be modeled as a series combination of a solid-state photovoltaic cell and a metal/electrolyte interface. A crucial factor in their performance is the efficacy of charge transfer at the overlayer/electrolyte interface. In the presence of fast kinetics at this interface, performance approaching that of the corresponding solid-state device can be realized. Kinetic hindrance to charge transfer at the overlayer/electrolyte interface manifests as overvoltage losses that reduce the photovoltage gained at the heterojunction. An important advantage with the use of heterojunction electrodes in PEC systems is the possibility of solar energy storage, which is obviously not offered by the corresponding solid-state device. Further improvements in catalytic modification of the ITO surface are, however, needed before the performance of PEC systems based on the Si/ITO heterojunction can match that of solid-state devices based on this interface.

Acknowledgment. This research was partially supported by a grant (XS-0-9272-1) from the Solar Energy Research Institute.

Registry No. Si, 7440-21-3; silicon oxide, 11126-22-0; indium tin oxide, 50926-11-9; Pt, 7440-06-4; RuO$_2$, 12036-10-1.

Recoil Tritium Reactions with 1,2-Difluoroethylenes

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Abstract: Recoil tritium reactions with *cis*- and *trans*-CHF═CHF have been studied. The results indicate that the majority of the tritium-labeled parent molecules are formed via the direct T-for-H substitution process and that the geometric isomers are formed via unimolecular isomerization of the excited parent molecules. On the other hand, the recoil tritium addition process will give rise to an excited radical that immediately converts to a bridged complex. Such a bridged complex may either isomerize to effect a net 1,2 F-atom migration to give CHT═CF$_2$ as the final product or expel an F-atom to form CHT═CHF.

Recoil tritium atoms interact with π bonds in olefins very readily, giving rise to tritium-labeled radicals.[1–10] With enough excitation, such radicals may decompose by eliminating certain chemical entities to restore the π bond and form either the original or a different olefinic species as the final product.[4,5] Otherwise, it may be scavenged or it may undergo typical chemical interactions of free radicals in the reaction system. In the literature there are a number of studies devoted to the reactions of recoil tritium atoms with alkenes, but similar studies with substituted olefins are extremely rare.[1–10] In 1961, Urch and Wolfgang investigated the *cis*- and *trans*-dichloroethylene systems and obtained C$_2$H$_2$TCl as the major product, which probably arose from the following addition–elimination mechanism.[11]

$$\mathrm{T + CHCl{=}CHCl \rightarrow (CHTCl{-}CHCl\cdot)^*} \qquad (1)$$

$$\mathrm{(CHTCl{-}CHCl\cdot)^* \rightarrow CHT{=}CHCl + Cl} \qquad (2)$$

For the very small amount of *cis*- and *trans*-CHCl═CTCl observed in their experiments, the ratio of the isomers is about a factor of 2 in favor of the retention of the original geometric configuration. Similar favoritism is also detected in the recoil tritium studies with *cis*- and *trans*-2-butene performed by Rowland and co-workers.[7,8] Very recently, King and Wai have extended the recoil tritium reactions with *cis*- and *trans*-1,2-dichloroethylene to the liquid phase and have shown that the ratio of the isomers is more than a factor of 10 in favor of the isomer with the original configuration.[12] This means that hot T-for-H substitution at the ethylenic C–H bond proceeds with almost complete retention of configuration.

In the present work, recoil tritium reactions with *cis*- and *trans*-CHF═CHF have been studied. The results indicate that the majority of the tritium-labeled parent molecules are formed via the direct T-for-H substitution process. It confirms that substitution at the ethylenic C–H bonds proceeds predominantly with retention of configuration.[12] Furthermore, the results show that the CHTFCHF· radical formed from the recoil tritium addition process will undergo a 1,2 F shift to give CHT═CF$_2$ as a final decomposition product.[13] Although the shift of Cl and Br atoms in free radicals has been well established for at least two decades,[14,15] this is definitely the first unambiguous evidence for the occurrence of the F-atom shift in fluorine-containing radicals.[16,17]

Experimental Section

General Procedure. These experiments were performed by using the standard techniques employed in studying recoil tritium reactions.[1,18] Gaseous samples of the desired pressure that contained ^{3}He, the parent compound, and the desired additives were prepared by standard high-vacuum techniques and sealed in bulbs of about 20 mL in volume. The samples were irradiated at the Texas A&M Nuclear Science Center reactor for 10 min with a neutron flux of about 1×10^{13} n cm^{-2} s^{-1}. A set of 10 samples were generally irradiated with a rotisserie to normalize the neutron flux of the samples. In some sets, two pure *n*-C$_4$H$_{10}$ samples were included as standards to allow for the calculation of absolute yields of products. In all these experiments tritium was produced in situ via

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(5) K. L. Mahan and J. K. Garland, *J. Phys. Chem.*, **75**, 1031 (1971).

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(17) See, for example, W. J. Feast, R. R. Hughes, and W. K. R. Musgrave, *J. Fluorine Chem.*, **10**, 585 (1977).

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Table I. Recoil Tritium Reactions with *trans*-CHF=CHF at Various Pressures

	gas pressure, torr								
trans-CHF=CHF	44	84	80	181	186	266	376	393	779
^{3}He	8	16	21	16	16	16	21	16	21
total pressure	52	100	101	197	202	282	397	409	800
	relative yields[a]								
HT	100	100	100	100	100	100	100	100	100
HC≡CT	103	97	87	95	102	101	77	100	92
CT≡CF	79	70	225[b]	*c*	70	69	169[b]	66	62
$CHT{=}CF_2$	172	136		114	111	104		96	63
CHT=CHF	234	228	213	241	240	234	258	232	230
trans-CHF=CTF	168	169	164	190	192	192	205	202	208
cis-CHF=CTF	90	84	90	102	88	87	96	90	83

[a] The HT yields were normalized to 100. [b] Not separated. [c] Not measured.

the nuclear transmutation, $^3He(n,p)^3H$. The tritium-labeled products were analyzed with a standard radiogas chromatographic setup.[18]

Gas Chromatographic Analysis. Four different columns were employed for the analysis: (i) an 8 ft Porapak-Q column operated at either 0 or 25 °C; (ii) a 30 ft Silicon Fluid-96 column operated at 55 °C; (iii) a 50 ft dimethylsulfolane (DMS) column operated at 25 °C; and (iv) a 50 ft propylene carbonate coated on alumina column operated at 0 °C. The Porapak-Q column at 0 °C was often used for the analysis of the major portions of the samples.

Identification of Fluoroacetylene. All of the tritium-labeled products were identified through their respective retention times on different columns with authentic samples. However, there was an unknown product that had a retention time close to that of C_2H_2. This tritium-labeled product was trapped out with liquid nitrogen during analysis. A large excess of H_2 was added to this unknown, and the mixture was passed through a Pd catalyst at 150 °C for hydrogenation. Gas chromatographic analysis indicated that the resultant product was C_2H_4TF. Since the unknown was definitely not C_2H_2TF, the only logical choice for its identity was therefore CT≡CF.

Chemicals. *cis*- and *trans*-CHF=CHF were obtained as a 1:3 mixture from PCR, Inc. It was gas chromatographically separated with a 15 ft DMS column, which gave a complete separation between the two isomers. The compounds were normally purified again prior to sample preparation.

Helium-3 (99.9%) was obtained from Monsanto Research Corporation. 1,1-Difluoroethylene (99.0%) was obtained from Matheson. Helium-4 (99.995%) and oxygen (99.6%) were both obtained from Air Reduction Incorporated. Each gas was used without further purification except for several cycles of degassing for the condensable compounds.

Results

Product Spectrum from Recoil Tritium Reactions with *cis*- and *trans*-CHF=CHF. Recoil tritium reactions with *cis*- and *trans*-CHF=CHF have been carried out, and the product spectra from such systems are shown in Figure 1. The detected tritium-labeled products include HT, CT≡CF, CH≡CT, C_2H_2TF, $CHT{=}CF_2$, *trans*-CHF=CTF, and *cis*-CHF≡CTF.

For comparison purposes, some experiments of recoil tritium reactions with $CH_2{=}CF_2$ have also been performed. For nonscavenged samples at 800 torr, the tritium-labeled products and relative yields (in parentheses) are HT (180), CH≡CT (7), CT≡CF (8), C_2H_2TF (16), $CHT{=}CF_2$ (100), *trans*-CHF=CTF (1.6), and *cis*-CHF=CTF (2.3). This product spectrum is essentially what one would expect for such fluoroalkene systems: (i) a low HT yield due to the strong C—H bonds; (ii) some decomposition products such as CT≡CF and CH≡CT; (iii) a low C_2H_2TF yield due to the very strong C—F bonds; and (iv) very small amounts of structural isomers of the parent compound as products. Numerically, the total yield of *trans*- and *cis*-CHF=CTF relative to that of $CHT{=}CF_2$ was only 4%.

The product spectra derived from *cis*- and *trans*-CHF=CHF as shown in Figure 1 definitely contain some surprising features. In the first place, the structure isomer, $CHT{=}CF_2$, was produced in very high yields. Secondly, the apparent T-for-F substitution product, C_2H_2TF, actually has the highest yield among the products. Furthermore, the relative amounts of the decomposition products are more than what has been observed in the $CH_2{=}CF_2$ system. Of course, the present systems possess the additional interest that cis and trans geometric isomerization is feasible.

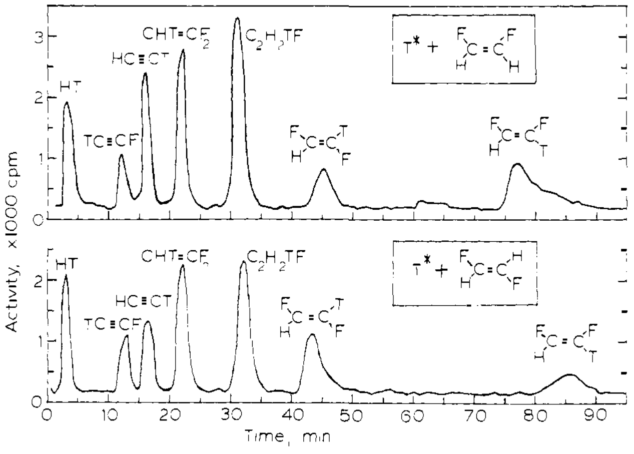

Figure 1. Radiogas chromatograms of products derived from recoil tritium reactions with *cis*- and *trans*-CHF=CHF.

Table II. Recoil Tritium Reactions with *cis*-CHF=CHF at Various Pressures

	gas pressure, torr						
cis-CHF=CHF	31	44	78	175	375	506	771
^{3}He	20	8	20	21	20	16	20
total pressure	51	52	98	196	395	522	791
	relative yields[a]						
HT	100	100	100	100	100	100	100
HC≡CT	115	115	108	98	124	128	114
CT≡CF	61	82	61	169[b]	72	75	63
$CHT{=}CF_2$	175	170	118		105	107	90
CHT=CHF	241	244	235	268	302	311	296
trans-CHF=CTF	76	88	70	85	98	104	98
cis-CHF=CTF	174	180	152	177	228	253	232

[a] The HT yields were normalized to 100. [b] Not separated.

Pressure Effects. The product variations as a function of pressure are summarized in Tables I and II for recoil tritium reactions with *trans*- and *cis*-CHF=CHF, respectively. Since it has been demonstrated that HT yields serve well as a pressure-independent standard in recoil tritium systems,[19] the product yields in both tables are all expressed relative to the yield of HT of 100. The pressure range employed is 50–800 torr. It is obvious from the data that the yield of $CHT{=}CF_2$ shows the most significant pressure dependence. Its yield decreased with increasing pressure by a factor of 2 or more in the above-mentioned range for both *trans*- and *cis*-CHF=CHF systems. The other major observation is that in both cases the yields of the tritium-labeled parent compounds increase with pressure by about 20–30%. For the yields of the other tritium-labeled products, no obvious variation trends are displayed.

When the normalized yields of the tritium-labeled products relative to that of HT in these two tables are compared, the values

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(19) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

Table III. Oxygen Effect on Recoil Tritium Reactions with *trans*-CHF≡CHF at Constant Total Pressures

	gas pressure, torr					
trans-CHF=CHF	779	746	705	625	464	138
O_2	0	42	51	161	332	638
^{3}He	21	20	20	20	20	23
total pressure	800	808	806	806	816	799
	relative yields[a]					
HT	343	343	338	270	184	164
HC≡CT	315	326	354	303	324	342
CF≡CT	214	229	231	184	229	261
$CHT{=}CF_2$	276	275	344	356	283	324
CHT=CHF	790	855	799	725	862	792
trans-CHF=CTF	715	718	712	744	706	717
cis-CHF=CTF	285	282	288	256	294	283

[a] The sum of the *trans*-CHF=CTF and *cis*-CHF=CTF yields is normalized to 1000.

derived from *cis*-CHF=CHF are generally higher than those from its trans isomer. This indicates that the HT yields of the two systems are not identical, and a higher HT yield is probably derived from *trans*-CHF=CHF. Since the moderating effect of such geometric isomers should be similar, this observation in turn means that the C—H bond in *trans*-CHF=CHF is weaker than that in its cis counterpart.[20,21]

It is also noted in Tables I and II that for the yields of *trans*- and *cis*-CHF=CTF, the tritium-labeled parent compound is always in favor over its geometric isomer by a ratio in excess of 2:1.

Effect of O_2 as a Scavenger. The effect of O_2 as an additive on the product yields subsequent to recoil tritium reactions with *trans*-CHF=CHF is shown in Table III. The total pressures of these samples are held constant while the percentage of O_2 varies from 0 to about 80%. Because the HT yield is likely to contain a low energy contribution and therefore might be scavenger sensitive, while the T-for-H substitution is likely to be a totally hot process,[1-3] the data in Table III are normalized relative to the sum of *trans*- and *cis*-CHF=CTF yields of 1000.

When the first three samples of Table III are compared, it is obvious that the addition of 5% O_2 has essentially no effect on the product yields. Even the HT yield stays constant and is not diminished by the presence of an effective scavenger. This indicates that none of the products listed in Table III are formed via thermal tritium atoms and that the CHF=CHF systems are very efficiently self-scavenged. The thermalized T atoms in the pure systems may add to the double bonds of CHF=CHF to give CHTF—CHF· radicals that may eventually become polymeric species.

As larger amounts of O_2 are added to the samples, the HT yield steadily decreases from 343 to 164. This indicates that about half of the H-abstractions are initiated by rather low energy T atoms. The other product yields are still unchanged with further O_2 addition. In fact, the *trans*-CHF=CTF to *cis*-CHF=CTF ratio stays very constant at about 7/3 throughout the whole O_2 concentration range.

Effect of He as a Moderator. In Table IV, the effects of a large excess of ^{4}He as a moderator on the products derived from *trans*-CHF=CHF are shown. Table V gives results from similar moderated systems when 2 torr of O_2 was included in each sample. The data are again expressed relative to the sum of *trans*- and *cis*-CHF=CTF yields of 1000. It is seen from Table IV that as the energy spectrum of the reacting T atoms is lowered, the relative yields of HT, $CHT{=}CF_2$, and CHT=CHF all increase very sharply. The relative yield of CH≡CT also rises. But both the relative yield of CT≡CF and the trans/cis ratio of CHF=CTF remain unchanged. On the other hand, as shown in Table V, essentially all of the surplus in yields of $CHT{=}CF_2$ and part of the surplus in yields of CHT=CHF are eliminated with the inclusion of 2 torr of O_2. In fact, the $CHT{=}CF_2$ yield decreases with moderation in the presence of O_2. However, this apparent decrease may actually be due to an increase in the total pressure of the system instead of due to moderation. Since the amount of *trans*-CHF=CHF was maintained constant in these samples and an increasing amount of ^{4}He was added, the sample with the highest moderation also has the highest pressure. As seen in Table I, the yields of $CHT{=}CF_2$ do decrease at higher pressures.

Table IV. Helium Effect on Recoil Tritium Reactions with *trans*-CHF=CHF at Constant Parent Pressures

	gas pressure, torr					
trans-CHF=CHF	29	33	32	35	32	34
^{3}He	21	19	19	19	19	19
^{4}He	0	49	123	209	449	823
% ^{4}He	0	49	71	90	90	94
	relative yields[a]					
HT	567	1255	1825	2001	2427	2329
HC≡CT	526	603	685	797	1159	1105
CT≡CF	366	432	350	360	372	339
$CHT{=}CF_2$	985	1227	1690	1827	2096	1567
CHT=CHF	1069	1128	1389	1626	1993	1670
trans-CHF=CTF	690	717	699	730	696	678
cis-CHF=CTF	310	283	302	270	304	323

[a] The sum of the *trans*-CHF=CTF and *cis*-CHF=CTF yields is normalized to 1000.

Table V. Helium Effect on Recoil Tritium Reactions with *trans*-CHF=CHF at Constant Parent Pressures in the Presence of O_2

	gas pressure, torr				
trans-CHF=CHF	30	28	29	28	30
^{3}He	21	21	21	21	21
O_2	2	2	2	2	2
^{4}He	0	107	206	413	801
% ^{4}He	0	68	80	89	94
	relative yields[a]				
HT	744	814	984	1197	1713
HC≡CT	545	577	646	697	983
CT≡CF	336	332	350	348	410
$CHT{=}CF_2$	709	769	796	661	685
CHT=CHF	1147	1296	1540	1682	1208
trans-CHF=CTF	578	676	709	690	712
cis-CHF=CTF	422	324	291	310	288

[a] The sum of the *trans*-CHF=CTF and *cis*-CHF=CTF yields is normalized to 1000.

Absolute Yields. The sum of the absolute yields of the observed products from the *trans*-CHF=CHF sample with a total pressure of 409 torr (listed in Table I) was measured as 41% and that from the *cis*-CHF=CHF sample with a total pressure of 522 torr (listed in Table II) was measured as 42%. The missing portions of the absolute yields should be partially due to the unmeasured F-abstraction product, TF, and partially due to some undetected polymeric products derived from the combination of the tritium-labeled radicals with the parent compounds. In addition, TF also can be formed from the decomposition of either excited tritium-labeled molecular products or hot radicals such as CHTFCHF· that are readily formed from the recoil tritium addition process.

Discussion

Formation of Tritium-Labeled Parent Compounds and Their Geometric Isomers. In recoil tritium reactions with *cis*- and *trans*-CHF=CHF the tritium-labeled parent compounds and their geometric isomers can be formed via two major mechanisms.

(1) Direct Substitution. The observed CHF=CTF in the *cis*- and *trans*-CHF=CHF systems can be formed by direct T-for-H substitution. The substitution may proceed either with retention of the original geometric configuration to give the tritium-labeled parent compound or with inversion of the configuration to give the geometric isomer as the tritium-labeled product. These two

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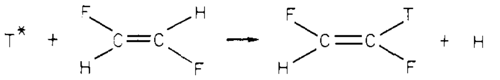
[20] J. W. Root, W. Breckenridge, and F. S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965).

[21] E. Tachikawa and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 4767 (1968).

possibilities are illustrated in eq 3 and 4 with *trans*-CHF=CHF as the starting parent.



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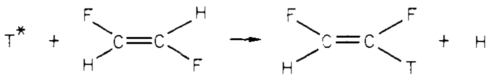
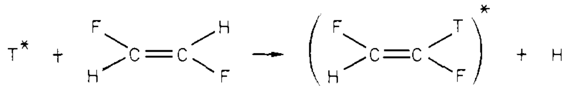


(4)

Judging from the knowledge in the literature, substitution with inversion is a rather unlikely process. For T-for-H substitution at carbon atoms with sp^3 hybridization, the percentage retention was observed to be greater than 99.5% by Palino and Rowland when the compound *meso*-$(CHFCl)_2$ was employed.[22] For T-for-H substitution at carbon atoms with sp^2 hybridization, the recent work by King and Wai with *cis*- and *trans*-CHCl=CHCl in the liquid phase has shown that greater than 90% of the substitution proceeds with retention.[12] However, even in the light of such results, the possibility of a minor contribution from the substitution with inversion process cannot be totally ruled out for the present CHF=CHF systems. Although the presence of a more rigid double bond and a stronger C—F bond may not aid the course of inversion during substitution, the smaller F atoms in these molecules may increase the chance for the attack of T atoms from the opposite side of the leaving H atoms.

Even in the absence of a substitution with inversion process, it is likely that a major fraction of the geometric isomer is originated from the direct T-for-H substitution process through isomerization. It has been well documented that subsequent to the hot T-for-H substitution a median of 5 eV of excitation energy will be deposited in the resultant tritium-labeled products.[19]



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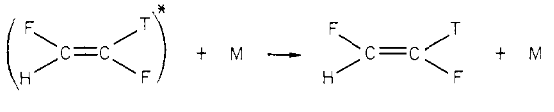

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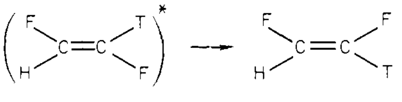
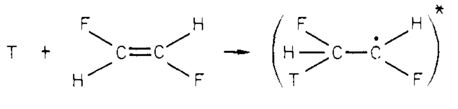


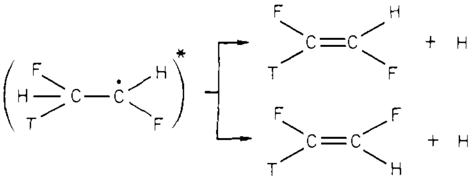
(7)

Such highly excited molecules formed in reactions such as (5) may either be stabilized by collisions to give the tritium-labeled parent or isomerized to give the geometric isomer.

(2) Addition–Elimination Process. The two isomers can also be formed via the addition–elimination mechanism. Tritium atoms add to the double bond of CHF=CHF to give a tritium-labeled 1,2-difluoroethyl radical that decomposes through H-elimination to give both *cis*- and *trans*-CHF=CTF as possible products. This is again illustrated with *trans*-CHF=CHF as the parent compound. The C—C bond in the tritium-labeled 1,2-difluoroethyl radical shown in eq 8 should have essentially free rotation.



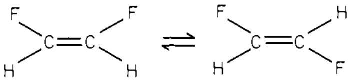
(8)



(9a)

(9b)

Therefore, the relative occurrence of reactions 9a and 9b, and thus the relative yields of the tritium-labeled parent compound and its geometric isomer, will depend on the competition between the decomposition rate and the rotation rate: (i) In the case where the lifetime of the radical is much shorter than the rotational time, reaction 9a will be the only observed event and thus no geometric isomer will be detected. (ii) In the case where the lifetime of the radical is long in comparison with the rotational time, an equilibrium mixture of the two geometric isomers characteristic of their thermodynamic stability should be obtained. At 298 K, the equilibrium constant for the cis to trans isomerization as shown in eq 10 has been reported as 0.21, indicating that *cis*-CHF=CHF



(10)

is the thermodynamically stable form.[23] This means that if the radicals are long-lived, the cis/trans product branching ratio should be larger than unity, and the same cis/trans ratio should be obtained from either *cis*- or *trans*-CHF=CHF as the starting reactant. (iii) In the case when the lifetime of the radical and the rotational time of the C—C bond are comparable, different cis/trans product branching ratios will be obtained when the two geometric isomers are employed as reactants. Since the cis compound is the thermodynamically stable form and should be formed in a higher yield from the rotating radicals, the cis/trans product ratio derived from *cis*-CHF=CHF as parent should have a higher value than the trans/cis ratio derived from *trans*-CHF=CHF as parent. In other words, the percentage isomerization in the *cis*-CHF=CHF system should be lower than that in the *trans*-CHF=CHF system.

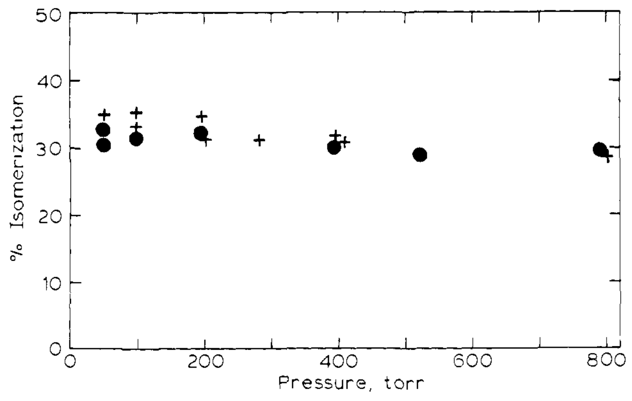


Figure 2. Percentage conversion to geometric isomers at various pressures subsequent to recoil tritium reactions with *cis*- and *trans*-CHF=CHF: (●) percent *trans*-CHF=CTF from *cis*-CHF=CHF; (+) percent *cis*-CHF=CTF from *trans*-CHF=CHF.

The experimental results in Table I and II indicate that both the trans/cis product ratio from *trans*-CHF=CHF and the cis/trans product ratio from *cis*-CHF=CHF are about 7:3. The percentage geometric isomerization in both systems can conveniently be evaluated from these product ratios. In Figure 2, such percentages are plotted as a function of pressure for both systems. It is obvious that the two percentages are essentially identical at about 30% for the whole pressure range. These results are inconsistent with what would have been observed if the addition–elimination mechanism was predominant. For the three situations of the addition–elimination mechanism mentioned above, the results disagree with the first one because a quantitative yield of the geometric isomer is definitely obtained. The results disagree with the second one because the trans/cis product ratios from the two parent compounds are definitely not identical. In fact, the two values are reciprocals of each other. The results also disagree with the third situation because the cis/trans product ratio from *cis*-CHF=CHF is not higher than the trans/cis product ratio from *trans*-CHF=CHF and the percentage isomerizations are not lower for the *cis*-CHF=CHF system.

The observed experimental results are more consistent with the assumption that the substitution–isomerization mechanism is the

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[22] G. F. Palino and F. S. Rowland, *J. Phys. Chem.*, **75**, 1299 (1971).

[23] N. C. Craig and E. A. Entemann, *J. Chem. Phys.*, **36**, 244 (1962).

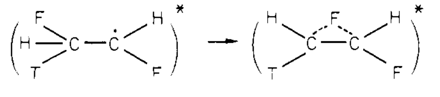
predominant one in forming the tritium-labeled parent compounds and their geometric isomers in these $CHF{=}CHF$ systems. The excited tritium-labeled molecules subsequent to T-for-H substitution may either be stabilized to give the parent compound or isomerized to give the geometric isomer. Kinetically, for $CHF{=}CHF$, the rate constant k(cis → trans) has been measured as $10^{13.17}e^{-62800/RT}$ s^{-1}, while the rate constant k(trans → cis) has been measured as $10^{12.98}e^{-60100/RT}$ s^{-1}.[24] Since both the activation energies and the A factors are similar for these two isomerization processes, it is expected that the extent of isomerization subsequent to substitution should also be similar. This explains well the observation that the trans/cis product ratio from *trans*-$CHF{=}CHF$ and the cis/trans product ratio from *cis*-$CHF{=}CHF$ are both about 7/3. Quantitatively, the observed 30% isomerization is consistent with what would be expected from unimolecular reaction theories if the median excitation is about 5 eV and the stabilization pressure is 1 atm. Additional support for the substitution–isomerization mechanism can be found in the pressure effect of the percentage isomerization as shown in Figure 2. For both $CHF{=}CHF$ systems, this percentage decreases slightly with increasing pressure. The decreasing trend is what would have been expected for the pressure effect on the competition between reactions 6 and 7, the stabilization and isomerization processes. However, the small magnitude of the effect indicates that other mechanisms may also contribute significantly to their yields.

The above discussion has established that the direct T-for-H substitution process definitely operates in the $CHF{=}CHF$ systems and is responsible for the formation of the majority of the $CHF{=}CTF$ products. But in no way does it deny the occurrence of the recoil tritium addition reactions to double bonds as shown in eq 8. Nor have we established that the substitution process predominates over the addition process in the overall product spectrum. All that we have shown so far about the addition process is that reaction 9 is not responsible for the formation of the majority of the $CHF{=}CTF$ products.

Formation of $CHT{=}CF_2$ via Fluorine Atom Shift in the CHTFCHF· Radicals. What is the fate of the CHTFCHF· radicals formed in eq 8 if they do not decompose to give $CHF{=}CTF$ as shown in (9)? One possibility is to add to other molecules of $CHF{=}CHF$ to give dimers or polymers. Although dimers are not observed during back-flush experiments, the 40% total absolute yield observed means that polymerization is definitely plausible. Another possible route is to eliminate TF to give an unlabeled $CHF{=}CH\cdot$ radical. Such an elimination will serve to deplete the observed absolute yield of the system, but it will not affect the measured relative yields of the tritium-labeled products. In addition, the fact that $CHT{=}CF_2$ was observed as a major product in the systems indicates the probable occurrence of a novel process in that the CHTFCHF· radicals undergo an F-atom shift prior to decomposition.

As seen in the tables, the $CHT{=}CF_2$ yields are of similar magnitude as those of *trans*- and *cis*-$CHF{=}CTF$. Its yield relative to those of the parent compounds decreases sharply with increasing pressure and remains essentially unchanged with the addition of O_2 as a radical scavenger. When He was added as a moderator its yield increases sharply, but the increase can be easily supressed by a small amount of O_2. This means that a hot radical such as (CHTFCHF·)* formed via the interaction of low energy T atoms is likely to be its precursor.

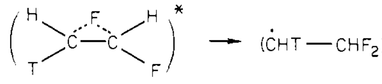
The formation of $CHT{=}CF_2$ can be explained with the following mechanism. The hot CHTFCHF· radical formed in reaction 8 via the recoil tritium addition process may be immediately converted into a bridged complex as shown in (11). The single electron on the first carbon interacts with an unbonded electron pair of the F atom on the second carbon to form the bridge. Such a bridge formation process must be fast enough to compete with reaction 9, the decomposition of the excited radical through C–H bond cleavage. Similar bridged complexes have been proposed during the past decades to explain the observed shift of chlorine and bromine atoms in free radicals.[14,15]


(11)

The bridged complex formed in (11) could break down in two different ways: one follows the reverse reaction of (11) to return to CHTFCHF· radical, and another is to convert into $CHF_2CHT\cdot$ radical as in (12). The relative occurrence of these two routes depends on the relative enthalpy of formation of these two radicals, $CH_2FCHF\cdot$ and $CHF_2CH_2\cdot$. The fact that large quantities of $CHT{=}CF_2$ were observed as product indicates that eq 12 takes place very readily. The hot $CHF_2CHT\cdot$ radicals formed in (12) can then decompose with a C—H cleavage to give $CHT{=}CF_2$ as the final product (eq 13). A concerted step to convert the

$$(CHT{-}CHF_2\cdot)^* \rightarrow CHT{=}CF_2 + H \qquad (13)$$

bridged complex directly to $CHF{=}CF_2$ is less likely because it requires the cleavage of a C—H σ bond and the formation of a C—F σ bonds and a C—C π bond to occur simultaneously.


(12)

One of the necessary conditions for the conversion of a fluorinated radical to a bridged complex is that F atoms must be present on the carbon neighboring the one with the unbounded electron to facilitate the electronic interaction. As indicated under Results, in the corresponding system of recoil tritium reactions with $CH_2{=}CF_2$, the observed yields of $CHF{=}CTF$ only amount to about 4% relative to those of the tritium-labeled parent compound. In some previous publications, it was observed that thermal H atoms always add preferentially to the carbon of a fluoroethene that has fewer F atoms attached to it.[25-28] In the case of $CH_2{=}CF_2$, the H atom adds almost exclusively at the $={CH_2}$ group.[25,26] Therefore, it is expected that the tritium atom addition reaction should also take place almost exclusively at this carbon (eq 14). Since there is no F atom on the second carbon of the

$$T^* + CH_2{=}CF_2 \rightarrow (CH_2T{-}CF_2\cdot)^* \qquad (14)$$

resultant $CH_2TCF_2\cdot$ radical, it is difficult for it to form a bridged complex to facilitate the 1,2 F-shift process. (As a result, it decomposes without radical isomerization to give $CHT{=}CF_2$ as the final product.) This explains the low yield of $CHF{=}CTF$ when recoil tritium reacts with $CH_2{=}CF_2$, in contrast with the high yield of $CHT{=}CF_2$ when recoil tritium reacts with $CHF{=}CHF$.

Theoretically, all the CHTFCHF· radicals formed in eq 8 are energetically capable of decomposing via eq 9 to give $CHF{=}CTF$ because the energy released in eq 8 is essentially identical with the minimum energy requirement for the decomposition in eq 9: a C—T bond is formed in (8) and a C—H bond is broken in (9). The total excitation of the CHTFCHF· radical must be equal to the exothermicity of the addition reaction plus the kinetic energy carried by the reacting T atom. Since the radical isomerization sequence shown in eq 11 and 12 does not consume any energy, the hot CHF_2–CHT· radical undergoing decomposition in eq 13 should have an excitation essentially identical with that of the CHTF–CHF· radical formed in eq 8, provided that the processes are fast enough to avoid collisional stabilization. From the results of the pressure studies, it is observed that the yield of the decomposition product from eq 13, $CHT{=}CF_2$, exhibits a sharp pressure dependence in the 0.1–1.0-atm range. This means that the precursors of the decomposition have lifetimes in the range

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(24) P. M. Jeffers and W. Schaub, *J. Am. Chem. Soc.*, **91**, 7706 (1969).

(25) J. P. Kilcoyne and K. R. Jennings, *J. Chem. Soc., Faraday Trans. 1*, **70**, 379 (1974).

(26) P. M. Scott and K. R. Jennings, *J. Phys. Chem.*, **73**, 1521 (1969).

(27) L. Teng and W. E. Jones, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1267 (1967).

(28) L. Teng and W. E. Jones, *J. Chem. Soc., Faraday Trans. 1*, **69**, 189 (1973).

of 10^{-9} s. It transcribes into an excitation energy not far above the exothermicity of the addition process, eq 8. *In* other words, the excitation of the hot radicals giving rise to $CHT{=}CF_2$ is mainly derived from the exothermicity of the addition reaction instead of received from the reacting T atoms. Therefore, it can be concluded that it is the low energy (above thermal, but below, say, 5 eV) T atoms that add to $CHF{=}CHF$ to give hot radicals leading to the formation of bridged complex and eventually $CHT{=}CF_2$. The same conclusion can also be alternatively arrived at from the results of the moderator studies: the relative yield of $CHT{=}CF_2$ was enhanced when large excess of He was added to decrease the energy spectrum of the reacting tritium atoms.

The above discussion also hinted that the time required for the formation of the bridged complex is likely to be much less than 10^{-9} s.

Formation of CHT═CHF. In the system of recoil tritium reactions with $CH_2{=}CF_2$, the apparent T-for-F substitution product, $CH_2{=}CTF$, only amounts to 16% relative to the T-for-H substitution product, reflecting the effect of a strong C—F bond for both the direct substitution reaction, (15), and the addition–decomposition reactions, (16) and (17). However, as shown under Results, the yield of $CHT{=}CHF$ is always the highest among products in the systems of recoil tritium reactions with $CHF{=}CHF$. This apparent T-for-F substitution product again can be formed from either the direct substitution reaction (18), or the addition–decomposition reaction sequence, (8) followed by (19).

$$T^* + CH_2{=}CF_2 \rightarrow CH_2{=}CTF + F \tag{15}$$

$$T^* + CH_2{=}CF_2 \rightarrow (CH_2{-}CTF_2\cdot)^* \tag{16}$$

$$(CH_2{-}CTF_2\cdot)^* \rightarrow CH_2{=}CTF + F \tag{17}$$

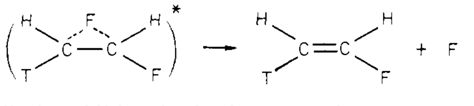
$$T^* + CHF{=}CHF \rightarrow CHT{=}CHF + F \tag{18}$$

$$T^* + CHF{=}CHF \rightarrow (CHTF{-}CHF\cdot)^* \tag{8}$$

$$(CHTF{-}CHF\cdot)^* \rightarrow CHT{=}CHF + F \tag{19}$$

When the $CH_2{=}CF_2$ and $CHF{=}CHF$ systems are compared, for the direct T-for-F substitution processes, reaction 18 should be more efficient than reaction 15 because there is only one instead of two F atoms on the carbon where substitution takes place.[29] However, the direct T-for-F substitution process even in the absence of other F atoms at the substitution site is a rather inefficient reaction owing to the strength of the C–F bond.[29,30] For the addition reaction, there is no doubt that reaction 8 is much more efficient than reaction 16.[25-28] However, because of the relative strength of the C–H and the C–F bonds, the resultant CHTF–CHF· radical from (8) *is* expected to decompose via C–H bond cleavage as shown in (9) instead of C–F bond cleavage as indicated in (19). Judging from these, none of the common reaction channels as shown above could account for the extremely high yield of $CHT{=}CHF$ derived from the recoil tritium reactions with $CHF{=}CHF$.

One plausible explanation is that $CHT{=}CHF$ is derived from the bridged complex formed in reaction 11. The precursor of this bridged complex CHTFCHF· radical should be readily formed from the addition reaction, (8). It is probable that if the bridged complex possesses sufficient excitation, the two partial C–F bonds could cleave simultaneously for the F atom to be ejected in favor of forming a π bond. This F-atom expulsion process is shown in eq 20.



(20)

Overall, the addition–bridged complex formation process, (8) followed by (11), should involve lower energy tritium atoms. The extremely highly energetic reaction adduct from reaction (8) is capable of carrying out reaction 9 directly. The low energy nature of the reaction products derived from the bridged complex are supported by the observation in Table IV that the yields of both $CHT{=}CF_2$ and $CHT{=}CHF$ increase significantly with He moderation. However, between these two products, the formation of $CHT{=}CHF$ should be a somewhat higher energy process. For the bridged complex formed in (11), the more energetic ones are likely to cleave the partial bonds to undergo reaction 20, while the less energetic ones are likely to undergo the isomerization reaction (12) to give $CHT{-}CHF_2\cdot$. With the additional excitation derived from the exothermicity of (8), the more energetic bridged complex could complete the F-atom expulsion process, eq 20, in a time scale considerably shorter than the collision time of the reacting systems. This explains the lack of a significant pressure dependence for the $CHT{=}CHF$ yields. On the other hand, the less energetic bridged complex should require a much longer period of time to undergo the F-atom shift reaction, eq 12, and the H-elimination reaction, eq 13. This explains why the $CHT{=}CF_2$ yields are very pressure sensitive.

Another contrast in behavior between the $CHT{=}CF_2$ and the $CHT{=}CHF$ yields is that, although both of their yields were tremendously increased by He moderation, the *increase* in the $CHT{=}CF_2$ yield was essentially suppressed by 2 torr of O_2 while the *increase* of $CHT{=}CHF$ was only partially lowered by the inclusion of O_2. This again is consistent with the supposition that the former is formed via the decomposition of a rather low energy radical while the latter is formed from the direct decomposition of the bridged complex without the involvement of an immediate radical precursor.

Formation of the Acetylenes. Both $CT{\equiv}CF$ and $CH{\equiv}CT$ are decomposition products of this recoil tritium system. They are both formed in rather high yields, but their modes of formation are quite different.

The predominant mode for the formation of $CT{\equiv}CF$ should be the decomposition of highly excited $CHF{=}CTF$ molecules subsequent to the hot T-for-H substitution reaction as shown in eq 5 and 21.

$$T^* + CHF{=}CHF \rightarrow (CHF{=}CTF)^* + H \tag{5}$$

$$(CHF{=}CTF)^* \rightarrow F{-}C{\equiv}C{-}T + HF \tag{21}$$

On the other hand, there are two possible modes with which $CH{\equiv}CT$ could be formed. The first route involves the decomposition of highly excited $CHT{\equiv}CHF$ molecules subsequent to the hot T-for-F substitution reaction as shown in eq 18 and 22.

$$T^* + CHF{=}CHF \rightarrow (CHT{=}CHF)^* + F \tag{18}$$

$$(CHT{=}CHF)^* \rightarrow CT{\equiv}CH + HF \tag{22}$$

However, the contribution of this mechanism is expected to be limited because of the strong C—F bonds and thus the inefficient T-for-F substitution. It is more likely for $CH{\equiv}CT$ to be formed by the second route, which involves the addition of very energetic tritium atoms to $CHF{=}CHF$, and leads to extremely excited CHTFCHF· radicals that undergo a consecutive decomposition to give $CH{\equiv}CT$ as the final product. In this reaction sequence, the extremely excited CHTFCHF· radicals formed in reaction 8 also first give rise to an excited bridged complex as in eq 11. But after the F-atom expulsion reaction as shown in eq 20, the resultant $CHT{=}CHF$ molecules are still very excited. As a result, they undergo further HF elimination as shown in eq 22 to give $CH{\equiv}CT$ as the final product.

Both $CH{\equiv}CT$ and $CT{\equiv}CF$ yields are not sensitive to pressure variation in the range of 50–800 torr. The collisional frequencies corresponding to these pressures are not high enough to stabilize such highly excited molecules and radicals. The molecular nature of the formation of these products and the involvement of only hot radicals are also in agreement with the observation in Table III that both of their yields are insensitive to scavenger concentrations.

The He-moderation results in Tables IV and V are also consistent with the above mechanisms for the formation of $CT{\equiv}CF$ and $CH{\equiv}CT$. The yield of $CT{\equiv}CF$ relative to those of CH-

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(29) R. A. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **85**, 1050 (1963).

(30) Y.-N. Tang, E. K. C. Lee, E. Tachikawa, and F. S. Rowland, *J. Phys. Chem.*, **75**, 1290 (1971).

$F{\equiv}CTF$, the T-for-H substitution products, stays constant with moderation either in the presence or the absence of O_2. This implies that $CT{\equiv}CF$ is also formed by primary recoil tritium substitution reactions as shown in eq 5 and 21 and that these T-for-H and T-for-F substitutions have similar energy dependence. On the other hand, the increase in the $CH{\equiv}CT$ yield with He moderation parallels those of $CHT{=}CF_2$ and $CHT{=}CHF$, indicating the similarity in their formation mechanism. Such common behavior lends support to the notion that $CH{\equiv}CT$ is formed via the excited bridged complex, as discussed earlier in this section.

However, certain features about these two less important products are not easily explainable. For example, it is difficult to account for their rather high yields in the recoil tritium reaction with $CHF{=}CHF$ systems. In the corresponding $CH_2{=}CF_2$ system, their yields relative to the T-for-H substitution product are at least a factor of three to five less.

The HT Yield. The HT to $CHF{=}CTF$ ratios from both *cis*- and *trans*-$CHF{=}CHF$ systems are both around 0.3, in comparison with a HT/C_2H_3T ratio of 0.23 from recoil tritium reactions with C_2H_4[10] and a HT/CH_3T ratio of 0.79 from the corresponding CH_4 system.[31] The rather low HT yield implies that the $D(C{-}H)$ values in $CHF{=}CHF$ are likely to be well above 100 kcal mol^{-1}.

The results also show that the HT yield decreases with the addition of O_2 as a scavenger and increases sharply with He moderation. Both of these observations are consistent with the notion that H abstraction by recoil tritium atoms is a rather low energy process.[1-3]

Conclusion

Among other features, the two main conclusions of this work on recoil tritium reactions with *cis*- and *trans*-$CHF{=}CHF$ are as follows: (i) the tritium-labeled parent compound is formed mainly from the direct T-for-H substitution process while the geometric isomer is formed via unimolecular isomerization of the excited tritium-labeled parent compounds; (ii) the recoil tritium addition process will give rise to an excited radical, which immediately converts into a bridged complex. Such a bridged complex may isomerize to effect a net 1,2 F-atom migration to give $CHT{=}CF_2$ as the final product. It can also either expel an F atom to form $CHT{=}CHF$ or undergo further decomposition to give $CH{\equiv}CT$ through HF elimination.

Acknowledgment. This work is kindly supported by the Robert A. Welch Foundation. The technical help of Deborah L. Morris is also appreciated.

Registry No. *cis*-$CHF{=}CHF$, 1630-77-9; *trans*-$CHF{=}CHF$, 1630-78-0; tritium, 10028-17-8.

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(31) D. Seewald and R. Wolfgang, *J. Chem. Phys.*, 47, 143 (1967).

Resonance Raman Spectra and Electronic Structure of the μ-Disulfur-Bridged Diruthenium Complex $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ and Related Systems[1]

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Abstract: The resonance Raman spectra of the μ-disulfur-bridged complex $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$, **1**, has been determined. An excitation profile reveals that the intense, totally symmetric Ru–S stretching vibration, which is the dominant feature of these spectra, is coupled to a single, intense, low-energy electronic transition (λ 715 mm, ϵ 14990) involving electrons delocalized over the Ru–S–S–Ru core. These observations establish that the Ru–S–S–Ru unit in this and certain related complexes is an electronically unique, independent chromophore. The suggested assignment for this transition, based on a qualitative molecular orbital description of the π-bonding in **1**, involves the promotion of an electron from a π-antibonding b_g orbital to a π-antibonding a_u orbital. It further follows that the only reasonable formulation of the electronic configuration in this molecule is Ru(III)–S–S–Ru(III). The utility of these observations, concepts, and conclusions as they relate to the electronic structure of other μ-dichalcogenide-bridged complexes is discussed.

Early studies of μ-dichalcogenide-bridged transition metal complexes concentrated on peroxo- and superoxo-bridged species with the aim of establishing categories of geometry and bonding.[2a,b] In turn, these investigations have provided insights about the nature of dioxygen-transition metal coordination.

More recently, attention has begun to focus on μ-dichalcogenide-bridged complexes in general, i.e., compounds which, as a class, are characterized by a M–X–X–M (X = S, Se, Te) linkage. Among the earliest characterizations of such complexes are those of Taube and co-workers,[3] who prepared the complex tetrabromo-μ-disulfurdecaaminodiruthenium, $[(H_3N)_5RuSSRu(NH_3)_5]Br_4$, **1**, along with a series of related homologues, $[(L)(H_3N)_4RuSSRu(NH_3)_4(L)]^{n+}$, and those of Siebert and Thym,[4] who reported the synthesis and partial characterization of hexapotassium μ-disulfurdecacyanodicobalt(III), $K_6[(NC)_5CoSSCo(CN)_5]$, and hexapotassium μ-diseleniumdecacyanodicobalt(III), $K_6[(NC)_5CoSeSeCo(CN)_5]$. Following these and subsequent studies,[5-7] the initial novelty of μ-dichalcogenide-

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[†] Rutgers University.

[‡] Bell Laboratories.

(1) This research was supported by DOE contract DE-AS05-80ER-1062 and NSF Grant 80-17405.

(2) (a) Cf. Lever, A. B. P.; Gray, H. B. *Accounts Chem. Res.* **1978**, *11*, 348, and references therein. (b) Martin, R. L. "New Pathways in Inorganic Chemistry"; Cambridge University Press, 1968. (c) DiSalvo, F. J.; Waszczak, J. V. *Phys. Rev.* **1981**, *B23*, 457. (d) Mononuclear ruthenium species serve as precursors to **1**; also compound **1** undergoes spontaneous decomposition in solution to a complex mixture of uncharacterized ruthenium-containing products.

(3) Brulet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758.

(4) Siebert, H.; Thym, S. *Z. Anorg. Allg. Chem.* **1973**, *399*, 107.

(5) For a review of earlier as well as subsequent papers, see: Kuehn, C. G.; Isied, S. S. *Prog. Inorg. Chem.* **1979**, *27*, 153.

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