than it is in the red form. Models of the possible structures confirm that the only other configuration in which the "extra" oxine bonding is similar is that with the nitrogen hydrogen bonded to one of the uranyl oxygens instead of an adjacent ligand oxygen. This configuration has a less dense packing in the ligand coordination plane, which may account for the lower thermal stability of the orange form.

In solution both the red and orange forms of $UO_2Ox_2 \cdot HOx$ are converted at high pH to the complex anion $UO_2Ox_3^-$, in which all three oxinates act as bidentate ligands. Although previous studies[7,8,13] have concluded that the $UO_2Ox_3^-$ structure is retained under acidic conditions, the present work establishes that both the red and orange forms of $UO_2Ox_2 \cdot HOx$ yield solvated UO_2Ox_2 and free oxine in DMSO solutions. However, titrations of $UO_2Ox_3^-$ with acid indicate the presence of a species that is a stronger acid than free oxine.[7,8,13] A possible explanation is that at the equivalence point the keto form of the "solvate" oxine is stabilized by coordination through the oxygen atom to uranium to give a protonated ring nitrogen (and stronger acid than free oxine). Neutralization of this proton frees the ring nitrogen to occupy a coordination site on the uranium atom. The nmr spectrum of the complex anion (Figure 2D) indicates that all three ligands are bound equivalently which implies that the uranyl group has a coordination number of 6 in this compound. Because of steric considerations, the three ligands probably are twisted, "propeller fashion," out of the plane normal to the linear uranyl group.

Earlier workers[7] have suggested that the red color which results from the dissolution of the olive green UO_2Ox_2 complex is due to the decomposition of the "normal" chelate

$$3UO_2Ox_2 \xrightarrow{\text{solvent}} UO_2^{2+} + 2UO_2Ox_3^-$$

However, the nmr data establish that there is no decomposition of UO_2Ox_2 and that it is $UO_2Ox_2 \cdot HOx$ which decomposes to give solvated UO_2Ox_2 and free oxine. The color change associated with dissolution of the green chelate probably is due to coordination by the solvent because the complexes of higher coordination number are red in both solid and solution phases. The maroon trihydrate may contain the three water molecules in the coordination sphere also because high temperatures are required for their removal. This is consistent with other observations that the uranyl group tends to coordinate "extra" donor molecules.[20-22]

Acknowledgment.—This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(11-1)-34, Project No. 45.

---

(20) H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **4**, 375 (1947).
(21) L. Sacconi, G. Caroti, and P. Paoletti, *J. Chem. Soc.*, 4257 (1958).
(22) M. Bartušek and L. Sommer, *J. Inorg. Nucl. Chem.*, **27**, 2397 (1965).

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Fluxional Behavior of Group IV Trimethylindenyl Compounds

By P. E. RAKITA and A. DAVISON

Received December 19, 1968

The indenyltrimethyl compounds of silicon, germanium, and tin have been investigated by variable-temperature proton magnetic resonance spectroscopy and shown to be fluxional molecules. For $(CH_3)_3SnC_9H_7$ the complete range from limiting high- to limiting low-temperature behavior was observed. The presence of tin to ring hydrogen coupling confirms the *intra*molecular nature of the rearrangement. Relative signs of the proton–proton and tin–proton coupling constants in $(CH_3)_3SnC_9H_7$ have been determined.

Our studies[1] of main group cyclopentadienyl compounds showed, for all of the tin compounds studied, only limiting, high-temperature, "dynamic" spectra even as low as −100°. Furthermore, as expected, only average values of ^{117}Sn and ^{119}Sn-H coupling constants were observed for ring methyl protons and the ring hydrogens. In view of the observation of Cotton and coworkers[2] that $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_9H_7)$ apparently exhibits nonfluxional behavior, we felt the scope of our investigation should be extended to include the σ-indenyl compounds of the group IV elements.

Experimental Section

General Data.—All manipulations were carried out under a dry N_2 atmosphere or *in vacuo*. Infrared spectra were recorded as liquid films between KBr plates on a Perkin-Elmer 337 spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6-D spectrometer. Nmr spectra were obtained at 60 MHz utilizing a Varian Associates A-60 spectrometer equipped with a variable-temperature probe. Temperature calibrations were made with methanol or ethylene glycol. The spectra of indenyltrimethylsilane and -germane were recorded on neat liquids, while those for indenyltrimethylstannane were recorded in 50% v/v CS_2 in the range 0 to −60° and as the neat liquid from 0 to +140°. Cyclohexane was used as an internal reference.

Preparation of Indenyltrimethylsilane.—A modification to the published procedure[3] was used to obtain indenyltrimethylsilane

---

(1) A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968).
(2) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).
(3) L. H. Sommer and N. S. Marans, *ibid.*, **73**, 5138 (1951).

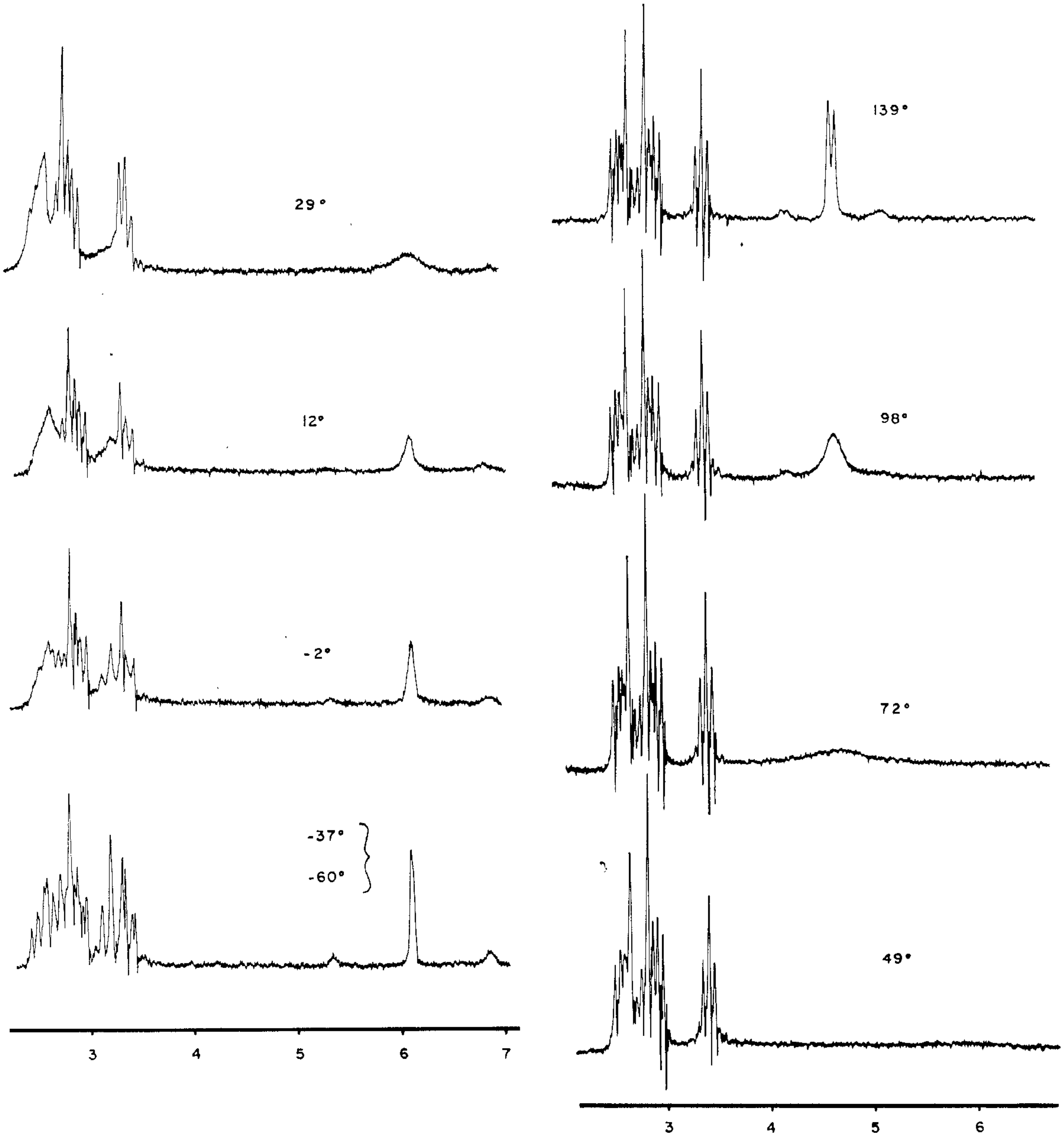


Figure 1.—The proton magnetic resonance spectra of indenyltrimethylstannane, $(CH_3)_3SnC_9H_7$, in the region τ 2–7 at various temperatures. Spectra below 0° were recorded on a 50% v/v solution in CS_2; the others, as neat liquids.

in 55% yield. The product, a clear liquid, bp 87° (4 mm), $n^{25.5}D$ 1.5404 [lit.[3] bp 87° (4 mm), $n^{20}D$ 1.5423], turns pale yellow on standing for 1–2 days at −15°. *Anal.* Calcd for $C_{12}H_{16}Si$: C, 76.53; H, 8.56. Found: C, 76.51; H, 8.56. The mass spectrum showed the molecular ion ($C_{12}H_{16}{}^{28}Si$) at *m/e* 188. The infrared spectrum showed: 3117 (w), 3065 (m), 3015 (w), 2953 (s), 2896 (m), 1621 (w), 1600 (w), 1573 (w), 1527 (w), 1443 (s), 1423 (w), 1400 (w), 1353 (w), 1262 (m), 1250 (s), 1221 (m), 1190 (m), 1110 (w), 1020 (s), 975 (m), 930 (w), 877 (m), 832 (vs), 790 (m), 757 (s), 726 (w), 710 (m), 690 (w), 610 (m) cm^{-1}.

Preparation of Indenyltrimethylgermane.—Indenyllithium was prepared by adding distilled indene in diethyl ether to butyllithium in hexane and stirring for 12 hr. To the resultant yellow solution was added a slight excess of chlorotrimethylgermane in ether and the mixture was stirred at reflux for 7 hr. Lithium chloride was filtered off under nitrogen and the ether and hexane were distilled at atmospheric pressure. Vacuum distillation yielded a colorless liquid, bp 72° (0.8 mm), $n^{23}D$ 1.5605. *Anal.* Calcd for $C_{12}H_{16}Ge$: C, 61.90; H, 6.93. Found: C, 61.76; H, 7.27. The mass spectrum showed the molecular ion ($C_{12}H_{16}{}^{74}Ge$) at *m/e* 234. The infrared spectrum showed: 3116 (vw), 3069 (m), 3018 (vw), 2975 (m), 2910 (m), 1522 (w), 1453 (w), 1445 (s), 1402 (w), 1352 (w), 1236 (m), 1220 (m), 1193 (w), 1110 (vw), 1018 (m), 1000 (m), 978 (s), 929 (w), 858 (w), 820 (vs), 789 (w), 754 (vs), 727 (w), 710 (s), 595 (s), 560 (m), 533 (w), 429 (m) cm^{-1}.

Preparation of Indenyltrimethylstannane.—The compound $(CH_3)_3SnC_9H_7$ was prepared in a similar manner to indenyltrimethylgermane. It was obtained as a very pale yellow liquid after two distillations at 64° (0.15 mm) $n^{21}D$ 1.5941. Unlike the corresponding silicon and germanium compounds, indenyltrimethylstannane is extremely water sensitive. *Anal.* Calcd for $C_{12}H_{16}Sn$: C, 51.67; H, 5.78. Found: C, 51.04; H, 6.00. The mass spectrum showed molecular ion ($C_{12}H_{16}{}^{120}Sn$) at *m/e* 280. The infrared spectrum showed: 3097 (w), 3064 (m), 3045 (vw), 2982 (m), 2917 (s), 2850 (m), 1700 (w), 1675 (vw), 1608 (vw), 1589 (w), 1505 (w), 1452 (m), 1440 (vs), 1418 (vw), 1380 (vw), 1353 (w), 1313 (w), 1284 (w), 1223 (s), 1194 (m), 1184 (w), 1153 (vw), 1141 (w), 1105 (w), 1063 (w), 1013 (m), 979 (w), 935 (vs), 919 (vs), 854 (s), 778 (vs), 760 (vs), 744 (vs), 728 (s), 710 (s), 629 (vw), 587 (vw), 555 (w), 521 (s), 498 (m), 420 (s) cm^{-1}.

Results

Proton Magnetic Resonance Spectra.—The variable-temperature proton nmr spectra of the $(CH_3)_3MC_9H_7$ compounds (M = Si, Ge, and Sn) are displayed in Figures 1–3. Only in the case of indenyltrimethylstannane were we able to observe the complete range of limiting low- to limiting high-temperature spectra. At temperatures below −37°, $(CH_3)_3SnC_9H_7$ exhibits a spectrum characteristic of a "static" σ-indenyl compound. The four aromatic hydrogens give a complex ABCD pattern at $\tau \sim 2.75$. The olefin protons show the AB pattern of an ABX spectrum centered at τ 3.31. The tertiary X proton is a complex peak at τ 6.13 ($|J_{^{117}Sn,^{119}Sn-H}|$ = 91 Hz). The trimethylstannyl resonance occurs at τ 10.08 ($|J_{^{117}Sn-H}|$ = 51.5 Hz and $|J_{^{119}Sn-H}|$ = 54 Hz). Integration gives the expected 4:1:1:1:9 ratios. As the temperature is raised from −37°, the resonances at τ 3.20 and 6.13 first broaden and then collapse completely by +49°. At the same time the aromatic resonances at τ 2.75 undergo changes and at temperatures above +49° a symmetric AA′BB′ pattern results. The resonance centered at τ 3.42 also changes. At −2° it is a complex asymmetric pattern which at higher temperatures is transformed into a symmetric triplet (3.5 Hz, relative intensity 1, $|J_{^{117}Sn,^{119}Sn-H}|$ = 12 Hz). Above +72° a new resonance appears at a position midway between the original resonances at τ 3.2 and 6.1. At temperatures greater than ~140° the "dynamic" spectrum is obtained. The new peak at τ 4.66 is a well-resolved doublet (the X part of an AX_2 system J_{AX} = 3.5 Hz) of relative intensity 2 with tin satellites ($|J_{^{117}Sn,^{119}Sn-H}|$ = 54.5 Hz) unresolved. The resonance of the trimethylstannyl group with its tin coupling remains unaltered throughout the temperature range.

A similar pattern of behavior is observed for indenyltrimethylgermane (see Figure 2). However, the onset of the changes described above is approximately 135° higher and as a consequence the full range of spectral changes was not observed. At temperatures below +134° the spectrum is that characteristic of a σ-indenyl group with peaks at $\tau \sim 2.8$ (aromatic multiplet), τ 3.35 (AB part of ABX due to olefinic hydrogens), τ 6.50 (X part due to tertiary hydrogen), and a singlet at τ 10.02 (trimethylgermyl protons). In the temperature range 134–167° the same general pattern of behavior as that already described for the tin compound occurs. In fact the spectrum of indenyltrimethylgermane at 134° is identical in every respect with that of indenyltrimethylstannane at −2°.

Similarly for indenyltrimethylsilane the spectral changes do not begin to manifest themselves until about +180° where parts of the spectrum have just begun to broaden. The resonances at τ 3.27, 3.59, and 6.71 resemble the corresponding ones in the tin spectrum at −2°.

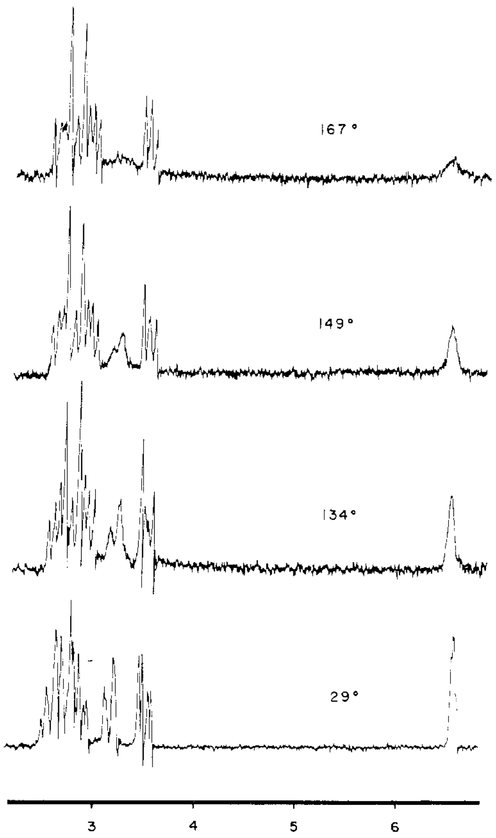


Figure 2.—The proton magnetic resonance spectra of indenyltrimethylgermane, $(CH_3)_3GeC_9H_7$, in the region τ 2–7 at several temperatures.

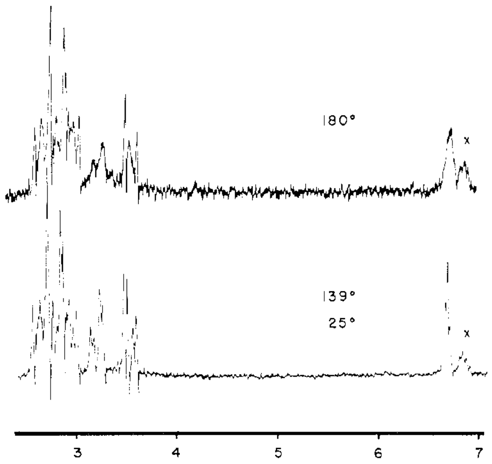


Figure 3.—The proton magnetic resonance spectra of indenyltrimethylsilane, $(CH_3)_3SiC_9H_7$, in the region τ 2–7 at three temperatures. The impurity (×) occurs at τ 6.91.

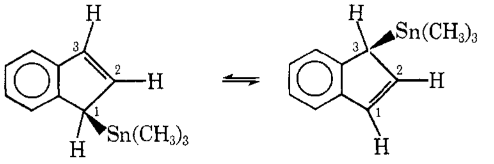
The proton nmr spectrum of a neat sample of allyltrimethylstannane was recorded at 35 and at 150° with no observable change. Another sample of allyltrimethylstannane containing a small amount of bromotrimethylstannane likewise showed no change at both temperatures.

Mass Spectra.—All three indenyltrimethyl compounds had peaks in their mass spectra which correspond to the molecular ions $C_{12}H_{16}M^+$. The fragmentation patterns for all three compounds were very similar. The most prominent peaks were the $(CH_3)_3M^+$

ions. Other prominent peaks included $C_{11}H_{13}M^+$, $C_9H_7M^+$, $C_2H_6M^+$, CH_3M^+, $C_9H_8^+$, $C_9H_7^+$, M^+ (M = Si, Ge, Sn).

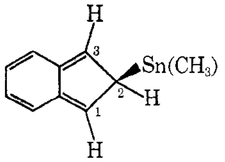
Discussion

The nmr spectra of indenyltrimethylstannane below −37° (Figure 1) are characteristic of a "static" σ-bonded structure. The spectra undergo considerable change and eventual simplification as the temperature is increased. From the appearance of the spectra in the two limits, slow exchange "static" and fast exchange "dynamic," and the observation of tin to proton coupling in both limits, we can readily interpret the changes as follows. There is an intramolecular rearrangement occurring which has the effect of interchanging the trimethylstannyl group between positions 1 and 3 on the five-membered ring of the indene moiety. This conclusion follows from the simplicity of the spectrum in the fast-exchange limit and is independent of the fine details of the mode of rearrangement. However, a suprafacial shift of the $Sn(CH_3)_3$ group gives rapid equilibration of the enantiamorphs Ia and Ib

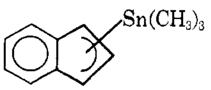


Ia Ib

Further, in the absence of hydrogen migration,[4] we can make the following chemical shift assignments for the slow-exchange spectra, *viz.*, for Ia: H(1), τ 6.13; H(2), τ 3.42; H(3), τ 3.20. Similar conclusions and assignments can be made for the spectra of the germanium (Figure 2) and silicon (Figure 3) analogs. From this and previous work[2] on σ-indenyl groups we find that $|J_{12}| > |J_{13}|$, a situation similar to that found[5] in indene. The chemical shift of the proton H(2) remains essentially constant[6] throughout the averaging process and the eventual triplet structure ($J = 3.5$ Hz) arises from the average of the coupling constants $(|J_{12}| + |J_{23}|)/2$. This can *only* occur if the coupling constants J_{12} and J_{23} have the same sign ($J_{12} \sim \pm 1.5$ Hz and $J_{23} \sim \pm 5.4$ Hz); *cf.* the case of indene.[5] These observations are consistent with but are not proof of the intramolecular exchange taking place *via* 1,3 jumps. However, a rapid equilibration *via* 1,2 jumps having intermediates such as II or III would give rise to the same spectral changes and cannot, on the basis of the present work, be conclusively ruled out.



II



III

We were able to achieve our original objective, namely, the measurement of ^{117,119}Sn–H coupling constants for the different C_5 ring hydrogens of the indenyl group. Using the average value $|J_{^{117,119}\mathrm{Sn-H(1)\ and\ H(3)}}| = 54.5$ Hz from the high-temperature spectrum and the value of $J_{^{117,119}\mathrm{Sn-H(1)}} = \pm 91$ Hz from the slow-exchange spectrum, we calculate $J_{^{117,119}\mathrm{Sn-H(3)}} = \pm 18$ Hz (or ∓200 Hz). The latter value can be rejected because the satellites would have been clearly observable in the low-temperature spectrum. The remaining coupling constant, $|J_{^{117,119}\mathrm{Sn-H(2)}}| = 12$ Hz, was observed directly in the +139° spectrum. We note in this case that $|J_{^{117,119}\mathrm{Sn-H(3)}}| > |J_{^{117,119}\mathrm{Sn-H(2)}}|$ and that the tin–proton coupling is of the same sign for H(1) as for H(3).

It is interesting to observe, if we assume that the olefinic resonances in a σ-C_5H_5 group occur at the same relative positions as those found in the corresponding σ-indenyl derivatives, we must then conclude in cyclopentadienyltrimethylsilane the rearrangement[7] occurs by 1,2 jumps. This conclusion we feel may be fortuitous in view of the sensitivity of the position of resonances of the H(2) and H(3) protons on the indene to the nature of the attached group.[2]

Acknowledgments.—We thank the Alfred P. Sloan Foundation for a fellowship to A. D., 1967–1969, the National Science Foundation for a predoctoral fellowship to P. E. R., 1966–1968, Mr. R. L. Lambert for assistance with the mass spectra, and Dr. T. F. Jula for the sample of allyltrimethylstannane.

---

[4] The molecule pentamethylcyclopentadienyltrimethylgermane, $(CH_3)_3GeC_5(CH_3)_5$, undergoes a rapid intramolecular rearrangement of the five-membered ring which cannot occur by hydrogen migration: A. Davison and P. E. Rakita, unpublished work; see also ref 1.

[5] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

[6] The constancy of the chemical shift for the H(2) proton in dynamic allylic compounds undergoing 1,3 jumps is well known: G. M. Whitesides, J. E. Norlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962); K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc.*, **88**, 4387 (1966).

[7] At 100-MHz the upfield portion of the olefinic proton signal, which would be assigned to H(2) and H(5), collapses more rapidly as the temperature is increased: A. Davison and P. E. Rakita, unpublished work.