a similar displacement of β-diketonate anions from palladium(II) has been observed to cause H–D exchange with $CDCl_3$.[15] This route can successfully explain the formation of protonated cyclopentadienyl complexes from the deuterated starting material, and the observed dependence on water concentration, since base catalysis is again involved.

A second possibility is transfer of a hydride from the cyclopentadienyl ring to palladium. This could also result in H–D exchange, such a process perhaps being facilitated by phosphine migration to the ring.[16] Formation of a hydridopalladium species by this route should be reversible and could cause complete deuteration of the cyclopentadienyl ring. Alternatively, protonation of the cyclopentadienyl ring and elimination of cyclopentadiene could in principle occur, although this is unlikely to be reversible and no obvious proton source is available.

Finally, it is possible that some (though not all) of the H–D exchange involving the ring protons is catalyzed by $[PdL_n]$. Addition of 0.17 mol equiv of $[Pd(P\text{-}n\text{-}Bu_3)_3]$ to a solution of I in acetone-d_6/D_2O caused almost quantitative exchange within the cyclopentadienyl ring, while the appearance of signals at δ 2.10 (quintet) and 3.50 (br s) indicated the formation of CHD_2COCD_3 and HOD (or H_2O), respectively. The fact that H–D exchange between water and the solvent has been observed to proceed independently of any change in cyclopentadienyl proton intensity, however, means that such a route for exchange of the ring protons could not be fast compared to the other process(es) involving the ring. Indeed, during the deuteration of I in the presence of $[Pd(P\text{-}n\text{-}Bu_3)_3]$ II was also observed, indicating that P-n-Bu_3 dissociation occurs, thereby opening the way for alternative mechanisms to operate here also.

Investigations of other cyclopentadienyl systems are being undertaken at present. Addition of tertiary phosphines to solutions of $[Ni(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NC_6H_5)]$ did not result in any isotopic exchange, but $[Pd(\eta^5\text{-}C_5H_5)(C_6H_5)(P\text{-}n\text{-}Bu_3)]$ reacted with P-n-Bu_3 in deuteriochloroform to yield some protonated solvent. A series of complexes $[Pt(\eta^5\text{-}C_5H_5)R(PR^1{}_3)]$ also reacted with $PR^1{}_3$ to give $CHCl_3$, the rate of H–D exchange decreasing in the orders $PR^1{}_3 = PMe_2Ph > PMePh_2$ and R = $p\text{-}Me_2NC_6H_4 > p\text{-}MeOC_6H_4 > C_6H_5 > CCl{=}CCl_2$.

These reactions present some interesting possibilities for the generation of deuterated or partially deuterated organic and organometallic molecules under very mild conditions, as well as providing an approach to the activation of water toward synthetically useful reactions, and work is currently in progress in these directions.

Acknowledgment. Thanks are expressed to Johnson Matthey for generous loans of palladium salts, and the award of a Faculty Research Fellowship by the University of Missouri—St. Louis (G.K.A.) is gratefully acknowledged.

Registry No. I, 85453-00-5; $Pd(PMePh_2)_4$, 24981-80-4; P-n-Bu_3, 998-40-3; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0; H_2O, 7732-18-5; $Pd(P\text{-}n\text{-}Bu_3)_3$, 52359-13-4; $Pd(PMePh_2)_4$, 24981-80-4.

---

[15] Okeya, S.; Nakamura, Y.; Kawaguchi, S. *J. Chem. Soc., Chem. Commun.* **1977**, 914; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3396.

[16] See, for example: Munro, G. A. M.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1976**, 134.

Synthesis and Decarboxylation Mechanism of the Chiral Rhenium Formate $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$

James H. Merrifield[1a] and J. A. Gladysz*[,1b,2]

Departments of Chemistry, University of California
Los Angeles, California 90024
and University of Utah
Salt Lake City, Utah 84112

Received March 8, 1983

Summary: Formate $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ (**1**) decarboxylates to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**2**) without PPh_3 dissociation, with retention at rhenium, with k_H/k_D (112 °C) = 1.55 ± 0.19, $\Delta H^\ddagger$ = 26.8 ± 0.6 kcal/mol, and $\Delta S^\ddagger$ = −6.3 ± 1.3 eu.

Catalyst-bound formates have been proposed as intermediates in some water gas shift reactions,[3,4] the iridium-catalyzed isomerization of methyl formate to acetic acid,[5] transfer hydrogenations involving formate ion,[6] metal-catalyzed decarboxylations of formic acid,[7] and CO_2/H_2 reactions.[8] Consequently, the chemistry of transition-metal formate complexes has been of intense recent interest.[4,9] In this communication, we report the synthesis of the first optically active formate complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ (1) and mechanistic details on its decarboxylation to hydride $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (2).

Reaction of racemic $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[10] (3) with 1.5 equiv of 88% aqueous HCO_2H in CH_2Cl_2 at −24 °C gave, after workup and CH_2Cl_2/hexane recrystallization, red needles of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)\cdot 0.75CH_2Cl_2$ ($1\cdot 0.75CH_2Cl_2$) in 79% yield (eq 1). Subsequent rapid CH_2Cl_2/hexane precipitation gave solvate free 1. The presence of the formate ligand was indicated by a ^1H NMR resonance at δ 8.06, a ^{13}C NMR resonance at 171.4 ppm, and IR $\nu_{C=O}$ at 1616 (s) and $\nu_{H\text{-}CO_2}$ at 2850 (w,

---

[1] (a) University of California. (b) University of Utah.

[2] Address correspondence to this author at the University of Utah. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

[3] (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *Ibid.* **1981**, *103*, 2699. (c) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *Ibid.* **1981**, *103*, 3411. (d) Slegeir, W. A. R.; Sapienza, R. S.; Rayford, R.; Lam, L. *Organometallics* **1982**, *1*, 1728.

[4] (a) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (b) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *Ibid.* **1981**, *103*, 3223. (c) Darensbourg, D. J.; Rokicki, A. *Ibid.* **1982**, *104*, 349. (d) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (e) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.*, in press.

[5] Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693.

[6] Bar, R.; Sasson, Y.; Blum, J. *J. Mol. Catal.* **1982**, *16*, 175.

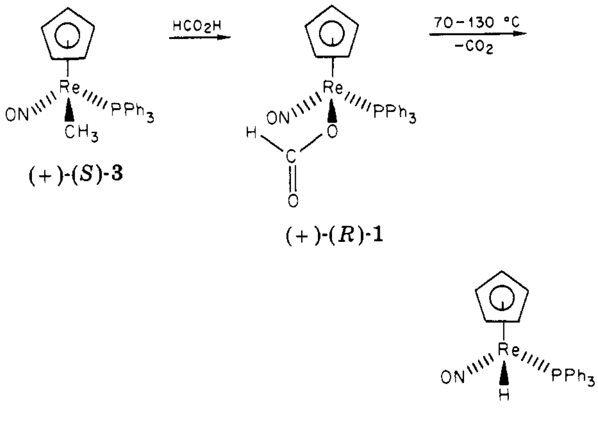
[7] (a) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59, and references therein. (d) Madix, R. J. *Adv. Catal.* **1980**, *29*, 1.

[8] (a) Ramaroson, E.; Kieffer, R.; Kienneman, A. *J. Chem. Soc., Chem. Commun.* **1982**, 645. (b) Certain data have also been intepreted as evidence for formates in the Cu/ZnO- or ZnO-catalyzed conversion of CO/H_2 to methanol: Ueno, A.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1971**, *67*, 3585. Klier, K. *Adv. Catal.* **1982**, *31*, 243.

[9] (a) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295. (b) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1982**, *234*, C5. (c) Poonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. (d) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662. (e) Roberts, D. R.; Geoffroy, G. L.; Bradley, M. G. *J. Organomet. Chem.* **1980**, *198*, C75.

[10] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

0276-7333/83/2302-0782$01.50/0



(+)-(*S*)-3

(+)-(*R*)-1

(+)-(*S*)-2

(1)

Table I. Rate of Decarboxylation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ (1)

substrate (additive)	temp, °C	10^4k_{obsd},[a] s^{-1}
(±)-1	90	0.23 ± 0.01
(±)-1	100	0.67 ± 0.07
(±)-1[b]	100	0.68 ± 0.05
(+)-(*R*)-1	100	0.66 ± 0.05
(±)-1	112	2.03 ± 0.08
(±)-1-d_1	112	1.31 ± 0.05
(±)-1-d_{15}	112	2.30 ± 0.09
(±)-1	115	2.72 ± 0.08
(±)-1	117	3.28 ± 0.13
(±)-1 (1.7 equiv of PPh_3)	117	3.08 ± 0.16
(±)-1 (2.5 equiv of PPh_3)	117	3.16 ± 0.14
(±)-1[c]	117	12.76 ± 0.62
(±)-1	134	14.53 ± 0.41

[a] From monitoring the disappearance of the C_5H_5 ^1H NMR resonance of 1 and the appearance of the C_5H_5 ^1H NMR resonance of 2 vs. Ph_3SiCH_3 internal standard. $[1]_0$ was ca. 0.145 M in toluene-d_8 unless noted. [b] $[1]_0$ was 1.5 times that in the preceding experiment. [c] CD_3CN solvent.

$\nu_{D\text{-}CO_2}$ 2125 cm^{-1}) cm^{-1} (all data in chloroform).[11] An identical reaction of (+)-(*S*)-3[12,13] with HCO_2H gave (+)-1, $[\alpha]^{25}{}_{589}$ 529° (*c* 0.72, $CHCl_3$), as a red powder. Other acid Re–CH_3 cleavages of (+)-(*S*)-3 have been shown by X-ray crystallography to proceed with >98% retention at rhenium.[14] Accordingly, the ORD/CD spectra of the (+)-1 obtained in eq 1 indicate *retention* at rhenium,[15] which corresponds to the *R*[12] absolute configuration.[16]

When 1 was heated to 70–130 °C in toluene, it cleanly decarboxylated to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (2, 96% isolated).[8] This reaction was ^1H NMR monitored in sealed tubes in toluene-d_8 and followed the rate law $-d[1]/dt = d[2]/dt = k_{obsd}[1]$ through three $t_{1/2}$ and over a range of temperatures (Table I). These data yielded the apparent activation parameters $\Delta H^{\ddagger} = 26.8 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -6.3 \pm 1.3$ eu, and $\Delta G^{\ddagger}_{298K} = 28.7 \pm 0.7$ kcal/mol.

The labeled formates $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCDO)$ (1-d_1) and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(OCHO)$ (1-d_{15}) were synthesized analogously to 1. As shown in Table I, 1-d_1 decarboxylated more slowly than 1: k_H/k_D (112 °C) = 1.55 ± 0.19. Recovered 1-d_1 showed no intramolecular deuterium scrambling.

The rate of decarboxylation of 1 in CD_3CN at 117 °C was ca. 4 times faster than that in toluene-d_8 (Table I). However, the rate was not affected by added PPh_3. To rigorously test the possibility of PPh_3 (or free ion ^-OCHO) dissociation at any point in the decarboxylation mechanism, 1-d_1 and 1-d_{15} were codecomposed. Mass spectral analysis of recovered 1-d_x and the resulting 2-d_x showed ≤8% of d_0 or d_{16} crossover products.

Optically active (+)-(*R*)-1 decarboxylated at the same rate as (±)-1. The resulting hydride was also optically active and ORD/CD spectra indicated[13-15] it to be (+)-(*S*)-2 (*retention*). However, the optical rotation of 2 depended upon the decarboxylation temperature (112 °C, 50% conversion, $[\alpha]^{25}{}_{589}$ = 17° (*c* 0.52, CH_2Cl_2); 75 °C, ca. 40% conversion, $[\alpha]^{25}{}_{589}$ = 53° (*c* 0.49, CH_2Cl_2)). Recovered (+)-(*R*)-1 showed no sign of racemization. No chemical or spectroscopic optical purity assay for 2 has been found to date.

The decarboxylation of 1-d_1 was accompanied by a product scrambling process which may be related to the preceding optical activity loss. Analysis of the 2-d_1 resulting from a 75 °C decarboxylation (ca. 82 h) by ^2H NMR showed the presence of deuterium in both the hydride (84 ± 3%) and cyclopentadienyl (16 ± 3%) ligands. Continued heating of this sample at 135 °C gave, after 2 days, a near-statistical (14 ± 3):(86 ± 3) ratio of Re–D to C_5H_4D.[17] No ^2H incorporation or scrambling was noted when 1 or 1-d_{15} were decarboxylated in toluene-d_8.

Hydride 2 was heated to 100 °C in toluene under 2000 psi of CO_2 for 3 days. No 1 formed; >95% of 2 was recovered. Formate isomer $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH)$[10] showed no sign of reaction over the course of 8 h in toluene-d_8 at 112 °C. Hence it can be rejected as an intermediate in eq 1.

The preceding data provide several startling contrasts to decarboxylation mechanisms of previously synthesized formate complexes. In Darensbourg's $(CO)_5Cr(OCHO)^-$, $(CO)_5W(OCHO)^-$, and $(\eta\text{-}C_5H_5)Fe(CO)_2(OCHO)$ systems,[4] ^{13}CO exchange was much faster than decarboxylation. The rate of decarboxylation of the former was retarded under CO.[4e] Hence CO dissociation was proposed as the initial step. Since our crossover experiments show that no PPh_3

---

(11) Data on 1: mp 126–127 ((±)-1) and 134–136 ((+)-(*R*)-1) °C; IR (cm^{-1}, $CHCl_3$) $\nu_{H\text{-}CO_2}$ 2850 (w), $\nu_{N{=}O}$ 1670 (s), $\nu_{C{=}O}$ 1616 (s); ^1H NMR (δ, $CDCl_3$) 8.06 (s, 1 H), 7.50–7.26 (m, 15H), 5.29 (s, 5H); ^{13}C NMR (ppm, $CDCl_3$) 171.4 (s, OCHO), phenyl carbons at 134.0 (d, J_{CP} = 11.2 Hz), 132.7 (d, J_{CP} = 55.1 Hz), 130.6 (s), 128.5 (d, J_{CP} = 11.0 Hz); 90.7 (s, C_5H_5); mass spectrum (*m/e*, 16 eV) 589 (M^+, ^{187}Re, 2%), 545 ($M^+ - CO_2$, 100%), 467 (74%). Anal. Calcd for $C_{24}H_{21}NO_3PRe\cdot0.75CH_2Cl_2$: C, 45.57; H, 3.48; N, 2.15; P, 4.75. Found: C, 45.84; 3.66; N, 2.21; P, 4.85.

(12) Designations (+)- and (–)- refer to rotations at 589 nm. Absolute configuration assignments (*R*, *S*) follow published conventions: (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (b) Sloan, T. *Top. Stereochem.* **1981**, *12*, 1.

(13) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(14) Merrifield, J. H. Ph.D. Thesis, UCLA, 1983.

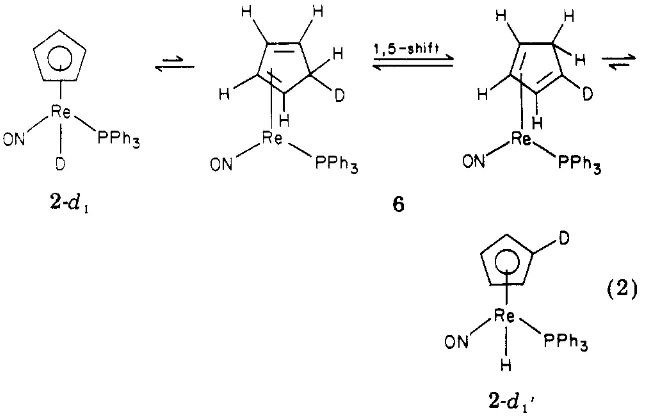
(15) The sign of the ORD or CD spectrum at >500 nm (or the sign of the region between the two *x*-axis crossings) correctly gives the absolute configuration in 29 of the 30 optically active $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds examined to date.[13,14]

(16) (a) Additional data on the optical purity and configurational assignment of (+)-(*R*)-1 are as follows. Reaction of (+)-(*S*)-3 with HCl gives (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (retention, $[\alpha]^{25}{}_{589}$ 307°), as determined by subsequent conversion with $AgPF_6$/(–)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (retention)[16b] to (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ (>99% diastereomerically pure by ^1H NMR; overall retention shown by X-ray structure).[14,16c] Treatment of (+)-(*R*)-1 with $(CH_3)_3SiCl$ also yields (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$, $[\alpha]^{25}{}_{589}$ 300°. This bounds the optical purity of (+)-(*R*)-1 as ≥98%; since the $(CH_3)_3SiCl$ cleavage likely proceeds with retention at rhenium, this provides further support that (+)-(*S*)-3 → (+)-(*R*)-1 proceeds with retention. (b) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251. (c) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.*, in press.

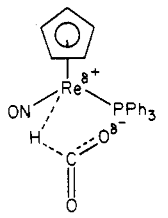
(17) Interestingly, when $LiAlD_4$ was substituted for $LiAlH_4$ in our previously reported synthesis of 2 ($[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-/(CH_3)_3N^+O^-/LiAlH$, 25 °C),[10] the Re-D to C_5H_4D ratio was ca. 30:70. This suggests that $\eta\text{-}C_5H_5$ is the preferred site of hydride attack.

dissociation occurs in 1 or 2 or during their interconversion, the corresponding mechanism for the decarboxylation of 1 can be excluded.

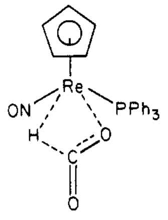
Remaining possibilities for the mechanism of decarboxylation of 1 include (1) η-C_5H_5 slippage followed by hydride migration to rhenium, (2) NO bending followed by hydride migration to rhenium, (3) hydride migration to η-C_5H_5 with η^2-CO_2 generation, (4) formate dissociation to give a tight ion pair, followed by hydride transfer to rhenium, and (5) concerted hydride migration to rhenium and CO_2 expulsion. We interpret the k_H/k_D as a *primary* kinetic isotope effect.[18] Hence η-C_5H_5 slippage and NO bending are excluded as rate-determining (but not preequilibrium) steps. Possibility 3 seems likely to give scrambled and/or racemic product (see eq 2). Any tight ion pair (possibility 4) would have to be configurationally stable, not dissociate, and form in a preequilibrium step. However, this mechanism would uniquely account for the greater ease of decarboxylation of 1 as compared to (η-C_5H_5)Re(NO)(PPh_3)(COOH). Furthermore, it has precedent in the S_Ni decarboxylation of thiocarbonates ROC(=O)SR′ and related organic compounds.[19] Structure 4 is a representation of the transition state for the rate-determining hydride-transfer step in this mechanism. It differs only slightly from the transition state for concerted decarboxylation, 5. We do not feel that our solvent effect and $\Delta S^{\ddagger}$ data rigorously distinguish between 4 and 5.



(2)



4



5

We speculate that deuterium scrambling (if chiral) in 2-d_1 proceeds as shown in eq 2. Intermediate 6 would have several possible facile racemization pathways. Both metal to η-C_5H_5 hydride migration and exo-1,5-hydride shifts in η^4-C_5H_6 ligands are precedented.[20] Davies and Felkin used a mechanism very similar to that in eq 2 to account for deuteride scrambling from iron to η-C_5H_5 in (η-C_5H_5)-Fe($PPh_2CH_2CH_2PPhCH_2CH_2PPh_2$)(D).[20b]

In summary, formate 1 decarboxylates without PPh_3 dissociation and with retention at rhenium. The mechanism differs from those proposed for the decarboxylation of other formate complexes. Additional experimental tests of some of the suggestions put forth in this communication are in progress.

Acknowledgment. We thank the Department of Energy for support of this research and Mr. G. Bodner for valuable assistance. FT NMR measurements made use of spectrometers obtained via NSF departmental instrumentation grants. J.H.M. thanks the Chevron Corp. and the regents of the University of California for fellowships.

---

[18] For leading references on isotope effects in four-centered transition states, see: Vitale, A. A.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 7341.

[19] (a) Kice, J. L.; Scriven, R. L.; Koubek, E.; Barnes, M. *J. Am. Chem. Soc.* **1970**, *92*, 5608. (b) Kice, J. L.; Hanson, G. C. *J. Org. Chem.* **1973**, *38*, 1410.

[20] (a) Whitesides, T. H.; Shelly, J. *J. Organomet. Chem.* **1975**, *92*, 215. (b) Davies, S. G.; Felkin, H.; Watts, O. *J. Chem. Soc., Chem. Commun.* **1980**, 159. (c) Knox, G. R.; Nutley, M.; Pauson, P. L.; Toma, S.; Watts, W. E.; Elder, P. A.; Griffiths, R. *J. Chem. Res., Miniprint* **1981**, 1901-1918.