react with 1 equiv of pyridine to give a white monoadduct that at 25 °C (by ^{1}H NMR) appears to be in equilibrium with the pyridine-free tantalacycle. With time in the presence of greater than 1 equiv of pyridine dark red solutions are obtained; no product(s) has (have) yet been identified.

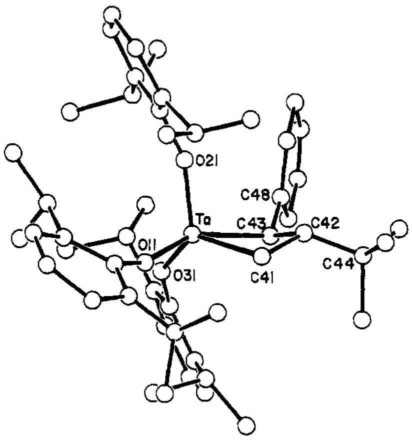

Figure 1. A view of one of the two crystallographically independent molecules of $TaCHPhCH(CMe_3)CH_2[O\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_3$. Spheres of arbitrary radius are employed in order to allow a clear view of the ligand system.

$Ta(CHCMe_3)(DIPP)_3(THF)$ reacts with 1 equiv of styrene in <30 min in ether to give a single product (by ^{1}H NMR) that can be isolated as orange crystals in only ~60% yield[12a] due to its high solubility. ^{1}H and ^{13}C NMR data[12b] suggested that the product was a metallacycle of empirical formula $Ta[C_3H_4(C_6H_5)(CMe_3)](DIPP)_3$ in which either the phenyl group or the *tert*-butyl group was bound to a β-carbon atom (δ 42.9 (d, J_{CH} = 125 Hz)). An X-ray structural study[13] showed that the β-substituent is the *tert*-butyl group (Figure 1) and that therefore (most likely) one of two possible initial tantalacyclobutane complexes loses an olefin, which then re-adds to the incipient alkylidene complex; one of the two possible sequences is shown in eq 1. Overall $TaCHPhCH(CMe_3)CH_2(DIPP)_3$ is approximately halfway between a square pyramid and a trigonal bipyramid. The Ta-C_α bond lengths average 2.18 (2) Å, and the ring is *bent* ($C_\alpha TaC_\alpha/C_\alpha C_\beta C_\alpha$ dihedral angle ~28°).[14] The phenoxide ligands have Ta–O–C angles

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(2) (a) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. (c) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (d) 1-Sila-3-zirconacyclobutane complexes have been prepared: Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651.

(3) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

(4) Tantalacyclobutane complexes have been proposed as intermediates in a number of systems.[5] None has been observed.

(5) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. (c) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.

(6) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

(7) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(8) Anal. Calcd for $TaC_{45}H_{69}O_4$: C, 63.20; H, 8.15. Found: C, 63.13; H. 8.09.

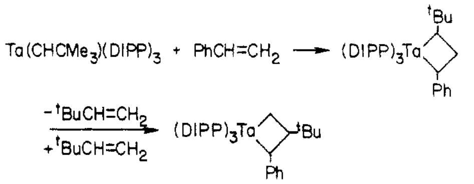
(9) $\delta(H_\alpha)$ 5.73, $\delta(C_\alpha)$ 227.1 ($J_{CH\alpha}$ = 95 Hz).

(10) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

(11) Anal. Calcd for $TaC_{39}H_{57}O_3$: C, 62.05; H, 7.63. Found: C, 62.21; H, 7.58.

(12) (a) Anal. Calcd for $TaC_{49}H_{69}O_3$: C, 66.34; H, 7.86. Found: C, 66.61; H, 7.63. (b) ^{1}H NMR (C_6D_6): δ 3.10–2.85 (m, area 2), 2.17 (d, area 1, J_{HH} = 12 Hz), 1.57 (m, area 1). ^{13}C NMR δ 81.9 (d, J_{CH} = 133 Hz), 63.8 (t, J_{CH} = 129 Hz), 42.9 (d, J_{CH} = 125 Hz).

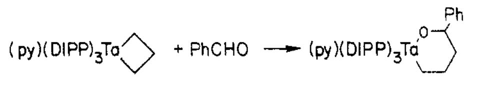
(13) (a) Crystal data: space group $P2_1/n$ with a = 21.338 (11) Å, b = 11.699 (5) Å, c = 37.198 (23) Å, β = 102.66 (5)°, Z = 8, M_r 887.13 g, V = 9060.1 Å^3, ρ(calcd) = 1.301 g cm^{-3}. Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation. AXIAL photographs were taken on the diffractometer about each of the reciprocal axes to check that the unit cell lengths were correct. The program TRACER was run on the unit cell, calculated with 25 high angle reflections ($\sigma > 15^0$), and revealed no higher symmetry. Data collection, reduction, and refinement procedures can be found elsewhere.[13b] A total of 11816 reflections were collected in the range $3° < 2\theta < 45°$ with the 7831 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was carried out in two blocks (224 variables each) using SHELX-76. Final R_1 = 0.084 and R_2 = 0.115. A semiempirical absorption correction was applied (μ = 5.8 cm^{-1}). Two crystallographically independent but closely analogous molecules are present in the asymmetric unit. Only the Ta atoms were refined anisotropically. Most hydrogen atoms could be placed in calculated positions (C–H = 0.95 Å) and were constrained to ride on their respective carbon atoms. Hydrogen atoms on the TaC_3 ring carbon atoms could not be located and were ignored. A final difference Fourier map showed no significant features. (b) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* 1980, *19*, 3379.


(1)

ranging from 146 (1)° to 157 (1)°, typical of what has been found in other d^0-phenoxide complexes.[15] The tantalacyclic ring is readily broken up by THF (in large excess) to give $Ta(CHPh)(DIPP)_3(THF)$ (only)[16] in equilibrium with the tantalacycle.

When 100 equiv of *cis*-2-pentene were added to $Ta(CHCMe_3)(DIPP)_3(THF)$ in pentane, it was metathesized to both cis and trans products in 10 min. Thereafter no further activity was observed. We assume that trisubstituted tantalacycles are involved in the metathesis reaction but do not know yet whether they, or alkylidene complexes, dominate under the reaction conditions. Previous metathesis studies using tantalum complexes[5c] suggested that catalytic activity is limited as a result of rearrangement of the alkylidene ligand to an olefin.

Tantalacycles are potential "Wittig" reagents. For example, $\overline{\mathrm{TaCH_2CH_2C}}\mathrm{H_2(py)(DIPP)_3}$ reacts with 1.5 equiv of benzophenone at 60 °C in C_6D_6 in 35 min to give an 86% yield of 1,1-diphenylethylene (by NMR). However, it reacts with benzaldehyde at 25 °C for 60 min in ether to give an 80% yield of a white powder (crystallized from ether or pentane) that analyzes as $Ta(C_3H_6)(PhCHO)(DIPP)_3(py)$.[17] On the basis of ^1H and ^{13}C NMR results we propose that the oxytantallacyclohexane complex shown in eq 2 has formed.[18] The nature of the tantalacycle is an important factor in determining "Wittig" vs. "insertion" chemistry. For example, $\overline{\mathrm{TaCH_2CH_2C}}\mathrm{H_2(DIPP)_3}$ reacts with 1.5 equiv of acetone at 25 ° to give 100% insertion product (by NMR), but $\overline{\mathrm{TaCHPhCH(CMe_3)C}}\mathrm{H_2(DIPP)_3}$ reacts with acetone under identical conditions to give 86% of a *single* product ($Me_2C{=}CHPh$) and 91% $Me_3CCH{=}CH_2$ (by NMR), as one might expect for a more crowded tantalacyclic ring system.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Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant CHE 84-02892, and K.C.W. thanks the Dow Chemical Corp. for a predoctoral fellowship. We also thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10 RR02243).

Supplementary Material Available: Tables of final atomic coordinates and temperature factors for $\overline{\mathrm{TaCHPhCH(CMe_3)}}\mathrm{CH_2(DIPP)_3}$ as well as fully labeled diagrams for both of the crystallographically independent molecules in the asymmetric unit (6 pages); a listing of observed and calculated structure factors for $\overline{\mathrm{TaCHPhCH(CMe_3)C}}\mathrm{H_2(DIPP)_3}$ (47 pages). Ordering information is given on any current masthead page.

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(14) The ring in $\overline{\mathrm{WCH(SiMe_3)CH(SiMe_3)C}}\mathrm{H_2[N\text{-}2,6\text{-}C_6H_3(CHMe_2)_2][OCMe(CF_3)_2]_2}$ is bent by ~25°. Bis(cyclopentadienyl)titanacyclobutane complexes contain virtually planar TiC_3 rings.[2b]

(15) See, for example: Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

(16) In C_6D_6 $\delta(H_\alpha)$ 8.49, $\delta(C_\alpha)$ 221.1 ppm (d, $J_{CH} = 114$ Hz).

(17) (a) Anal. Calcd for $TaC_{51}H_{68}O_4N$: C, 65.15; H, 7.31. Found: C, 64.74; H, 6.87.

(18) Benzaldehyde has been observed to insert into the Hf–C_α bond in $Hf(\eta^5\text{-}C_5H_5)_2(C_3H_6)$[2c] and formaldehyde into the Zr–C_α bond in a 1-sila-3-zirconacyclobutane complex.[2d] ^1H and ^{13}C NMR spectra of $\mathrm{(DIPP)_3}\overline{\mathrm{TaCH_2CH_2CH_2CHPhO}}$ are very similar to those of the related hafnium and zirconium complexes.

Book Reviews

Chemistry of Pseudohalides. Edited by A. M. Golub, H. Köhler, and V. V. Skopenko. Elsevier, Amsterdam. 1986. 479 pages. $109.25.

This volume, the twenty-first in a series of monographs covering topics in inorganic and general chemistry, is an up-dated English translation of *Chemie der Pseudohalogenide*, edited by A. M. Golub and H. Köhler, and published in the German Democratic Republic in 1979. The updating is much more than cosmetic. Whereas the original German version generated 2705 references in the editors' attempt to cover all important publications on the inorganic chemistry of the pseudohalides up to 1974, the English version, which covers the pseudohalide literature up to the end of 1980, includes an impressive total of 4217 references. This whopping increase of 56%, in a scant 6 years, offers dramatic evidence of the extent of research activity in an area that some chemists would consider to be off the beaten track. Indeed, the most heavily referenced chapter (that on thiocyanates) experienced a doubling of references, from 812 to 1630, during that brief period.

Following a short introductory chapter, individual chapters are devoted to the chemistry of each of the ions normally thought of as being pseudohalides (N_3^-, CN^-, NCO^-/CNO^-, SCN^-, and $SeCN^-$) as well as to two that, while appropriate, are more obscure ($C(CN)_3^-$ [tricyanomethanide] and $N(CN)_2^-$ [dicyanamide]). The last chapter deals with a comparative characterization of the pseudohalides,including the acidity and structure of the hydropseudohalic acids, the solubility of metal pseudohalides and metal halides, the ligand characteristics and donor activity of the pseudohalides, and mixed complexes of linear and nonlinear pseudohalides.

The rich diversity found in the chemistry of the pseudohalides is largely derived from their ability to function as ambidentate ligands. The editors have left very few stones unturned in their thorough and well-organized review of the pseudohalides' inorganic chemistry. Every bonding possibility is explored for each ion. The profusion of tabulated single-crystal X-ray structural data included is especially noteworthy, in this context. Extensive coverage of IR and, where appropriate, NMR spectroscopic data is also provided. The factors determining the bonding mode adopted in a given situation are compared and critically evaluated.

All of the free pseudohalogens are described, as are the pseudohalide complexes of all the elements save carbon which, for obvious reasons, is given only passing mention. In addition, a variety of special applications are discussed, including the use of several of the pseudohalides in chemical analyses, organic syntheses, the chemical industry, environmental protection, biochemistry, and medicine.

The last of the chalcogen pseudohalides, $TeCN^-$, is conspicuous by its virtual absence. While not worthy of a separate chapter, more is known about it than is indicated by the three references cited in the text.

Of much greater concern is the fact that the coverage of the text is already 6 years out-of-date. Nonetheless, it should be a mandatory addition to every chemistry library, for no other text exists that approaches either its currency or its scope, as far as pseudohalide chemistry is concerned. It stands as a fitting tribute to Professor Golub, who died in 1977, shortly after the original manuscript had been completed.

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