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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Robert Edward Desinfecte II

ENTITLED: Addition and Substitution Reactions of

Fe₃Te₂(S)₃

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ADDITION AND SUBSTITUTION REACTIONS
OF
Fe₃Te₂(CO)₉

BY
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# TABLE OF CONTENTS

1. Introduction ................................................. 1-3
2. Figure 1 ................................................... 3
3. Experimental ............................................... 4-9
4. Results ................................................... 9
   - Scheme 1 ............................................... 9
   - Scheme 2 ............................................... 11
   - Figure 2 ............................................... 11
   - Figure 3 ............................................... 11
   - Scheme 3 ............................................... 12
   - Figure 4 ............................................... 13
5. Discussion ............................................... 15
6. Table of IR Absorptions ................................. 17
7. Scheme 1 (Diagram) ....................................... 18
8. Scheme 2, 3 (Diagram) .................................. 19
9. References ............................................... 20
Introduction

Iron chalcogenide cluster compounds are well known species first synthesized by Hieber, et. al. in 1956.\textsuperscript{1,2} Isoelectronic cobalt pnictogen clusters, first synthesized by Dahl, and Marko,\textsuperscript{3,4,5} are also known. In the iron-chalcogenide series both bimetallic and trimetallic clusters are known with the respective formulations: Fe\textsubscript{2}E\textsubscript{2}(CO)\textsubscript{6}, and Fe\textsubscript{3}E\textsubscript{2}(CO)\textsubscript{9}, where E = S, Se, Te.\textsuperscript{6} Various studies have been done in attempts to establish reactivity patterns. Some of these studies include making mixed metal clusters\textsuperscript{6}, looking at CO substitution rates,\textsuperscript{7,8} \textsuperscript{13}C NMR studies,\textsuperscript{9} and reactions with various ligands.\textsuperscript{7,10} It has also been found that Fe\textsubscript{3}E\textsubscript{2}(CO)\textsubscript{9}, for E = Te, exhibits a reactivity different from its S and Se analogs.\textsuperscript{10} Our study was designed to rationalize its different reactivity and to determine the extent, and location of ligand substitution.

Hieber, et. al.\textsuperscript{1,2} first synthesized both the bi and trimuclear iron clusters via the reaction of iron carbonyl ions (Fe(CO)\textsubscript{5} in methanolic KOH) with organic disulfides and diselenides, or alkali metal sulfides, selenides, and tellurites. In work by Stanghellini, et. al., the S, and Se congeners were found to undergo sequential substitution reactions with phosphine and arsine ligands only as far as the disubstituted derivatives.\textsuperscript{10} No trisubstituted derivatives were isolated and the starting materials decomposed with higher reaction temperatures. The reactivity of
the $S$, and $Se$ trinuclear compounds can be summarized as follows:

1) $Fe_2E_2(CO)_9 + L \rightleftharpoons Fe_3E_2(CO)_8L + CO$

2) $Fe_2E_2(CO)_6L + L \rightleftharpoons Fe_3E_2(CO)_7L_2 + CO$

$L = S, Se$

The Te compound was found to react similarly at room temperature, but with the initial reversible formation of an adduct:

$$Fe_3E_2(CO)_9 + L \rightleftharpoons Fe_3E_2(CO)_8L$$

purple \hspace{1cm} orange

$L = Te$

Stanghellini observed that with an excess of ligand, ($AsPh_3$, $P(n-$Bu)$_3$, $P(t-$Bu)$_3$), and moderate heating, the disubstitute analogous to that formed by the $S$ and $Se$ clusters was produced. (i.e., $Fe_3E_2(CO)_7L_2$)

Studies here focusing on the reactions of $Fe_3Te_2(CO)_9$ were investigated with the following ligands: triphenyl phosphine, ($Ph_3P$), dimethylphenylphosphine, ($Me_2PhP$), and tert-butyl isocyanide, ($t-$BuNC).

Other interesting problems with the $Fe_3E_2(CO)_9$ system are: 1) determining the location of ligand substitution, and 2) following the subsequent effects on the structure of the iron chalcogenide backbone. Previous studies outline a substitution pattern, and stereochemistry. The researchers
support these findings with $^{13}\text{C}$ NMR data. The proposed structure of the $\text{Fe}_5\text{Te}_2(\text{CO})_9$ adducts is as follows:

![Diagram of the proposed structure of the $\text{Fe}_5\text{Te}_2(\text{CO})_9$ adducts.]

Studies done here disagree with this structure, rather they predict this structure based on $^{31}\text{P}$, and $^{125}\text{Te}$ NMR spectra of the $\text{Fe}_5\text{Te}_2(\text{CO})_9$ adduct; $^{11,12}$ ($\text{L}=\text{PPh}_3$):

![Diagram of the predicted structure of the $\text{Fe}_5\text{Te}_2(\text{CO})_9$ adducts.]

*Figure 1, $\text{Fe}_5\text{Te}_2(\text{CO})_9\text{L}$*
Experimental

$^1H$ NMR spectra were recorded on either of two Varian instruments, one a 60 MHz, and the other a 90 MHz EM-390, using TMS as an internal standard. $^{31}P$ NMR spectra were recorded on a Varian XL-100 spectrometer in the Fourier transform mode with proton decoupling using an external D$_2$O lock with 85% H$_3$PO$_4$ as an external reference. IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer in cyclohexane or methylene chloride solutions. Microanalyses were performed by the School of Chemical Sciences analytical laboratory. Thin Layer Chromatography was performed on silica gel with 4:1 benzene/hexane as the eluent.

$\text{Fe}_3\text{Te}_2(\text{CO})_9$, 1

$\text{Fe}_3\text{Te}_2(\text{CO})_{10}$ was made by the modified Hieber method$^{13}$ and converted directly to $\text{Fe}_3\text{Te}_2(\text{CO})_9$ by refluxing for 0.5 hr. in hexane. This compound was recrystallized in CH$_2$Cl$_2$/MeOH. Yield: 2.97g (43%). Purity was checked by IR, and TLC. The $R_f$ on silica was 0.71.

$\text{Fe}_3\text{Te}_2(\text{Cl})_3\text{PPh}_3$, 1a

1a (1.5 mmol) of 1 was stirred at room temperature under N$_2$ with 0.39$\phi$ (1.5 mmol) of PPh$_3$ in 50ml of benzene for 5hr., when the reaction was judged complete after 2hr. by TLC. The solution had undergone a color change from dark purple to dark orange. The product, 1.23g (87.5%) was recrystallized from CH$_2$Cl$_2$/MeOH and characterized by IR.
and elemental analysis. Calculated for C_{27}Fe_{3}H_{15}O_{9}P_{2}: C, 34.61; H, 1.61; Fe, 17.88; P, 3.30. Found: C, 34.83; H, 1.57; Fe, 17.75; P, 3.66.

**Fe_{3}Te_{2}(CO)_{6}PPh_{3}, 1b**

1.23g (1.33 mmol) of 1a was refluxed in 50ml of hexane under N\textsubscript{2} with stirring. The reaction was judged complete after 2hr. by TLC, when the solution had gone from orange to dark purple. The solution was evaporated to dryness and recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/MeOH yielding 1.05g, (88%), of black crystals. The product was characterized by IR.

**Fe_{3}Te_{2}(CO)_{7}(PPh_{3})_{2}, 1c**

This compound was prepared from both 1a and 1b. First, 1b, (1.05g, 1.16 mmol) was dissolved in 50ml of hexane under N\textsubscript{2} and allowed to stir with 303mg, (1eq.) of PPh\textsubscript{3} for 10.5hr. The TLC showed that the reaction was incomplete with spots corresponding to the starting material 1b, an intermediate (probably the adduct Fe_{3}Te_{2}(CO)_{6}(PPh_{3})_{2}) and a third spot with an R\textsubscript{f} between the fast moving starting material and the slow moving adduct. The reaction mixture was then refluxed for 5hr. to yield the product with the intermediate R\textsubscript{f}. The solution was purified by column chromatography with Biobeads SX-4 gel as the stationary phase and benzene as the eluent. An intermediate fraction was taken and recrystallized from CH\textsubscript{2}Cl\textsubscript{2}/MeOH to yield 100mg, (7.5%), of black crystals of Fe_{3}Te_{2}(CO)_{7}(PPh_{3})_{2}. The product was characterized by IR and elemental analysis. Calc. for
Fe\textsubscript{3}Te\textsubscript{2}(C\textsubscript{7}H\textsubscript{4}C\textsubscript{3})\textsubscript{3}F\textsubscript{2}: Fe, 4.65; C, 45.17; H, 2.64; P, 5.42.
Found: Fe, 14.74; C, 44.68; H, 2.49; P, 5.75.

\textbf{Fe\textsubscript{3}Te\textsubscript{2}(Ph\textsubscript{3})\textsubscript{7}(t-BuNC). 1d}

100 mg of \textit{1d} (87.5 mmol) was stirred in 50 ml of benzene under N\textsubscript{2} with 15 \textmu l (\approx 2 eq) of t-BuNC. After 1 hr. TLC showed that the starting material was gone and 39 mg (36%) of a red orange powder that resisted recrystallization was recovered. It was characterized by IR, TLC, and elemental analysis. Its analysis was not close to the empirical formula Fe\textsubscript{3}Te\textsubscript{2}C\textsubscript{7}H\textsubscript{4}Cl\textsubscript{39} F\textsubscript{28}.

\textbf{Fe\textsubscript{3}Te\textsubscript{2}(CO)\textsubscript{9} + CH\textsubscript{2}N\textsubscript{2}}

100 mg (0.148 mmol) of \textit{1} was stirred in 50 ml of diethyl ether with 0.74 ml (1 eq) of a 0.2 M solution of CH\textsubscript{2}N\textsubscript{2} in diethyl ether. There was no reaction by TLC after 10 hr. and the starting material was recovered.

\textbf{Fe\textsubscript{3}Te\textsubscript{2}(Cl)\textsubscript{7}dpmm. 2}

1 g of \textit{1}, (1.48 mmol) in 50 ml of benzene was refluxed with stirring under N\textsubscript{2} with leq (0.57 g) of dpmm (bis-diphenyl-phosphino methane) for 0.5 hr., when the reaction was judged complete by TLC. The product was obtained as a dark powder, C, 4\textsubscript{1} (27%), from CH\textsubscript{2}Cl\textsubscript{2}/bech. The product was characterized by \textit{1}.
\( \text{Fe}_3\text{Fe}_2\text{Cl}_{7}dppm(t-\text{BuNC})_2 \), 2a

200mL of 0.2mmol of 2 was stirred in 50ml of benzene under \( \text{N}_2 \) with 30\( \mu \)l (0.2\( \mu \)mol) of \( t-\text{BuNC} \). The solution changed color instantly from dark purple to dark orange and after 2 hr. the solution was evaporated to dryness and recrystallized from \( \text{CH}_2\text{Cl}_2/\text{hexane} \). 120mg (55%) of an orange brown powder was isolated and characterized by TLC, IR, 1H NMR, and analytical data. Calc. for \( \text{Fe}_3\text{Fe}_2\text{C}_{27} \text{O}_7\text{P}_2\text{H}_{31} \): C, 40.91; H, 2.88; N, 1.79. Found: C, 40.31; H, 2.81; N, 1.20.

**Ph\(_2\)Ph, 3**

\( \text{Ph}_2\text{Ph} \) was prepared similar to the general method used to make trialkyl phosphines with lithium reagents.\(^4\) 1mol of dicyclohexyl complex in a dropping funnel was added over 0.5 hr. to a solution of \( \text{PhPhCl}_2 \) (0.5mol) under \( \text{N}_2 \) in 1 lb. of anhydrous ether in a three necked, three liter, round bottom flask kept at \(-78^\circ\text{C} \). The solution was allowed to warm to room temperature. 100ml of \( \text{Li}\text{Cl} \) was then cautiously added with stirring. The aqueous phase was removed via cannula. The ether was then distilled away at atmospheric pressure under \( \text{N}_2 \) flow. Benzene (50ml) was added to azeotropically distill away any \( \text{H}_2\text{O} \). The phosphine was then vacuum distilled from the original flask at \( \approx 12 \text{mm} \) at 65-70\(^\circ\text{C} \) with an \( \text{N}_2 \) bleed. The phosphine was then redistilled at \( \approx 10 \text{mm} \) and 55\(^\circ\text{C} \) under an \( \text{N}_2 \) bleed. Literature reports a b.p. of 76\(^\circ\text{C} \) at 12mm.\(^5\) The product was characterized by \( ^1\text{H} \) NMR and stored at \( 0^\circ \text{C} \) with an \( \text{N}_2 \) balloon.
Fe₃Te₂(Cu)ₓ(Phe₂Ph)ₙ, 4

0.5g of 1, (0.74mmol) was stirred in 50ml of benzene under N₂ with 0.5ml (0.5eq.) of 2. The reaction was instantaneous, forming a red orange solution. After 1 hr. TLC showed the starting material had been consumed. The solution was evaporated to dryness and eluted with 4:1 benzene/hexane on a preparative TLC plate.
Results

While it has been previously reported that compound 1 undergoes sequential addition, substitution reactions with phosphine ligands, the reaction has only been observed to go as far as the dissubstituted product.\textsuperscript{10} Several unstable trisubstituted complexes have been reported with pyridine, and piperidine acting on Fe\textsubscript{3}Fe\textsubscript{2}(CO)\textsubscript{9}.\textsuperscript{16}

The goal of our study was then to determine if substitution to a greater extent was possible without using more drastic conditions. The approach was to use more basic phosphines, t\textsuperscript{-}Bu, and ppm, a small chelating phosphine. It was hoped that structural changes inherent to these compounds, already substantially explained,\textsuperscript{12} could be followed and rationalized spectroscopically, (IR and NMR).

Scheme I

Compounds 1, 1a, 1b, and 1c (or similar derivatives) have all been made before.\textsuperscript{10,12} Some definitive studies have been done on 1a specifically. It was speculated by previous workers that the ligand in the Fe\textsubscript{3}Fe\textsubscript{2}(CO)\textsubscript{9}L adducts was bound directly to the Te atoms.\textsuperscript{9} A \textsuperscript{31}P NMR spectra of 1a shows a singlet downfield of free ligand bracketed by 2 weak pairs of satellites one of which is presumed to be $J_{\text{Te}, \text{P}}$, trans. The weak nature of this coupling is inconsistent with direct binding of the ligand to the Te atoms. The $^{125}\text{Te}$ NMR of this adduct shows 3 signals in a 2:1:1 ratio - the doublet being attributed to $J(125\text{Te}, 31\text{P})$, this coupling is the same as that between the $31\text{P}$ signal and the $125\text{Te}$
satellites in the $^{31}$P spectra. The crystal structure supports the NMR data. It places the PPh$_3$ ligand on an apical carbon (Fig. 1 b.3). $^{11,12}$

The synthesis of 1b was meant to confirm the ease of proceeding stepwise with addition, and substitution reactions of 1. Its IR was recorded.

1c was synthesized stepwise from 1b and directly from 1. The synthesis from 1, in good yield, was easily followed by TLC. 1a, b and presumably the adduct of 1b, Fe$_3$Te$_2$(O)$_8$ (PPh$_3$)$_2$ were all noted as intermediates. Longer reaction times did not afford a trisubstitute. The compound was characterized by IR, and $^{31}$P NMR. The room temperature $^{31}$P spectrum showed a singlet 72.53 ppm downfield from the H$_3$PO$_4$ standard flanked by small $^{129}$Te satellites, consistent with magnetically equivalent P atoms.

Though 1c would not undergo further addition or substitution with PPh$_3$, when treated with t-BuNC, it reacted quickly to give the orange colored solution characteristic of an adduct, but it did not analyze well and its TLC showed some impurities that might well have been removed chromatographically. If it had been purified a $^{31}$P NMR would indicate if the P atoms were equivalent or not and hence the location of the t-BuNC ligand determined.

An attempt to introduce a methylene group between the iron atoms in the cluster (analogous to the dppe coumpound) failed when C$_2$N$_2$ was stirred with 1. The solution was not heated, but perhaps heat or UV light would have initiated the reaction.
Scheme 2

A second attempt to proliferate ligand substitution or addition on 1 was directed on compound 2, which has been previously reported along with a $^{31}$P NMR spectrum. The spectrum, a pair of doublets (each inequivalent P splitting the other into two lines) shows that the two P atoms are inequivalent, which is consistent with the proposed structure. (Fig. 2)

Again, treatment of 2 with t-BuNC turned the dark purple solution instantly orange, giving the adduct 2a which gave a good analysis. Its 1H was recorded and the 60MHz $^1$H NMR showed a singlet at 1.2ppm (t-butyl protons) and a broad multiplet at 7.2-7.4ppm (phenyl protons) which integrated to approximately the correct ratio (the sample was not concentrated enough - hence two methylene protons were not visible). A $^{31}$P NMR spectrum was recorded but it would establish the position of the ligands. The probable structure is as follows: (Fig. 3)
Scheme 3

Our final attempt to polysubstitute 1, involved the idea that the more basic, and least sterically hindered ligand would have the best chance of providing an isolable, greater than doubly substituted derivative. Dimethylphenyl-phosphine was chosen because it was felt the even more basic trialkyl phosphines would be difficult to crystallize. Hence, PPhMe₂ was synthesized and its purity checked by ¹H NMR which showed a singlet at 1.4 ppm (5.6H methyl) and a broad multiplet 7.4-7.6 (5 1 phenyl). This compound was stored under an H₂ balloon at 0°C. In reactions this ligand was dispensed by gas tight syringe into de-aerated solvents.

PPhMe₂, 4, reacted with 1 at room temperature, and formation of the adduct was indicated by TLC. When the solution was heated to reflux the adduct gradually disappeared and two new spots, a slow moving orange one, and the other a faster moving purple one. This purple compound was the major product and after separation by preparatory TLC lustrous black crystals were obtained. This compound was characterized by IR and ¹H NMR. The IR appeared analogous to that of the PPh₃ disubstitute, 1c. Though the peaks were shifted down in energy from the 1c. This is encouraging though, since PPhMe₂ is more basic than PPh₃ and a poorer π-acceptor, its νCO stretches are shifted to lower frequencies.¹⁹ The elemental analysis was high in carbon and hydrogen for Fe₇Te₂(CO)₇(PhMe₂)₂. The C, H percentages are slightly low
for the trisubstitute, Fe₃Te₂(CO)₆(PPhMe₂)₃:

<table>
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<th>Compound</th>
<th>C</th>
<th>H</th>
</tr>
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<tr>
<td>Fe₃Te₂(CO)₇(PPhMe₂)₂</td>
<td>30.86</td>
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<tr>
<td>4</td>
<td>34.61</td>
<td>2.98</td>
</tr>
<tr>
<td>Fe₃Te₂(CO)₆(PPhMe₂)₃</td>
<td>35.90</td>
<td>3.31</td>
</tr>
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</table>

If these two compounds have the same Kf on silica gel in a 4:1 benzene/hexane solvent system, then it is possible that 4 is a mixture of the two. If this is true, then 4 is ≈78% trisubstitute (based on carbon).

The ¹H NMR presents an interesting dilemma. The 60 MHz spectrum shows a broad multiplet in the phenyl region: 7.2-7.6ppm (integration=64), a doublet centered at 1.65ppm (J=8Hz), a singlet at 1.95Hz that looks like it has a doublet partner buried under a large acetone impurity peak at 2.1ppm. Each peak of the doublet centered at 1.65ppm has area 27. The singlet of the presumed obscured doublet has area 12. If it is a doublet, its total area would be 24. The ratio of the total area of methyl protons would then be 78/64 = 6.09/1, very close to the expected 6:1 ratio. The two postulated compounds are shown next:

![Figure 4](image)

A  
A disubstitute

B  
A trisubstitute
At room temperature thermal motion should provide sufficient rotation of the 2 methyl groups to render them equivalent. Then pure A (Fig. 4) should show one doublet ($^{31}$P coupling) and B (Fig. 4, should show two doublets in the ratio 2:1. The basal phosphine methyl groups on A and B could have the same chemical shift, then a mixture of A, and B would show a pair of doublets like the spectrum of 4. For 78% B the ratio of basal phosphine methyl groups to apical phosphine methyl groups would be ~3:1. The ratio on the spectrum is 2.2 to 1, which is reasonable. Another possibility is the existence of positional isomers, (phosphines in axial or equatorial positions, which has been demonstrated by $^{13}$C NMR. This would make the phosphine methyl groups of A (Fig. 4) inequivalent. It seems probable based on the analysis that a mixture of compounds exists. A $^{31}$P NMR would be useful for this compound(s), it should show a singlet at room temperature for A analogous to 2c, while B would probably be two singlets in a 2:1 ratio (the distance between basal and apical phosphine position should rule out coupling).
**Discussion**

The difference in reactivity for Fe$_3$L$_2$(CO)$_9$ for E=Te vs. E=S,Se has been attributed to the large covalent radius of Te (1.37\(\text{Å}\)) vs. 1.03 \(\text{Å}\) for S, and 1.23 \(\text{Å}\) for Se.\(^{11}\) The consequent long bond distance for E=Te in Fe$_3$L$_2$(CO)$_9$ translates to a tight Fe-Te-Fe bond angle (\(\approx 60^\circ\)), whereas this angle is 68° for E=Se, and 72° for E=S. Considering that addition reactions take place only for E=Te, it seems appropriate to model the Te cluster as a strained ring system analogous to an organic strained ring system. For instance, cyclopropane adds Br$_2$ in the presence of a catalytic amount of FeBr$_3$ in \(\approx 1\) minute to break the ring and form dibromopropanes.\(^{17}\)

The analogous reaction, with chlorine on cyclohexane, a compound with no ring strain proceeds to give only the substitution product cyclohexyl chloride in about 1.5 hr.

Analogously, the strained E=Te, Fe$_3$L$_2$(CO)$_9$ compound undergoes addition reactions to relieve the strain in one of two pairs of acute (\(60^\circ\)) Fe-Te-Fe bond angles (Scheme 1).

A reasonable mechanism previously proposed envisions ligand attack at a basal iron, and a rearrangement of iron-iron bonds and (formally) Te-Fe bonds to make the addition site the new apical iron.\(^{12}\) The substitution product can be imagined to form from the expulsion of a CO group at the apical Fe and subsequent rearrangement to place the ligand in a basal site (Scheme 1).

The adducts, with one pair of acute Fe-Te-Fe bond angles and two pairs of 98° angles, show no propensity to open up into a structure which would have 3 open Fe-Te-Fe bond angles...
(95°). This structure would correspond to a diadduct:

\[ \text{Fe(Te)} \]

The fact that previously known, monodentate chelating phosphine ligands show no tendency to add the free phosphorus atom to the metal cluster has been shown.\(^1\text{2}\)

\[ \text{Fe(Te)} \]

So apparently the relief of one pair of acute Fe-Te-Fe angles is sufficient to reduce the strain in this cyclic compound and allow it to react like other unstrained ring compounds, i.e. substitution.

Though attempts to add 3 ligands appeared to be successful, i.e. \(1\text{d}, 2\text{a}, 4\), these products were incompletely characterized. \(1\text{d}\), and \(4\) need to be purified. Separation by chromatographic methods would probably be sufficient. \(2\text{a}\) was isolated in relatively pure form but time limitations inhibited acquiring definitive variable temperature \(^{31}\text{P NMR}\) data to determine where the \(\text{t-buNC}\) ligand was substituted relative to the phosphine ligands. Further study with \(^{31}\text{P}\) and \(^{125}\text{Te NMR}\) would be helpful in elucidating the structure and stereochemistry of these compounds.
In Data, cm⁻¹ (cyclohexane or C₂H₂Cl₂ solutions)

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<th>Compound</th>
<th>ν CO</th>
<th>ν NC</th>
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<td>Fe₃Te₂(C₅H₄N)₉, ₁</td>
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Scheme 1

Method 1

Method 2
Scheme 2

Scheme 3
References