THE CHEMISTRY OF PARA-TOLYLIMIDOVANADIUM V TRICHLORIDE. SYNTHESIS AND CHARACTERIZATION OF DIALKYLDITHIOCARBAMATE AND RELATED DERIVATIVES AND OF BIS(ORGANOPHOSPHINE)VANADIUM IV COMPLEXES

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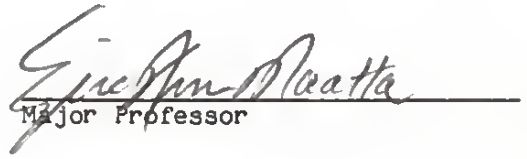

Major Professor

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LIST OF ABBREVIATIONS

acac	-	acetylacetonate
ca.	-	circa
cm	-	centimeter
d	-	doublet
dedtc	-	N,N-diethyldithiocarbamate
diphos	-	bis(diphenylphosphino)ethane
dmdtc	-	N,N-dimethyldithiocarbamate
dtc	-	N,N-dialkyldithiocarbamate
ESR	-	electron spin resonance
Et	-	ethyl group
g	-	grams
G	-	Gauss
GHz	-	Gigahertz
Hz	-	Hertz
IR	-	Infrared
m	-	multiplet
Me	-	methyl group
MHz	-	Megahertz
ml	-	milliliters
mmoles	-	millimoles
nm	-	nanometers
NMR	-	nuclear magnetic resonance
Ntol	-	para-tolylimido
Ø	-	C_6H_5
ppm	-	parts per million
q	-	quartet
R	-	alkyl group
s	-	singlet
t	-	triplet
THF	-	tetrahydrofuran

CHAPTER I

General Introduction

The investigation of complexes of early transition metals in high oxidation states continues to be subjected to thorough examination. Of the early transition metals, vanadium has a rich chemistry including compounds in all oxidation states from -1 to +5. Vanadium oxy-cations readily react to form compounds of interest because of their relatively simple magnetic and spectral properties. Among the more frequently considered ligands, sulfur and phosphorus have acted as donor atoms forming both monodentate and bidentate, thermally stable complexes. Vanadyl compounds of N,N-dialkyldithiocarbamates and organic phosphines have been prepared and well characterized in recent years. Reported here are the results of the synthesis and characterization of related dithiocarbamate and phosphine complexes of p-tolylimido vanadium.

The first vanadium N,N-dialkyldithiocarbamate reported was the vanadium (IV) compound $V(S_2CNEt_2)_4$ by Bradley and Gitlitz[1] in 1969. They prepared this complex by the addition of carbon disulfide to vanadium tetrakisdialkylamide.

$$V(NR_2)_4 + CS_2 \rightarrow V(S_2CNR_2)_4$$

R= Me, Et

These products are brown and thermally stable, but the dimethyl derivative decomposes upon heating.

An attempt at synthesizing a vanadium(II)dithiocarbamate compound was attempted by Larkworthy and coworkers[2] in 1970 when vanadium II salts were treated with aqueous solutions of sodium dithiocarbamates.

The brown products analyzed close to $V(dtc)_2$, but decomposition of the ligand and oxidation of the metal made the compound difficult to isolate in pure form.

The first successful isolation of a vanadyl N,N-dialkyldithiocarbamate complex was reported by Casey *et al.*,[3] in 1972. This Australian group synthesized the tri-substituted products of vanadium(V) with the formula $VO(dtc)_3$. The desired products were obtained by the oxidation reaction

$$VOSO_4 + Na(S_2CNR_2) \xrightarrow[H_2O]{H_2O_2} VO(S_2CNR_2)_3$$

R = Me, Et

The orange-brown products are air-stable in dry air and were characterized as being monomeric in nature.

In 1973, Bradley and coworkers[4] reported a reinvestigation of their previous vanadium(IV), $V(dtc)_4$ work, to report the newly detected presence of $V(dtc)_3$ during the synthesis of the tetrakis compound. They attributed their findings to the thermal instability of $V(dtc)_4$. A sample of the reddish-brown $V(dedtc)_4$ was heated under reflux for several hours in toluene to produce yellow-brown $V(dedtc)_3$.

$$V(dedtc)_4 \xrightarrow[\text{reflux}]{\text{toluene}} V(dedtc)_3$$

They also reported the synthesis of $VO(dtc)_2$ by the following reaction where the lithium N,N-diethyldithiocarbamate was obtained by addition of carbon disulfide to lithium diethylamide.

$$LiNEt_2 + CS_2 \rightarrow Li(dedtc)$$

$$VOSO_4 + Li(dedtc) \rightarrow VO(dedtc)_2$$

This grey compound was isolated and well-characterized.

Of the known vanadium dithiocarbamate compounds reported here, $V(dtc)_2$[2], $V(dtc)_3$[4], $V(dtc)_4$[1], $VO(dtc)_2$[4] and $VO(dtc)_3$[3], the vanadyl complexes are of great interest. It would be predicted that the isoelectronic vanadium p-tolylimido complexes should also be thermally stable and worthy of investigation. In Chapter II, the synthesis and characterization of the vanadium (V) dithiocarbamate compounds $V(Ntol)(dtc)_xCl_{3-x}$ where x = 1, 2, 3 is discussed.

The synthesis and characterization of μ-dithio-bis(tricarbonyliron) $(\mu\text{-}S)_2Fe_2(CO)_6$, was reported in 1958 by Hieber and Gruber[5]. The synthesis involved the reaction of iron pentacarbonyl with a methanolic solution of sulfur and sodium sulfide. It was shown in 1979[6] that the compound could be reacted with $LiEt_3BH$ to form the reactive ionic species $(\mu\text{-}LiS)_2Fe_2(CO)_6$. This compound could then be used to react with alkyl metal chlorides,

$$Li_2(S_2Fe_2(CO)_6) + R_2MCl_2 \rightarrow R_2MS_2Fe_2(CO)_6$$

and later[7] with metal tetrahalides.

$$Li_2(S_2Fe_2(CO)_6) + MX_4 \rightarrow X_2MS_2Fe_2(CO)_6$$

R. H. Holm and J. A. Kovacs[29] reported in 1986 the reaction of

$$Li_2(S_2Fe_2(CO)_6) + (NH_4)_3[VFe_2S_4Cl_4] \xrightarrow{Et_4N} (Et_4N)_3[VFe_6S_8(CO)_{12}]$$

the first reported vanadium compound containing the $S_2Fe_2(CO)_6$ moiety. Chapter III reports the preparation and identification of a heterotrimetallic complex of vanadium using $S_2Fe_2(CO)_6$ as a bidentate ligand, V(Ntol)(dmdtc)($S_2Fe_2(CO)_6$).

Complexes formed from β-diketones are numerous and have received extensive study for over 100 years. Acetylacetone, (acac), is the most commonly used β-ketone in these metal complexes which are numerous and easily synthesized. The vanadyl complex, $VO(acac)_2$, was first prepared in 1876 by Guyard[8] and then identified by Morgan and Moss in 1914.[9] X-ray crystal structure determination verified a tetragonal pyramidal structure and was reported by Dodge and coworkers[10] in 1961. In Chapter IV, the synthesis and characterization of the bisacetylacetonate complex $V(Ntol)(acac)_2Cl$ is described. $V(Ntol)(S_2P\emptyset_2)_2Cl$ is the final vanadium V compound to be reported in this text and it's synthesis and characterization are also found in Chapter IV.

It is generally recognized that organic phosphines may act as weak σ-pair donors toward transition metal atoms. In 1964 it was reported by Majandar and coworkers[11] that the product $VOCl_2 \cdot 2PPh_3 \cdot 2H_2O$ was isolated and identified, but later Selbin and Vigee[12] claimed this as erroneous, claiming the compound was actually a complex of triphenylphosphine oxide. Their report includes the synthesis of $VOCL_2 \cdot diphos \cdot H_2O$ by the following reaction

$$VOCl_2 \cdot xH_2O + diphos \rightarrow VOCl_2 \cdot diphos \cdot H_2O$$

The green solid was isolated and well characterized.

Published results during the early 1970's[11,12,13,14], reported failures to synthesize non-hydrated phosphine adducts of $VOCl_2$ or VCl_4. In 1978, Seddon and coworkers[15] reported successful isolation of the phosphine adducts, $VOCl_2(P\emptyset_2R)_2$, where (R = Me, $\emptyset$), by the reaction

$$VOCl_2(MeCN)_2 \xrightarrow[THF\ or\ MeCN]{P\emptyset_2R} VOCl_2(P\emptyset_2R)_2$$

In Chapter V, the synthesis and characterization of the related para-tolylimido vanadium(IV) phosphine complexes $V(Ntol)L_2Cl_2$ where L = PMe_3, $P\emptyset_3$, $PEt\emptyset_2$ and L_2 = diphos is described.

The vanadium V compounds $V(Ntol)L_2Cl$, where L = dmdtc, dedtc, acac, and $S_2P\emptyset_2$, were found to undergo reduction with Zn to form the vanadium (IV) products $V(Ntol)L_2$. Their syntheses and charazcterizations are described in Chapter VI.

The parent vanadium compound used in this study was prepared and characterized by Maatta in 1984.[16]

$$VOCl_3 + p\text{-tolylNCO} \rightarrow V(Ntol)Cl_3 + CO_2$$

The purple-black crystals are water sensitive, yet are thermally stable and provide a starting point to investigate vanadium (V) organoimido chemistry. Early investigations[16] showed the complex would form adducts $V(Ntol)Cl_3 \cdot L$, that it would react with potassium alkyloxides to form $V(Ntol)Cl_{3-x}(OR)_x$, where x = 1, 2, 3, and would react with NaC_5H_5 to form the π-bound arene complex $V(Ntol)(\eta^5\text{-}C_5H_5)Cl_2$.

This paper reports the ligand substitution reactions of $V(Ntol)Cl_3$, with Na(dtc), H(acac), $HS_2P\emptyset_2$, and $Li_2S_2Fe_2(CO)_6$, the reduction reactions with organic phosphines and Zn to form the vanadium(IV) complexes $V(Ntol)L_2Cl_2$, where L = PR_3 and L_2 = diphos, and the reduction reactions with Zn to form $V(Ntol)L_2$, where L = dtc, acac, or $S_2P\emptyset_2$.

Chapter II

Preparation and Purification of Starting Materials

Typical preparation and purification of starting materials are described herein.

I) para-Tolylimidovanadium V trichloride; $V(Ntol)Cl_3$[16]

$$VOCl_3 + p\text{-tolylNCO} \longrightarrow V(Ntol)Cl_3 + CO_2$$

p-Tolylisocyanate, (8.0 g, 60 mmoles), was combined with ca. 10 ml octane in a reaction flask containing a stir bar under a N_2 atmosphere. $VOCl_3$, (7.0 g, 40 mmoles), was added to ca. 50 ml octane and then added to the p-tolylisocyanate solution. The mixture was refluxed for 3 hours with CO_2 evolution resulting in a dark green solution. The octane was removed and the product evacuated at 110° overnight. Sublimation onto a water cooled probe from a 130°C oil bath yielded purple-black crystals. The product was analyzed by ^{1}H NMR, ^{51}V NMR, and mass spectroscopy and elemental analysis. (NOTE: Later investigations and preparations yielded results that provided information that sublimation was not necessary before subsequent reactions. The crude product appeared to be a mixture of brown and purple solids, but analysis indicated pure product. It could be assumed the brown solid is an oligomeric form of the desired $V(Ntol)Cl_3$ product). NMR data are found in Table 2-A and Table 2-D.

II) Sodium dimethyldithiocarbamate, $Na(S_2CN(CH_3)_2)$

CS_2, (15.0 ml, 250 mmoles), was syringed into a beaker at 0°C and allowed to stir. $HN(CH_3)_2/H_2O$, (43 ml, 250 mmoles), was then added and the solution turned an amber color with continued stirring. A solution of 50% NaOH, (10 g, 250 mmoles), was slowly added to the stirring solution over 5 minutes and produced a colorless solution. This solution was transferred to a 1-necked flask and the water was partially removed overnight by vacuum. As the water was being removed, a white precipitate collected on the sides of the flask. After 12 hours, the flask was heated to 110°C under continuous vacuum for 5 hours and the resulting dry white powder was washed by suction filtration using a Büchner funnel and three 25 ml aliquots of dried ethanol. The white crystalline product was analysed by IR and ^1H NMR spectroscopy to confirm the absence of H_2O and was stored in an N_2-filled dry box. ^1H NMR data are in Table 2-B.

III) Sodium diethyldithiocarbamate, $Na(S_2CN(CH_2CH_3)_2)$

$HN(CH_2CH_3)_2$, (25.9 ml, 250 mmoles), was added to 50 ml of CH_3CH_2OH in a beaker at 0°C and stirred. CS_2, (15.0 ml, 250 mmoles), was added to the ethanolic solution resulting in a golden colored solution. After 5 minutes, a 50% NaOH solution, (10.0 g, 250 mmoles), was cautiously added over 2 minutes and the desired product precipitated, producing a thick white solution. After stirring an additional 5 minutes at 0°C, the solution was filtered using a Büchner funnel and the product air dried for ~ 15 minutes. The product appeared fairly dry when transferred to a 500 ml 1-necked round bottom flask which was placed in an oil bath with a vacuum applied to remove the residual ethanol and to

drive off any coordinated water. After the product was heated for 4 hours at 105°C, the white crystalline product was transfered to a storage vial and kept in the N_2-filled dry box. The product was analyzed by IR and ^1H NMR spectroscopy to confirm the absence of water and provided proof of purity. ^1H NMR data are found in Table 2-C.

Experimental Section.

Synthesis of $V(Ntol)(S_2CN(CH_3)_2)Cl_2$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction vessel containing a stir bar and ca. 5 g Celite in the N_2-filled dry box. $NaS_2CN(CH_3)_2$, (0.273 g, 1.91 mmoles), was placed in a side arm and attached to the reaction flask. CH_2Cl_2, (ca. 25 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to ambient temperature with stirring. During the warm-up, the solution changed from purple to a dark green color. After 30 minutes, the $NaS_2CN(CH_3)_2$ was added and within one minute the green solution had turned an orange-red color. The product mixture stirred at room temperature for 30 minutes and was then filtered leaving NaCl and Celite on the filter frit. The filtrate was a red-orange CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_3)_2)Cl_2$. The CH_2Cl_2 was removed by vacuum and the product dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product which was washed and triturated with stirring for 15 minutes and then filtered, leaving the dark red-purple product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for the identity of

the product and purity by ^{1}H NMR, ^{51}V NMR, and Visible Spectroscopy. Data are found in Table 2-B, Table 2-D, and Table 2-E.

Synthesis of $V(Ntol)(S_2CN(CH_3)_2)_2Cl$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction flask containing a stir bar and ca. 5 g Celite in the N_2-filled dry box. $NaS_2CN(CH_3)_2$, (0.545 g, 3.81 mmoles), was placed in a side arm and attached to the reaction flask. CH_2Cl_2, (ca. 25 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. During the warm-up, the solution changed from dark purple to a dark green color. After 30 minutes, the $NaS_2CN(CH_3)_2$ was added and within 2 minutes, the green solution had turned an orange-red color. The product mixture was stirred at room temperature for 1 hour and then filtered leaving NaCl and Celite on the filter frit. The filtrate was an orange-red CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_3)_2)_2Cl$. The CH_2Cl_2 was removed by vacuum and the product dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product which was washed and triturated with stirring for 15 minutes and then filtered, leaving the dark red product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for proof of identity and purity by ^{1}H NMR, ^{51}V NMR, ^{13}C NMR, and Visible Spectroscopy. Data are found in Table 2-B, Table 2-D, Table 3-B, and Table 2-E.

Synthesis of $V(Ntol)(S_2CN(CH_3)_2)_3$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction flask containing a stir bar and ca. 5 grams of Celite in the N_2-filled dry box. $NaS_2CN(CH_3)_2$, (0.818 g 5.72 mmoles), was placed into a sidearm and attached to the reaction flask. CH_2Cl_2, (ca. 25 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. During the warm-up, the solution changed from purple to a dark green color. After 30 min, the $NaS_2CN(CH_3)_2$ was added and within 2 minutes the green solution had turned a red-orange color. After 30 minutes, the solution had gradually changed to a yellow color. The product mixture was stirred at room temperature for 90 minutes and then filtered leaving NaCl and Celite on the filter frit. The filtrate was a bright yellow colored CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_3)_2)_3$. The CH_2Cl_2 was removed by vacuum and the product was dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product which was washed and triturated with stirring for 15 minutes and then filtered, leaving the dark yellow product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for proof of identity and purity by ^1H NMR, ^{51}V NMR, Mass and Visible Spectroscopy and elemental analysis. Data are found in Table 2-B, Table 2-D, and Table 2-E.

For $V(Ntol)(dmdtc)_3 \cdot 1/4\ CH_2Cl_2$; $C_{16.25}H_{25.5}Cl_{0.5}N_4S_6V$

Found: C 36.11%, H 5.27%, N 9.87%

Calculated: C 36.28%, H 4.78%, N 10.41%

Synthesis of $V(Ntol)(S_2CN(CH_2CH_3)_2)Cl_2$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction flask containing a stir bar and ca. 5 grams of Celite in the N_2-filled dry box. $NaS_2CN(CH_2CH_3)_2$, (0.326 g, 1.91 mmoles), was placed in a sidearm and attached to the reaction flask. CH_2Cl_2, (ca. 25 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. During the warm-up, the solution changed from purple to a dark green color. After 30 minutes, the $NaS_2CN(CH_2CH_3)_2$ was added and within 2 minutes, the green solution had turned an orange-red color. The product mixture stirred at room temperature for 30 minutes and was filtered leaving NaCl and Celite on the filter frit. The filtrate was an orange-red CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_2CH_3)_2)Cl_2$. The CH_2Cl_2 was removed by vacuum and the product dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product. The dark red solid was washed and triturated with stirring for 15 minutes and then filtered leaving the dark red-purple product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for proof of identity and purity by ^1H NMR, ^{51} NMR, and Visible Spectroscopy and elemental analysis. Data are found in Table 2-C, Table 2-D, and Table 2-E.

For $V(Ntol)(dedtc)Cl_2$; $C_{12}H_{17}Cl_2N_2S_2V$

Found: C 38.92%, H 4.89%, N 7.59%

Calculated: C 38.41%, H 4.57%, N 7.47%

Synthesis of $V(Ntol)(S_2CN(CH_2CH_3)_2)_2Cl$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction flask containing a stir bar and ca. 5 grams of Celite in the N_2-filled dry box. $NaS_2CN(CH_2CH_3)_2$, (0.652 g, 3.80 mmoles), was placed in a sidearm and attached to the reaction flask. CH_2Cl_2, (ca. 25 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. During the warm-up, the solution changed from purple to a dark green color. After 30 minutes, the $NaS_2CN(CH_2CH_3)_2$ was added and within 3 minutes the green solution changed to a red-orange color. The product mixture stirred at room temperature for 60 minutes and was then filtered leaving NaCl and Celite on the filter frit. The filtrate was a red-orange CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_2CH_3)_2)_2Cl$. The CH_2Cl_2 was removed by vacuum and the product dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product. The dark red solid was washed and triturated with stirring for 15 minutes and then filtered leaving the dark red product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for proof of identity and purity by ^1H NMR, ^{15}V NMR, and Visible Spectroscopy and elemental analysis. Data are found in Table 2-C, Table 2-D, and Table 2-E.

For $V(Ntol)(dedtc)_2Cl \cdot 1/2CH_2Cl_2$; $C_{17.5}H_{28}Cl_2N_3S_4V$

Found: C 39.07%, H 5.53%, N 7.72%

Calculated: C 39.19%, H 5.23%, N 7.84%

Synthesis of $V(Ntol)(S_2CN(CH_2CH_3)_2)_3$

$V(Ntol)Cl_3$, (0.500 g, 1.91 mmoles), was added to a reaction flask containing a stir bar and ca. 5 grams of Celite in the N_2-filled dry box. $NaS_2CN(CH_2CH_3)_2$, (0.978 g, 5.72 mmoles), was placed into a side arm and attached to the reaction flask. CH_2Cl_2, (ca. 25 mL), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. During the warm up, the solution changed from purple to a dark green color. After 30 minutes, the solution had gradually changed to a dark yellow color. The product mixture stirred at room temperature for 90 minutes and was then filtered leaving NaCl and Celite on the filter frit. The filtrate was a bright yellow colored CH_2Cl_2 solution of $V(Ntol)(S_2CN(CH_2CH_3)_2)_3$. The CH_2Cl_2 was removed by vacuum and the product dried for 2 hours. n-Pentane was then vacuum distilled into the flask containing the dried product. The yellow solid was washed and triturated with stirring for 15 minutes and then filtered, leaving the dark yellow product on the filter frit. The pentane filtrate was colorless. The product was dried in vacuo for 3 hours and then stored in the N_2-filled dry box. The product was analyzed for proof of identity and purity by ^1H NMR, ^{51}V NMR, and Visible Spectroscopy and elemental analysis. Data are found in Table 2-C, Table 2-D, and Table 2-E.

For $V(Ntol)(dedtc)_3$; $C_{22}H_{37}N_4S_6V$

Found: C 43.60%, H 6.22%, N, 9.18%

Calculated: C 43.98%, H 6.21%, N 9.24%

Results and Discussion

$V(Ntol)(S_2CNR_2)_xCl_{3-x}$ $R = CH_3, CH_2CH_3$

$x = 1, 2, 3$

Analysis by ^1H NMR

The three protons in the tolyl-methyl group were found to be equivalent in all the imidovanadium dtc compounds studied. In the parent compound, $V(Ntol)Cl_3$, this proton resonance was exhibited at 2.5372 ppm. All the tolyl-methyl group signals in the dithiocarbamate compounds were found to exhibit an increasingly upfield shift with each additional dtc substitution of the three chlorine atoms. All the signals of the dmdtc derivatives were found to be just slightly upfield of the analogous dedtc compounds. Even though the tolyl-methyl protons are eleven atoms from the alkyl groups on the dtc ligands of the substituted vanadium compounds, the effects can be seen throughout the series that the dmdtc ligands are slightly better electron donors than are the dedtc groups. This is exhibited in the three pairs of dtc compounds where the dimethyl *vs* diethyl all show slight upfield shifts in the dimethyl derivatives: mono-substitution, 2.4317 ppm *vs* 2.4346 ppm, di-substitution, 2.4213 ppm *vs* 2.4278 ppm, and tri-substitution, 2.2687 ppm *vs* 2.2767 ppm. The increase in the upfield shifts are .0029 ppm, .0065 ppm, and .0080 ppm for each additional substitution. The other observation is the significant upfield shift the signals exhibit in the tri-substituted compounds versus the mono- and di-substituted products. This may be explained by the fact that in the mono- and di-substituted compounds, the dtc ligands lie mainly in the equatorial plane. However, upon substitution of the third chlorine atom by a dtc

ligand, the equatorial plane cannot accommodate all the sulfur atoms, and the third dtc ligand must coordinate with a sulfur atom in the axial position, trans to the nitrogen atom of the p-tolylimido moiety. The electron donation from the dtc ligand could then overlap with the dz^2 metal orbital providing a more efficient transport of electron density to the p-tolyl group. The upfield shift in the tri-substituted tolyl methyl proton signals clearly shows this phenomenon.

The next proton group analyzed was the dimethyldithiocarbmate methyl protons. In the sodium salt of dmdtc, the only signal exhibited is displayed at 3.2307 ppm due to the methyl protons. Upon substitution onto the vanadium atom, a downfield shift is shown versus the parent salt, in each compound. With each successive substitution, an upfield shift toward the parent peak value can be seen. The largest downfield shift is shown in the mono-substituted compound because there are two remaining chlorine groups on the vanadium atom, which draw electrons away from the metal center. Upon substitution by the second dmdtc ligand, the electron withdrawing capability of the one remaining chlorine atom vs the electron donating ability of the two dmdtc ligands is diminished and therefore the electron density donation per ligand is decreased showing an upfield shift in the methyl proton signal. This is seen as the signal shifts from 3.4407 ppm to 3.3563 ppm. Upon substitution by the third dmdtc ligand, only a very slight upfield shift in signal is noticed. This finding is difficult to explain with certainty, but changes in the vanadium environment must account for this shift, since one would expect an equal, if not greater, upfield shift to occur for the third substitution, since there are no electron withdrawing chlorine groups remaining and the vanadium atom now has

three electron donating dmdtc groups attached. Upon substitution the coordination number increases from six to seven and the compound transforms from a 16 electron complex to an 18 electron complex. These transformations are dramatic enough for a reliable explanation to be postulated. The p-tolyl methyl proton signal shifts upfield upon adding the third dmdtc ligand to the vanadium center, since the increased electron density from the third ligand is donated to the p-tolylimido moiety and away from the vanadium metal center.

One final observation about the signals exhibited by the dmdtc methyl protons, is that the signal displayed in the tri-substituted dmdtc compounds, exhibits inequality, due to the fact that the third ligand must substitute with one of the sulfur atoms coordinating in the axial position, trans to the imido-nitrogen atom. With the other dmdtc ligands lying in the equitorial plane of the compound, this renders the methyl protons unequal and thus produce a signal displaying a multiplet of peaks.

The α-CH_2 protons of the diethyldithiocarbamate ligands were also analyzed by ^1H NMR. To discuss the significance of their chemical shift behavior through the series of substitutions, the terminal methyl proton shift behavior must also be explained. For the parent salt, Na(dedtc), the spectrum exhibited is a triplet at 1.2454 ppm and a quartet at 4.0356 ppm. The signals displayed for the coordinated ligands show signals downfield from the parent salt for the terminal methyl protons, while the α-CH_2 protons exhibit upfield chemical shifts. The terminal methyl proton signals show this downfield shift for the same reasons the methyl protons of the dmdtc ligands displayed downfield shifts from their parent salt signal. The coordinated ligands donate electron

density to the vanadium atom, thus decreasing the electron density of the ligands, and especially of the terminal methyl protons. The greatest downfield shift is exhibited for the mono-substituted derivative, as with the dmdtc compound, because there are two remaining electron withdrawing chlorines to accept the electron density donation. The di-substituted signal then displays a slight upfield shift from the mono-substituted signal. This can be accounted for since there is only one remaining chlorine atom and two dedtc ligands donating electron density onto the metal center. The capacity of the vanadium atom to handle the increased electron density per ligand is diminished and therefore the ligand electron density donation is also decreased. This is shown as the signals appear at 1.3375 ppm for the mono-substituted dedtc derivative and at 1.2693 ppm for the di-substituted derivative. Both sets of signals appear as triplets showing equivalency amongst the protons. The conclusion is then reached, that for both compounds, the ligands must be bound in the equatorial plane.

The signals displayed for the α-CH_2 protons in these two compounds exhibit the opposite behavior. In the ^{51}V NMR analysis of these compounds, it was clearly shown that the dimethyl dtc ligands were slightly better electron donating ligands than were their diethyl counterparts. Since the methyl protons of the dmdtc ligands and the terminal methyl protons of the dedtc ligands exhibit the exact same behavior, yet the dmdtc ligand donate a greater electron density to the vanadium center, the difference must be with the α-CH_2 protons. Upon coordination to the metal atom, the α-CH_2 protons actually exhibit signals indicating an increase in electron density. Since the ligands display electron density donation and clearly the terminal methyl

protons show a decrease in electron density upon coordination, it can be assumed that the electron density lost by the three terminal methyl protons is shifted to the α-CH_2 protons, therefore increasing their electron density in the process. This may also explain why the dedtc ligands do not donate as much electron density to the vanadium center as the dmdtc ligands. This increase in electron density is shown in the signal position, as the peaks are shifted upfield from the parent salt signal. The parent signal appears as a 1:2:2:1 quartet, the mono-substituted compound signal is also displayed as a 1:2:2:1 quartet, but the 2 outside peaks are not quite resolved, and the di-substituted compound displays a doublet of quartets.

Coordination of the third dedtc to the vanadium atom adds complexity to the spectra, as there are now inequivalent ethyl groups due to coordination in the axial position. First, the terminal methyl proton signal exhibits a shoulder on the upfield side of the peak. The shoulder is small and is due to the dedtc ligand containing one sulfur coordinated in the axial position trans to the p-tolylimido nitrogen. It was discussed earlier in this text that there was significant electron density donation from the third dtc ligand through the d_{z^2} orbital to the p-tolyl moiety. Again, this is exhibited by the fact the shoulder lies to the upfield side of the peak. Both signals are displayed as triplets and are separated by .0961 ppm. The signal due to the α-CH_2 protons also displays an upfield shoulder again due to the third dtc coordinating out of the equitorial plane, forcing the inequivalency. These signals are separated by .0692 ppm and appear as unresolved multiplets.

The last set of signals exhibited by this series of compounds is the AB pattern located in the aromatic region of the spectra due to the ortho- and meta-carbon protons of the p-tolylimido moiety. The signals exhibit a second order spectra due to the fact that these two types of protons are involved in spin-spin coupling and the chemical shift difference of the two protons is large compared with their coupling constant. Since there is no change to the p-tolylimido moiety, throughout this series of compounds and the change in chemical environment due to ligand substitution is away from the tolyl-protons, there should not be dramatic changes seen in the signal patterns of these protons. The spin-spin coupling constant in the parent $V(Ntol)Cl_3$ compound is 7.80 Hz. This constant changes very little throughout the series with most values close to 8.00 Hz for both the dmdtc and dedtc derivatives. All the chemical shift values for the upfield doublet of the AB patterns are found upfield of the parent signal value of 7.2095 ppm, regardless of ligand alkyl group. This is easily explained since the parent compound has three electron withdrawing chlorines attached and upon substitution with electron donating dtc groups, an upfield shift due to the increase in electron density to the vanadium and thus to the p-tolyl ring would be expected. The values obtained are basically equal for either dtc ligand compound and show the pattern of increasing to ~7.08 ppm for the mono- and di-substituted products followed by a dramatic jump to ~6.90 ppm for the tri-substituted derivatives. This increase in electron density and upfield shift can be attributed by the dtc ligand coordinating through the axial position and allowing additional electron density to flow to the p-tolyl ring through the d_{z^2} orbital. The downfield doublet of the AB pattern exhibits an

unusual characteristic and should be carefully examined. In the mono-substituted derivatives, the doublet exhibits the predicted upfield shift form 7.4715 ppm in the parent $V(Ntol)Cl_3$ to 7.40 ppm due to the increased shielding created by the dtc ligand. However, upon substitution of the second dtc, the doublet makes a downfield leap past the value of the parent compound to 7.52 ppm. This seems confusing at first because the elimination of a chlorine and addition of a dtc ligand should push the signal further upfield. But, the lone chlorine is now forced into the axial position, trans to the p-tolylimido moiety and the overlap with the d_z^2 orbital of the vanadium allowing the electron withdrawing ability of the chlorine to be felt within the tolyl-ring, namely in the ortho positions. Since the chlorine is removing electron density from the ring at the ortho position, the signal shifts downfield, and the effect is so strong, the peak lies downfield of the parent peak, as well. This may be explained because the parent compound $V(Ntol)Cl_3$, has no chlorine atoms in the axial position and therefore no overlap through the d_z^2 orbital. But, once the chlorine atom is forced into that position, the resulting electron density withdrawal is significant. Finally, upon coordination of the third dtc, a dramatic reversal of electron flow heads back into the tolyl-ring and causes the signal to move upfield to -7.17 ppm. This shows the significant difference in electron density sharing properties of the two ligands involved.

This ^{1}H NMR spectral analysis has provided a bounty of information about the chemical properties and structure of the family of compounds

$V(Ntol)(S_2CNR_2)_xCl_{3-x}$ $\quad x = 1, 2, 3$

$\quad R = CH_3, CH_2CH_3$

It was found that the dimethyl dtc ligands were better electron density donating groups than the dedtc ligands and it was discovered that in the di-substituted derivatives that the dtc ligands lie in the equatorial plane, while forcing the chlorine atom into the axial position to act as an electron withdrawing group through the d_z^2 orbital of the vanadium metal center and effecting the electron density of the p-tolylimido ring. And finally, it was determined that upon coordination of the third dtc ligand to the vanadium atom, that it forms a sulfur bond to the metal in the axial position, trans to the p-tolylimido nitrogen atom which allows electron density to flow into the tolyl-ring through the overlap of the d_z^2 orbital on the vanadium atom.

$V(Ntol)(S_2CN(CH_3)_2)Cl_2$

Analysis by ^{13}C NMR

^{13}C NMR spectroscopy is a powerful analytical technique for determining the structures of organometallic compounds. In 1979,[17] van Gaal and co-workers reported the ^{13}C spectra data for seventy one dithiocarbamate compounds. The data obtained for the imidovanadium dithiocarbamates are in complete agreement with the values reported for similar compounds. The first signal encountered downfield from TMS appears at 21.721 ppm and is assigned to the p-tolyl methyl group. The

next signal appears at 39.750 ppm and is assigned to the dmdtc methyl groups. Since this is a single line, the dmdtc methyl groups must be chemically equivalent within the compound. van Gaal did not report any findings on dmdtc compounds, but a report by Chisholm and Extine[18] gives values near 35 ppm for the methyl groups of $M(O_2CN(CH_3)_2)_5$ type compounds. The next two peaks are exhibited at 126.738 ppm and 128.638 ppm and are due to the aromatic carbons in the p-tolyl ring. Values reported by van Gaal[17] for aromatic carbon signals are all within the 120 ppm to 130 ppm range with a few para position carbons lying slightly farther downfield. Aromatic carbons attached to a nitrogen atom exhibited signals from 137.0 ppm to 150.0 ppm and the peak in the vanadium spectrum at 140.722 can be accounted for by this carbon. The para-carbon of the p-tolyl ring showed no signal in this ^{13}C spectrum collected. This may be attributed to the fact this carbon has no bound protons. The final peak of the spectrum appears at 198.082 ppm and is the signal of the CS_2 dmdtc carbon. The intensity is very weak, but confirmable, and is in agreement with van Gaal as the reported values range from 191.7 ppm to 212.0 ppm for these particular carbons.

$V(Ntol)(dtc)_xCl_{3-x}$ x = 1, 2, 3

Analysis by ^{51}V NMR vs Visible Spectroscopy

Analysis of six family members of imidovanadium-ditihocarbamates was performed by a ^{51}V NMR study. The samples were prepared by forming solutions in $CDCl_3$ in an N_2-filled drybox and then sealed to prevent atmospheric oxidation. Good correlation was found between the corresponding dimethyl vs diethyl derivatives. For the mono-substituted compounds, the ^{51}V shift was found to be 288.9 ppm for the dimethyl

derivative and 301.4 ppm for the diethyl derivative. These values are closely related to the unsubstituted parent compound $V(Ntol)Cl_3$ where the chemical shift vs $VOCl_3$ was found at 305 ppm. The small upfield shift shows a slight increase in the electron density around the vanadium nucleus. The dimethyl derivative signal appears upfield of the diethyl derivative signal indicating that the methyl groups appear to have a slightly greater electron donating effect upon the dithiocarbamate ligand. Spectral data was also collected for the di-substituted compounds which showed an even greater electron density increase about the vanadium nucleus. The chemical shifts were found to be 161.1 ppm for the dimethyl derivative and 166.4 ppm for the diethyl derivative. Finally, spectral data was collected for the tri-substituted derivatives where a dramatic increase in the electron density around the vanadium nucleus was exhibited. The chemical shift values obtained were upfield from $VOCl_3$ at values of -573.6 ppm for the dimethyl derivative and of -565.1 ppm for the diethyl derivative. This dramatic increase may be explained by the increase in the coordination of the vanadium center from six to seven, or from the fact that the final chlorine of the parent compound was replaced, leaving only electron donating substituents on the metal center, providing an electron rich environment for the vanadium nucleus. Furthermore, the correlations found in the product analysis, reaffirmed the fact that the methyl groups effectively make the dithiocarbamate ligands slightly better electron contributors than the diethyl derivatives.

Line widths were also recorded in the ^{51}V spectral analysis and were found to be relatively large. A line width of 500 Hz is assigned to the parent compound and can be explained by the enhanced quadrupolar

broadening due to the lowering of the symmetry of the product produced by the p-tolylimido ligand. These line widths were all significantly large enough as to conceal the ^{51}V-^{14}N coupling, which has been reported to be ca. 100 Hz. The line widths are listed in Table 2-D and are found to range from 415 Hz to 2613 Hz for the series of dithiocarbamates being investigated and exhibit similar properties for related compounds.

Visible spectral data were also collected for this series of compounds. Solutions were made in the N_2-filled dry box using toluene as the solvent. Correlations and patterns were seen in the data collected as the related compound exhibited similar maximum values (λ_{max}). The mono-substituted compounds exhibited a single maximum peak and were found at 540 nm for the dimethyl derivative and at 530 nm for the diethyl derivative. The di-substituted compounds showed λ_{max} values at 505 nm and 520 nm respectively and the tri-substituted compounds exhibited single maximum peaks at 420 nm and 400 nm, also respectively. Although the precise assignment remains to be determined for these bands, it can be reasonably concluded they are best explained by ligand to metal charge transfer transitions. The dithiocarbamate ligands carry an electron from a molecular orbital to a molecular orbital centered mainly on the metal center during the transition. The energy required for this transition is thus reflected in the absorbtion of energy and the measurement is recorded as the λ_{max} value. This occurs when the metal ion possesses low-lying empty orbitals and the ligand has filled orbitals lying lower than the lowest unfilled metal orbitals.

A transition where an electron is transferred from one atom or group in the molecule to another is called a charge-transfer transition. The transition occurs between molecular orbitals that are essentially

centered on different atoms. This transition could involve excitation of an electron from a π bonding molecular orbital, consisting essentially of sulfur atomic orbitals, to a molecular orbital that is essentially a vanadium atomic orbital.

Chemical shift values δ_v increase in the order, Br < Cl < F, for the compounds VOX_3 and is explained in terms of decreasing paramagnetic contribution to the shielding constant δ_{para}.[19] This decrease is due to a) increased energy separation ΔE between the highest and lowest unoccupied molecular orbitals relevant to electron transitions in NMR experiments, b) decreased metal character of ground state and excited state molecular orbitals, and c) restricted expansion of the metal-electron sphere.[20,21]

The overall shielding under isotopic conditions can be expressed as

$$\sigma = \sigma_{dia} + \sigma_{para} + \sum_n \sigma_n$$

where σ_{dia} and σ_{para} are the local diamagnetic and paramagnetic contributions, and $\sum_n \sigma_n$ are non-local diamagnetic contributions.[22] Webb and co-workers[23] have shown the non-local terms are negligible. Variations in the overall shielding are dominated by variations in the paramagnetic term σ_{para}. This effect has it's origin in the residual paramagnetism imparted by excited states and acts as a deshielding contribution.[22]

The paramagnetic term extrapolated to zero is viewed by the spectroscopist as

$$\sigma_{para} = -\text{constant} \cdot \frac{\langle 1/r^3 \rangle}{\Delta E}$$

Figure 2-H shows the correlation between ^{51}V chemical shift and $1/\Delta E$ representing the wavelength of the lowest energy optical transition.

By relating the known information about ^{59}Co chemical shift theory[24] and correlation studies, a prediction is made that a linear correlation should exist between the λ_{max} values obtained from visible spectroscopy data with the values obtained in the ^{51}V NMR study. When plotted against each other, as seen in Figure 2-H, the correlation shows good alignment, but the values do deviate from being perfectly linear.

$V(Ntol)(S_2CN(CH_3)_2)_3$

Analysis by Mass Spectroscopy

A fairly high temperature was required to obtain a mass spectrum of this vanadium dithiocarbamate. The parent ion was detected and the base peak corresponded to the ligand fragment ion $(SCN(CH_3)_2)^+$. This is in complete agreement with the findings of Bradley, et. al.[4] when they examined the mass spectra of several metal dithiocarbamates and found similar results. The presence of the ion $V(S_2CN(CH_3)_2)_3^+$ in the spectrum is interesting, since the vanadium-nitrogen bond is thought to be relatively stable. The fragmentation pattern throughout the spectrum

exhibits conclusive evidence to confirm the synthesis of the desired product.

Table 2-A

Proton NMR Chemical Shift Assignments for $V(Ntol)Cl_3$

Atom	Chemical Shift (δ)
$NC_6H_4C\underline{H}_3$	2.5372, s
$NC_6\underline{H}_4CH_3$	7.3405, q

The spectrum was taken in $CDCl_3$ at ambient temperature.

Table 2-B

Proton NMR Chemical Shift Assignments
for the Dimethyldithiocarbamate derivatives

Compound		Chemical Shift (ppm)	Coupling Constant J(Hz)
Na(dmdtc)	$S_2CN(CH_3)_2$,	3.2307, s	
V(Ntol)(dmdtc)Cl_2	$NC_6H_4CH_3$,	2.4317, s	
	$NC_6H_4CH_3$,	7.2361, q	J_{AB} = 8.02
	$S_2CN(CH_3)_2$,	3.4407, s	
V(Ntol)$(dmdtc)_2Cl$	$NC_6H_4CH_3$,	2.4213, s	
	$NC_6H_4CH_3$,	7.3056, q	J_{AB} = 8.06
	$S_2CN(CH_3)_2$,	3.3563, s	
V(Ntol)$(dmdtc)_3$	$NC_6H_4CH_3$,	2.2687, s	
	$NC_6H_4CH_3$,	7.0430, q	J_{AB} = 8.14
	$S_2CN(CH_3)_2$,	3.3553, m	

All spectra were taken in $CDCl_3$ at ambient temperatures.

Table 2-C

Proton NMR Chemical Shift Assignments
for the Diethyldithiocarbamate derivatives

Compound	Chemical Shift (ppm)		Coupling Constant J(Hz)
Na(dedtc)	$S_2CN(CH_2\underline{CH_3})_2$	1.2454, t	
	$S_2CN(CH_2\underline{CH_3})_2$	4.0356, q	J_{H-H} = 7.04
V(Ntol)(dedtc)Cl_2	$NC_6H_4CH_3$	2.4346, s	
	$NC_6\underline{H_4}CH_3$	7.2382, q	J_{AB} = 7.92
	$S_2CN(CH_2\underline{CH_3})_2$	1.3375, t	
	$S_2CN(\underline{CH_2}CH_3)_2$	3.8536, d	J_{H-H} = 6.85
V(Ntol)$(dedtc)_2Cl$	$NC_6H_4CH_3$	2.4278, s	
	$NC_6\underline{H_4}CH_3$	7.3002, q	J_{AB} = 8.32
	$S_2CN(CH_2\underline{CH_3})_2$	1.2693, t	J_{H-H} = 7.06
	$S_2CN(\underline{CH_2}CH_3)_2$	3.7831, dm	
V(Ntol)$(dedtc)_3$	$NC_6H_4CH_3$	2.2767, s	
	$NC_6\underline{H_4}CH_3$	7.0258, q	J_{AB} = 8.08
	$S_2CN(CH_2\underline{CH_3})_2$ (equatorial-type)	1.2673, d	
	$S_2CN(CH_2\underline{CH_3})_2$ (axial-type)	1.1712, t	
	$S_2CN(\underline{CH_2}CH_3)_2$ (equatorial-type)	3.8157, m	
	$S_2CN(\underline{CH_2}CH_3)_2$ (axial-type)	3.7465, m	

All spectrum were taken in $CDCl_3$ at ambient temperatures.

Table 2-D

Vanadium Chemical Shift Assignments

Compound	Chemical Shift (ppm)	Line Width (Hz) ($\Delta\nu_{1/2}$)
$VOCl_3$	0	23
$V(Ntol)Cl_3$	305	500
$V(Ntol)(dmdtc)Cl_2$	288.9	439
$V(Ntol)(dedtc)Cl_2$	301.4	415
$V(Ntol)(dmdtc)_2Cl$	161.1	1868
$V(Ntol)(dedtc)_2Cl$	166.4	2613
$V(Ntol)(dmdtc)_3$	-573.6	1527
$V(Ntol)(dedtc)_3$	-565.1	1782

Chemical shifts are relative to external $VOCl_3/CDCl_3$ determined at 105.2 MHz as $CDCl_3$ solutions and at 25°C where positive values denote downfield shift.

Table 2-E

Visible Spectra Data for the dialkyldithiocarbamate compounds

Compound	λ_{max} (nm)
$V(Ntol)(dmdtc)Cl_2$	540
$V(Ntol)(dmdtc)_2Cl$	505
$V(Ntol)(dmdtc)_3$	420
$V(Ntol)(dedtc)Cl_2$	530
$V(Ntol)(dedtc)_2Cl$	520
$V(Ntol)(dedtc)_3$	400

All spectra were taken as solutions in dried and degassed toluene.

Table 2-F

Mass Spectral Data for
$V(Ntol)(S_2CN(CH_3)_2)_3$

Fragment	Calculated Mass	Observed Mass
$V(Ntol)(dmdtc)_3$	515.90	515.86
$V(dmdtc)_3$	410.90	410.88
$V(Ntol)(dmdtc)_2$	395.90	395.96
$V(N)(dmdtc)_2$	304.90	304.60
V(Ntol)(dmdtc)	275.90	276.98
$V(S_2CN)_2$	230.90	230.90
Ntol	105.0	105.98
$SCN(CH_3)_2$	88.0	87.96

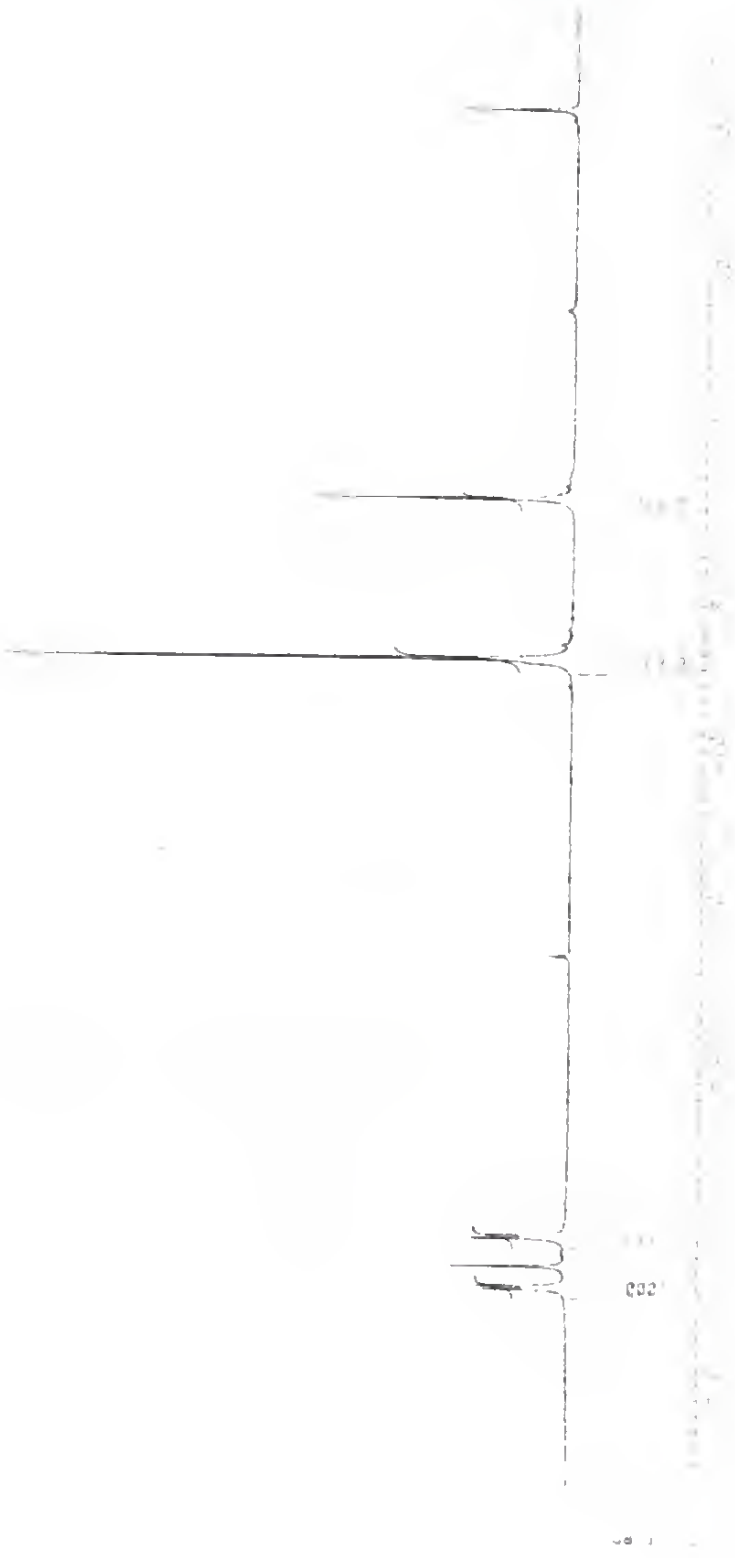

Fig. 2-A ^{1}H NMR Spectrum of (N,N-Dimethyldithiocarbamatopara-tolyl-imido vanadium V dichloride), ($CDCl_3$)

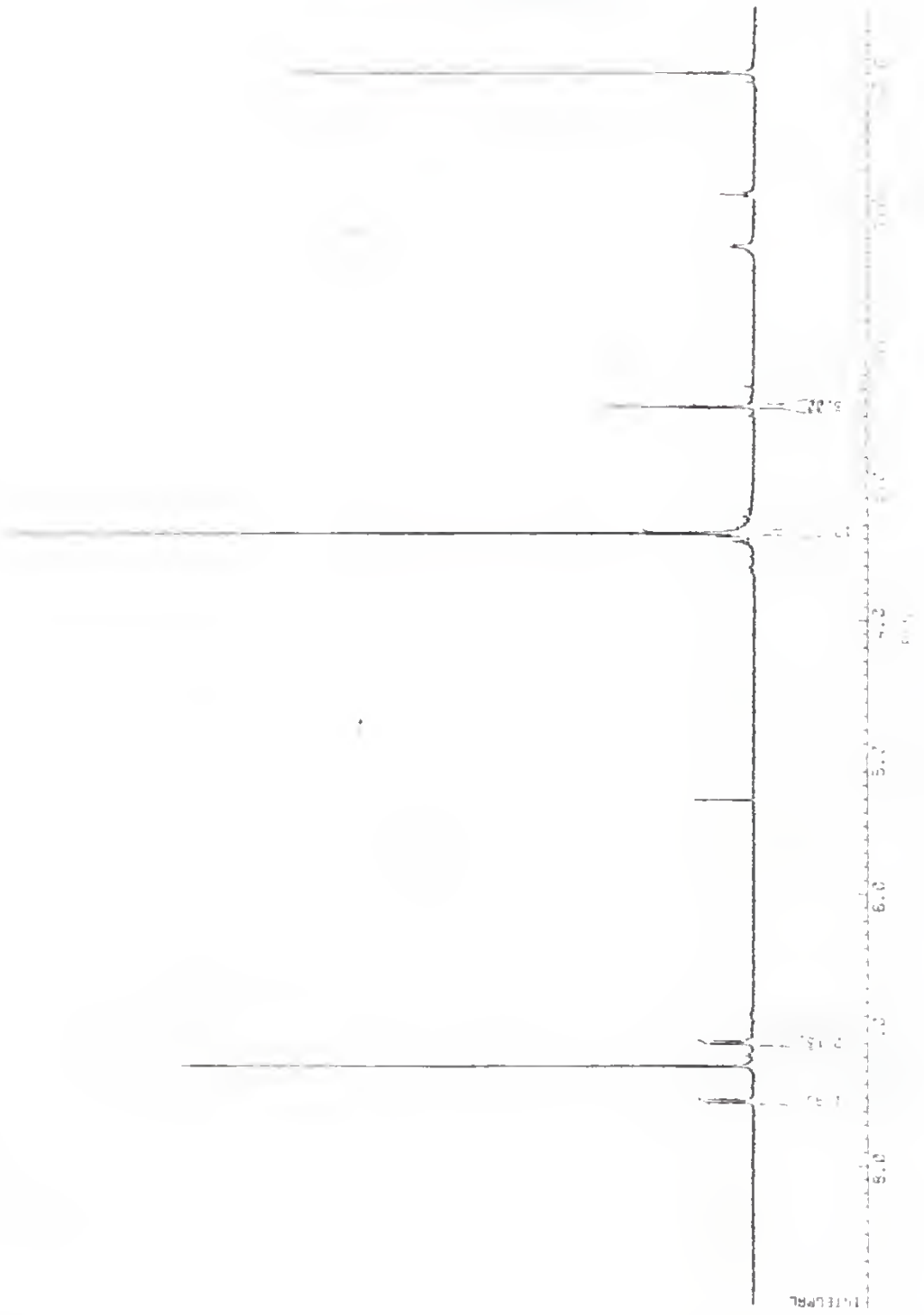

Fig. 2-B ^{1}H NMR Spectrum of (Bis(N,N-dimethyldithiocarbamato)para-tolylimido vanadium V chloride), ($CDCl_3$)

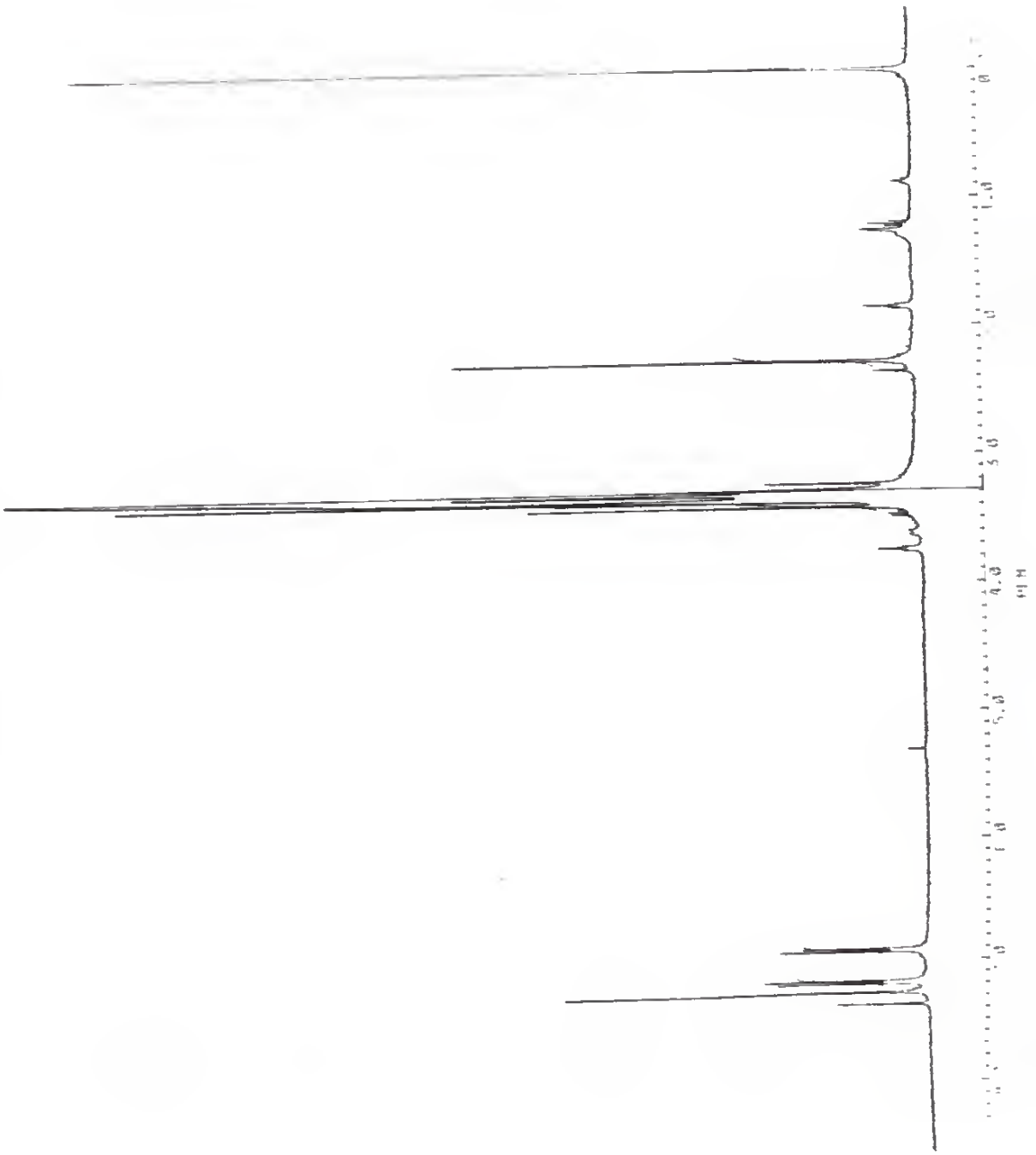

Fig. 2-C ^{1}H NMR Spectrum of (Tris(N,N-dimethyldithiocarbamato)para-tolylimido vanadium V), ($CDCl_3$)

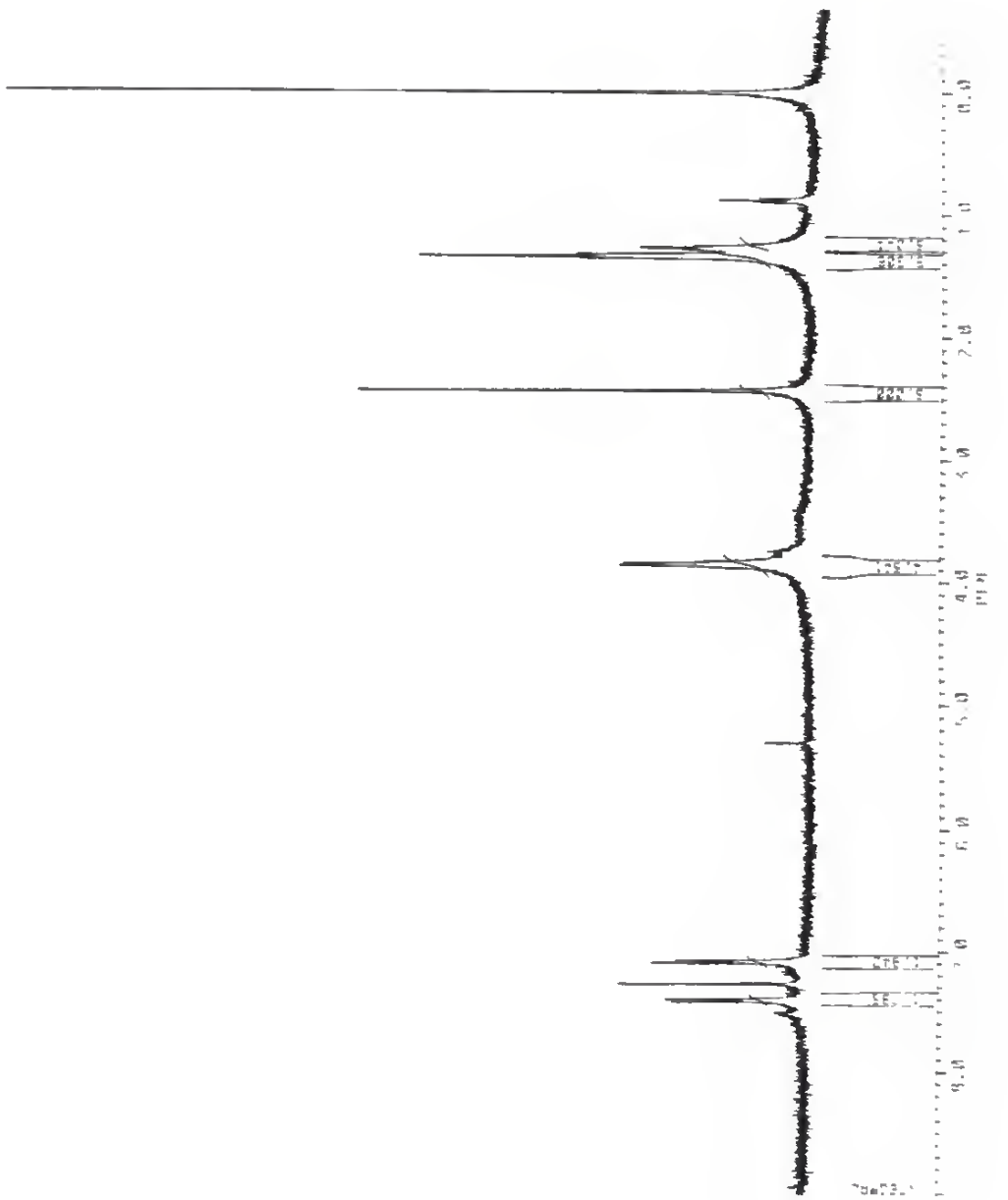

Fig. 2-D ^{1}H NMR Spectrum of (N,N-Diethyldithiocarbamato para-tolyl-imido vanadium V dichloride), ($CDCl_3$)

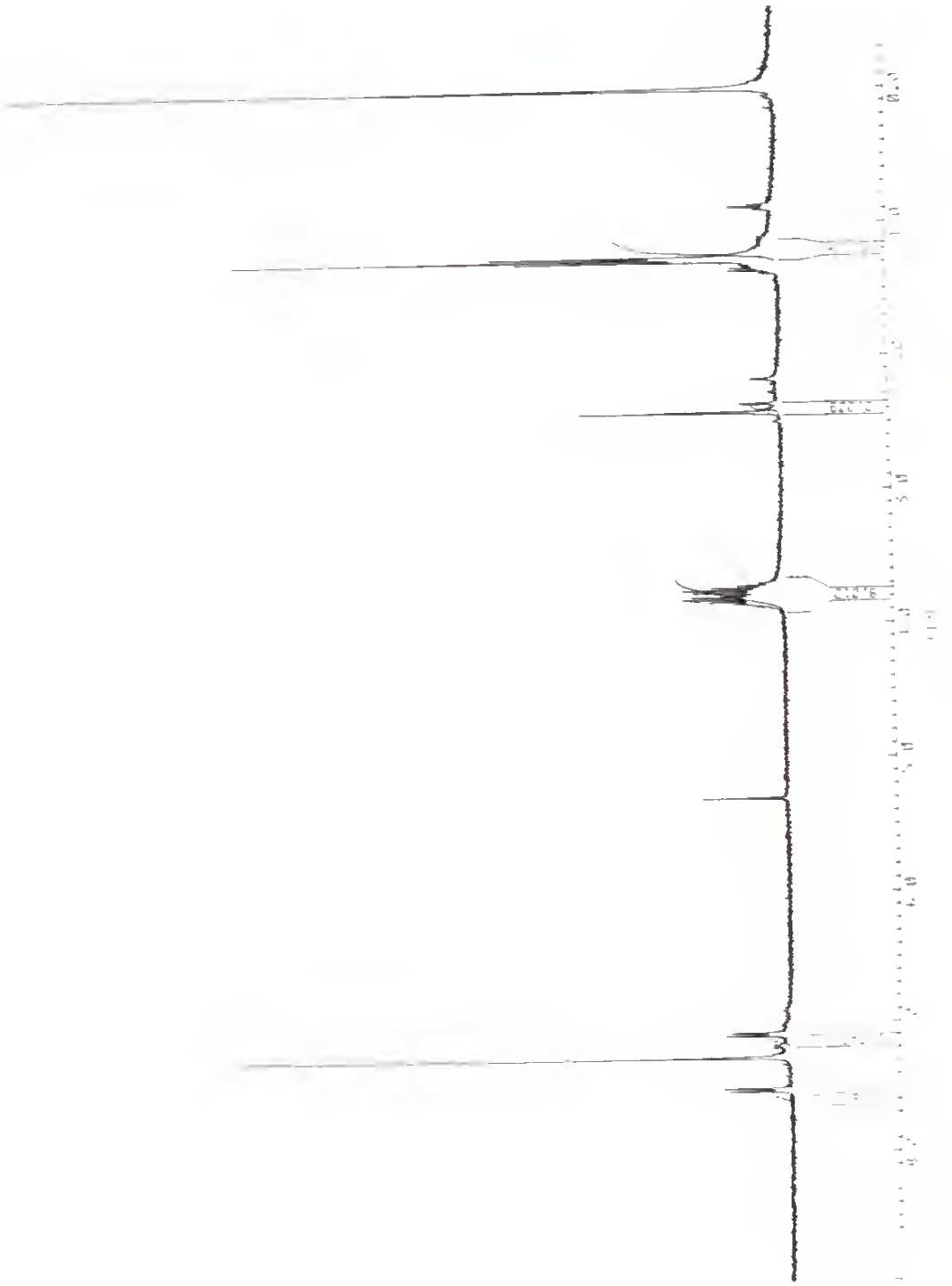

Fig. 2-E ^{1}H NMR Spectrum of (Bis(N,N-diethyldithiocarbamato) para-tolylimido vanadium V chloride), ($CDCl_3$)

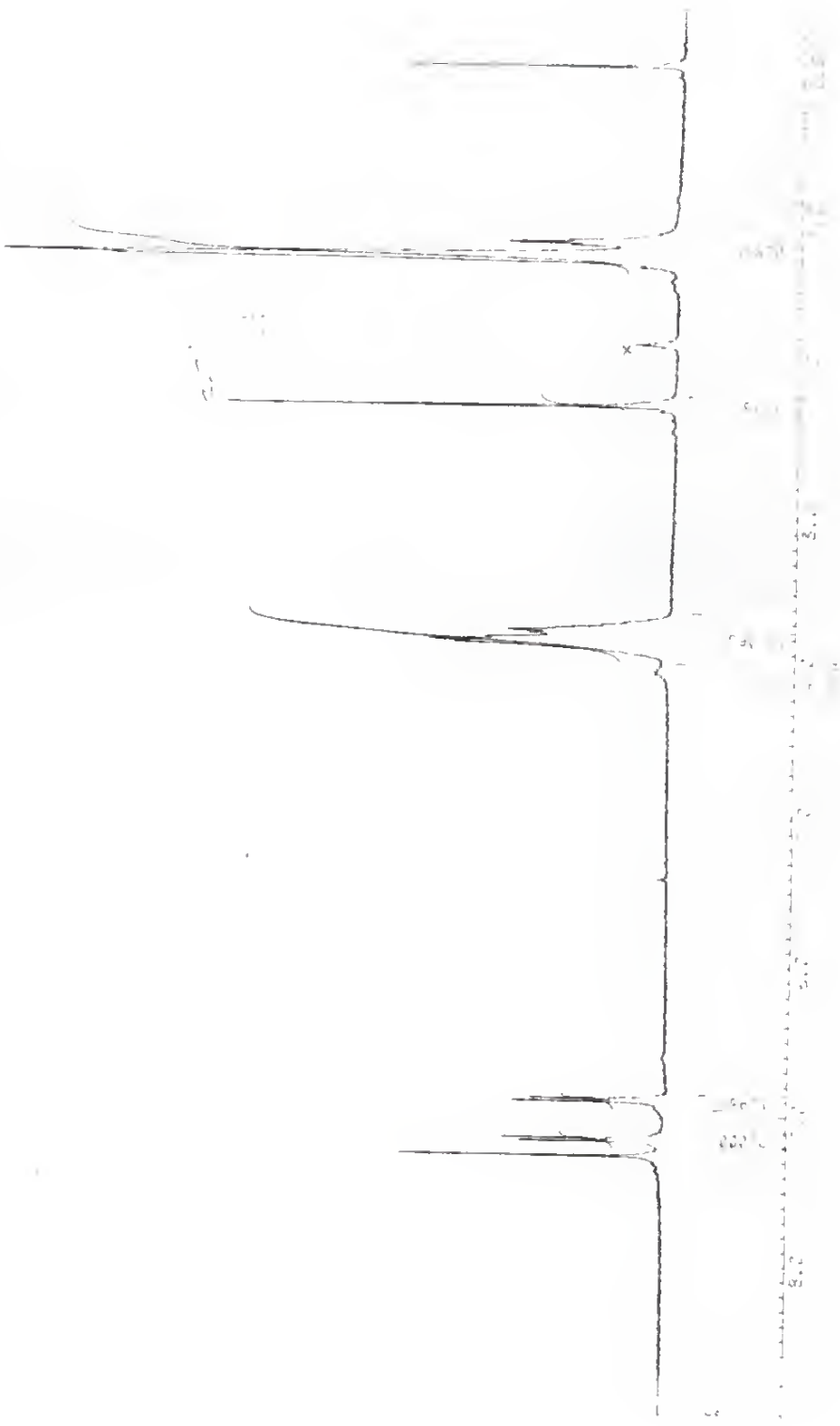

Fig. 2-F ^{1}H NMR Spectrum of (Tris(N,N-diethyldithiocarbamato) para-tolylimido vanadium V), ($CDCl_3$)

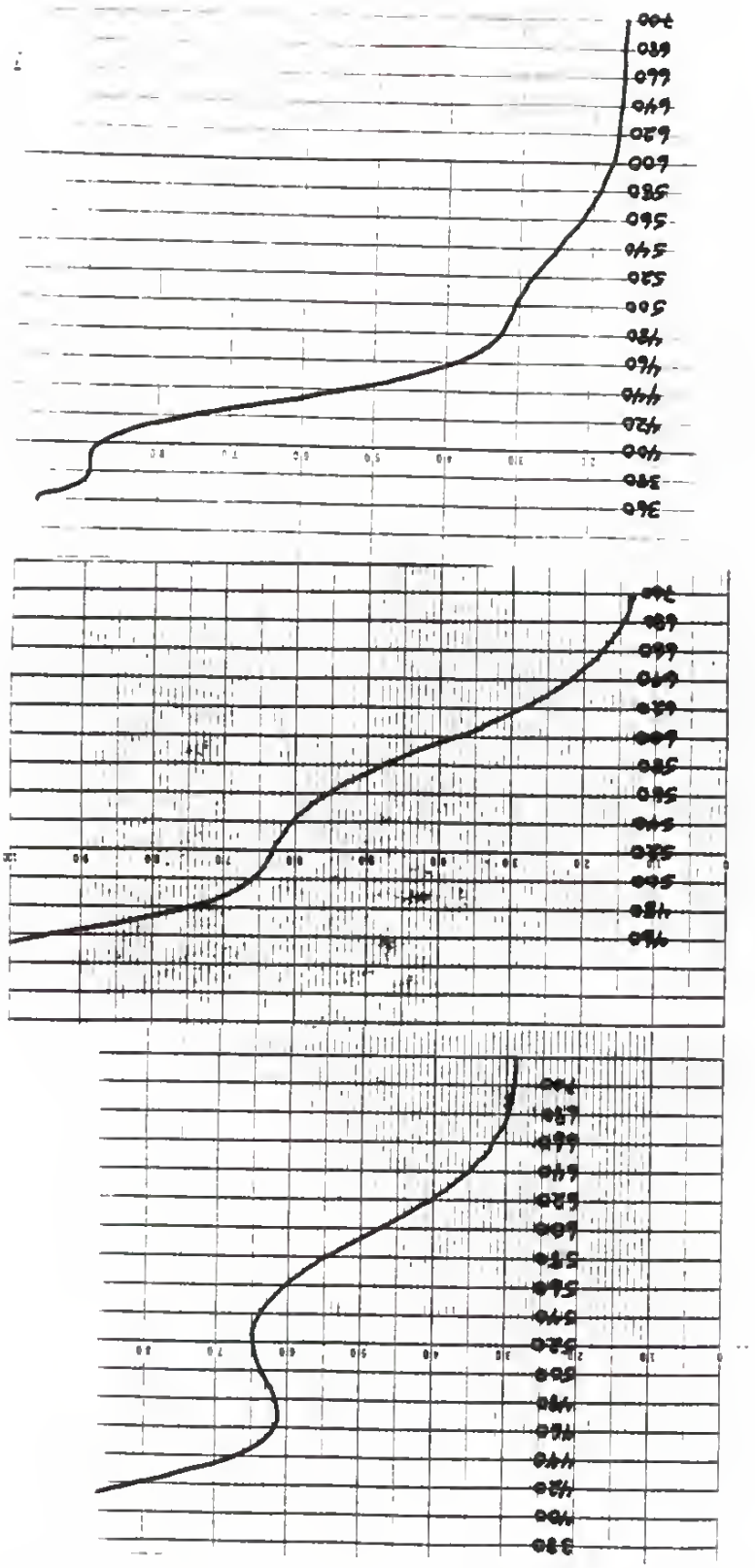

Fig. 2-G Visible Spectra of the Series $V(Ntol)(dedtc)_xCl_{3-x}$ x = 1, 2, 3 in toluene

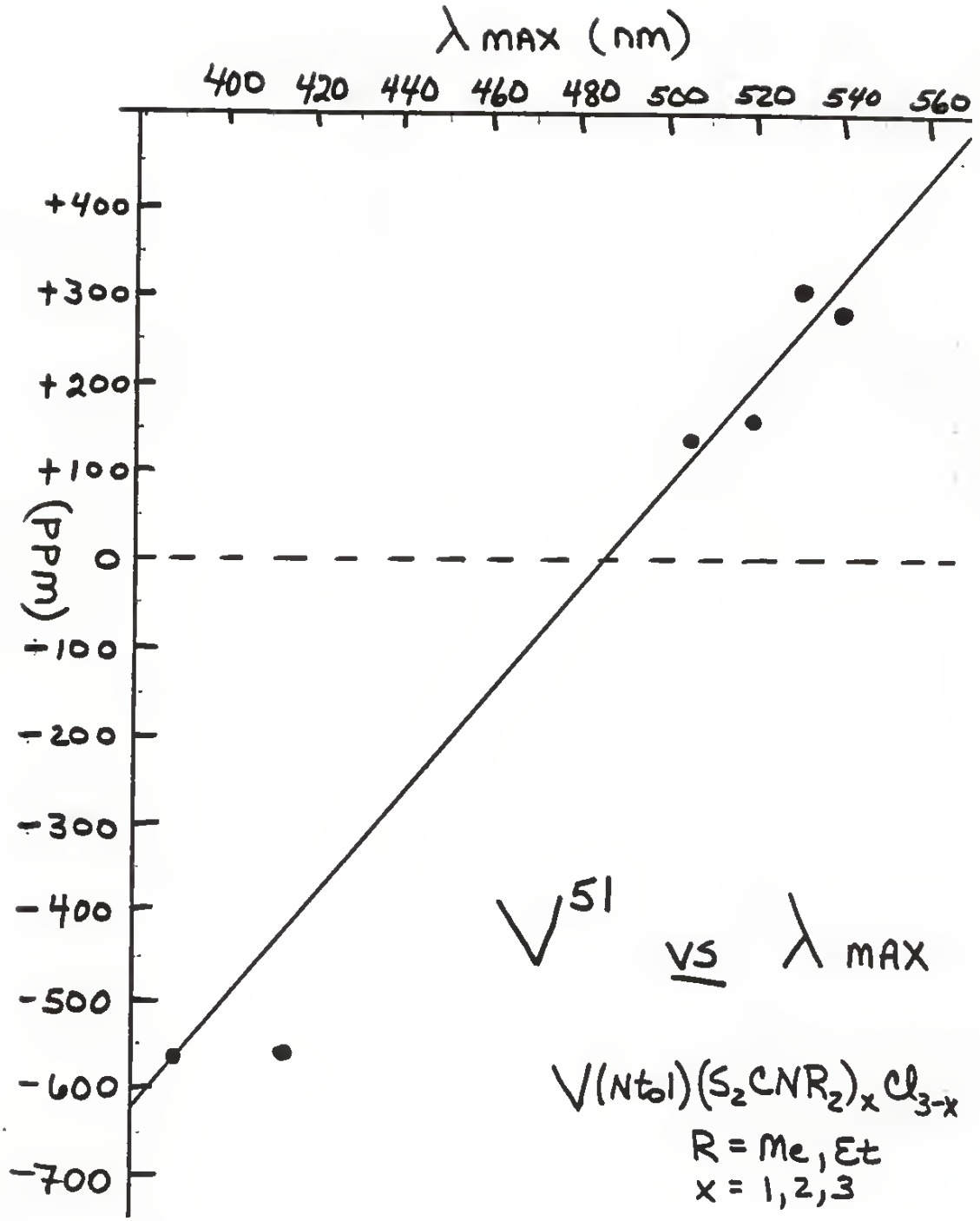

Fig. 2-H Linear Correlation of ^{51}V vs. λ_{max} for the series $V(Ntol)(S_2CNR_2)_xCl_{3-x}$ x = 1, 2, 3; R = Me, Et

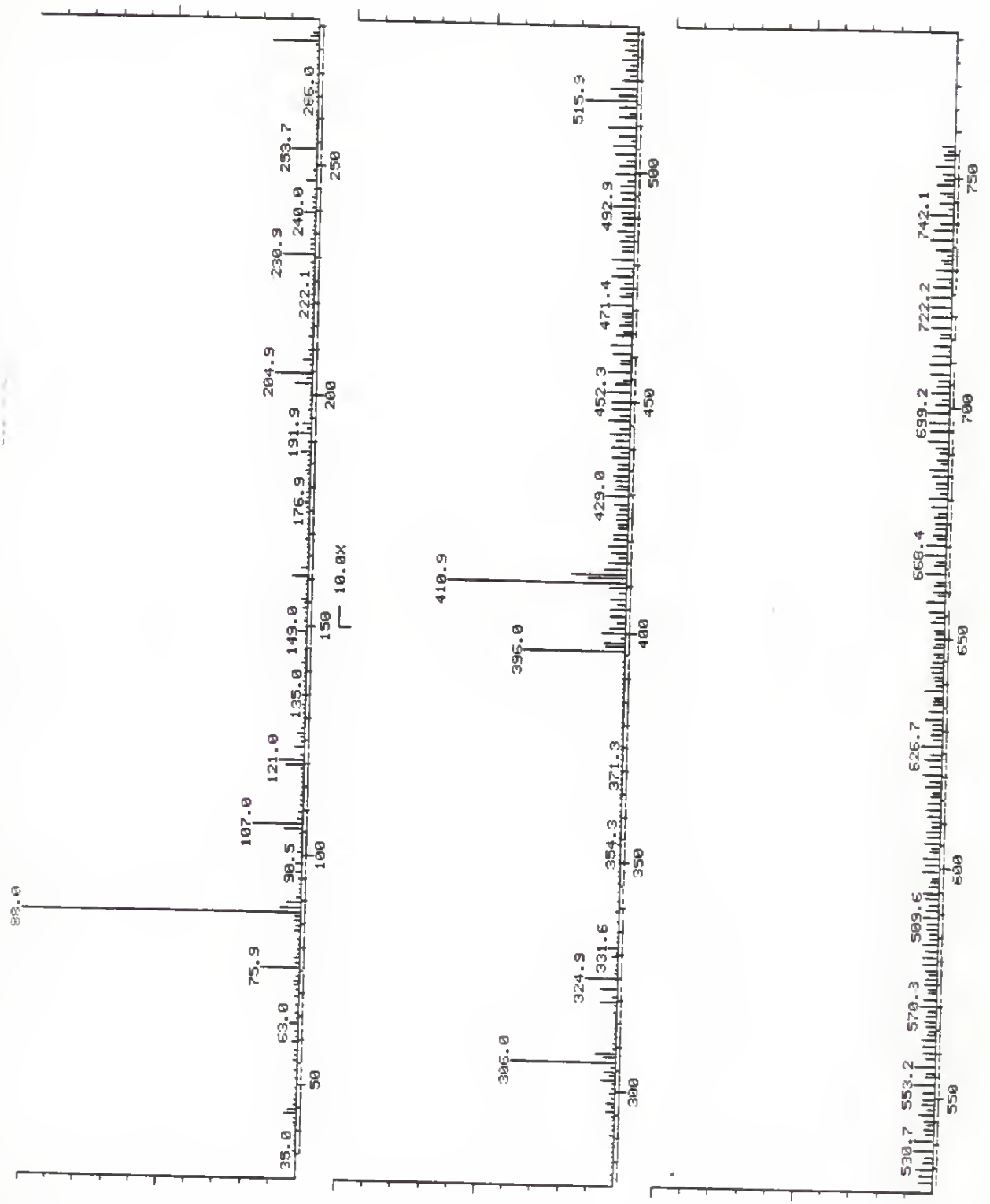

Fig. 2-I Mass Spectrum of Tris(N,N-dimethyldithiocarbamato)para-tolylimido vanadium V

Chapter III

Preparation of Starting Materials

μ-dithio-bis(tricarbonyliron), $S_2Fe_2(CO)_6$[5,7]

First, $Na_2S{\cdot}9H_2O$, (100 g, 416 mmoles), and 400 ml H_2O were mixed in a 1000 mL beaker on a hot plate and stirred for ~ 20 minutes until most of the solid had dissolved. 10 mL of a 50% solution of KOH was added and slowly warmed to *ca.* 70°C until all the solid $Na_2S{\cdot}9H_2O$ had dissolved. 55 g (1.72 mol) of sublimed sulfur was then added to the warm solution and stirred (for ~45 minutes), until all the sulfur had reacted. During this time, the solution changed from a colorless solution to a deep red color.

Second, a 3000 ml - 3 necked flask was flushed with N_2 in an ice bath at 0°C (for ~15 min). CH_3OH, 200 mL, was added to the reaction flask and N_2 bubbled through the solvent to remove any O_2, (for ~15 min), with vigorous stirring. $Fe(CO)_5$, (35 mL, 250 mmoles), was then added to the cooled degassed methanol resulting in a light brown colored solution that required vigorous stirring at 0°C and continuous N_2 bubbling until a homogeneous mixture resulted. Careful addition of 80 ml of 50% KOH solution to the cooled methanolic solution resulted in noticeable CO evolution. (NOTE: If the solution appears as a blood red color at this point, the solution has been contaminated with O_2 and must be discarded).

Thirdly, the Na_2S_5 solution was cooled to 0°C and degassed by bubbling N_2 through the solution. Careful addition of the Na_2S_5 solution to the methanolic iron carbonyl solution, (*ca.* 100 ml at a

time), produced considerable CO evolution and the large reaction vessel became filled with foaming reaction product. After cautious avoidance of contaminating the reaction mixture with air and all the Na_2S_5 mixture has been added, the solution stirred for 2 hours at 0°C.

Fourthly, a 5.8 M solution of HCl was prepared by combining 200 ml H_2O with 200 ml concentrated HCl. This solution was cooled to 0°C and degassed with N_2 bubbling for at least 15 minutes prior to addition to the reaction mixture. The acid solution was added to the methanolic iron carbonyl solution with EXTREME CARE! in 5 ml aliquots about every 10 minutes. The reaction mixture produced considerable frothing due to CO evolution and must be continuously stirred at 0°C and monitored often. The acid solution was added over 4-5 hours and the resulting brown solution stirred for an additional 1/2 hour to insure reaction completion.

Fifthly, in the open atmosphere, the brown precipitate was filtered using a course 150 ml Büchner funnel and washed with ca. 200 ml H_2O. The filtered brown sludge was transfered to a 500 ml one-necked flask and a vacuum was applied to the product mixture overnight to remove the H_2O. Occasionally, an extra 12-24 hours was needed to completely dry the sludge to form a brown powder. Extraction of the desired product was completed with pentane. The dried powder was split into 2 portions. To each, 600 mL of pentane was added and stirred vigorously for 15 minutes. The solution was filtered using a medium 150 ml Büchner funnel producing an orange-red filtrate and an insoluble dark brown solid. Reextraction of this brown solid was completed with an additional 600 mL of pentane and again stirring for 15 minutes. Filtration produced additional orange-red filtrate and insoluble brown solid. Repeated

extraction for a third and final time produced a weakly colored orange filtrate. The filtrates were combined forming a collective 3600 ml pentane solution of $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$. Removal of the pentane with a rotovap, resulted in a product that was a dark orange-red-brown solid.

Finally, this air-stable product mixture was transferred to a large sublimator and placed in a water bath. Static vacuum was applied to the sublimator, a dry ice/acetone mixture was added to the cold finger, and the water bath was warmed to 40°C. After 5 hours, the cold finger was withdrawn and the orange crystalline product was removed and stored in an air-tight flask. The cold finger was replaced under identical conditions for an additional 5 hours and orange crystals again formed on the sublimator probe. One final 5 hour sublimation yielded a small amount of addition product. The resulting orange crystalline $S_2Fe_2(CO)_6$, ~ 8 grams, was stored in the refrigerator indefinitely without noticeable decomposition. Analysis for conformation of purity was performed by IR, Mass, and ^{13}C NMR Spectroscopy. Data from these measurements are found in Table 3-D, Table 3-C, and Table 3-B.

Experimental Section

Synthesis of $V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$

$V(Ntol)(S_2CN(CH_3)_2)Cl_2$, (0.694 g, 2.00 mmoles), was placed into a side-arm reaction flask attachment and $S_2Fe_2(CO)_6$, (0.688 g, 2.00 mmoles), was placed in the bottom of the reaction flask containing a stir bar and ca. 10 grams of Celite. The side-arm was attached to the reaction flask in the N_2-filled dry box.

$Li(CH_3CH_2)_3BH/THF$, (4.00 mL, 4.00 mmoles), was placed in a 25 ml one-necked flask with a valve attached and then diluted to ca. 20 ml with additional THF. THF, (ca. 40 ml), was then vacuum distilled into the reaction flask. The orange solution was warmed to -78°C with a dry ice/acetone bath and allowed to stir until the solution was homogeneous. The $Li(CH_3CH_2)_3BH$ solution was added in ca. 5 ml alloquots every 15 minutes. At the midpoint of the additions, the solution changed from dark red to an olive green color. The resulting solution was allowed to stir at -78°C for an additional 15 minutes.

The $V(Ntol)(S_2CN(CH_3)_2Cl_2$ was then combined with the cold iron solution and the color instantaneously changed from olive green to a dark red color. The resulting reaction mixture was allowed to stir for ~15 minutes at -78°C after which time the dry ice/acetone bath was removed and the solution was allowed to slowly warm to room temperature with stirring. After 20 minutes, the color had changed from dark-red to a yellow-brown color. After 1 hour of stirring at room temperature, the THF was removed from the yellow-brown solution and the product dried for 1 hour. To the dark solid product, CH_2Cl_2, (ca. 50 ml), was added by vacuum distillation, the crude product was dissolved and then filtered leaving LiCl and Celite on the filter frit. The filtrate appeared as a red-orange-brown CH_2Cl_2 solution. As the solvent was being removed by vacuum, the solution became increasingly red in color. After all the CH_2Cl_2 was removed, the crude product was dried by vacuum for 1 hour. n-Pentane was then vacuum disilled into the flask containing the crude solid product to remove any unreacted $S_2Fe_2(CO)_6$ and to wash and triturate the product solid. The product was slightly soluble in n-Pentane and turned the solution a slight orange-red color. The wash

solution was filtered leaving a dark crystalline product on the filter frit and a slightly orange tinted pentane filtrate. The crystalline product was dried in vacuo for 2 hours and then stored in the N_2-filled dry box.

The product $V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$ was analyzed for identification and purity by ^{13}C NMR, ^{1}H NMR, Mass, and IR Spectroscopy. Data for these analyses are found in Table 3-B, Table 3-A, Table 3-C, and Table 3-D.

Results and Discussion

$V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$

Discussion of the Spectra

The heterotrimetallic compound was found to be an orange-brown powder, which could be stored in N_2-filled drybox, but spontaneously combusted upon exposure to the atmosphere. The product was isolated in >80% yield.

The infrared spectrum of the product exhibits the expected characteristic features. Shifts due to coordination from the unbound ligand to the parent moiety were also displayed. The carbonyl stretches were found in a region from 2061 cm^{-1} to 1967 cm^{-1}, containing 5 distinct bands. This is similar, but shifted to lower frequency due to coordination to the vanadium metal center, to the infrared bands found in the free $S_2Fe_2(CO)_6$ ligand.[7] The Fe-S stretches, present in the product spectrum, are shifted to lower frequencies from their original positions, found in the uncoordinated ligand at 615 cm^{-1}, 590 cm^{-1}, and 562 cm^{-1}. See Table 3-D. Stretching frequencies were also exhibited for the $S_2CN(CH_3)_2$ moiety at 1510 cm^{-1} and 1498 cm^{-1} for the thioureide bands, 1128 cm^{-1} due to the NR_2 band, and 1006 cm^{-1} due to the C-S band. Metal to sulfur bands were also detected, as there are six separate bonds within this product. The bands due to the four vanadium-sulfur bonds could be those found at 426 cm^{-1}, 398 cm^{-1}, and 368 cm^{-1}. The final major band at 968 cm^{-1} can be attributed to the vanadium-nitrogen stretching frequency. Most of the weaker bands can be attributed to the p-tolylimido moiety and CH_3 features.

The mass spectral data is particularly impressive as the parent ion appears at 619.60 daltons followed by a step-wise loss of each of the 6

carbonyl units. Also detected were the VS_2Fe_2, $S_2CN(CH_3)_2$ and Ntol fragments. Detailed fragmentation can be found in Table 3-C.

The proton NMR spectrum for this product is simple, as few protons are present and the spectrum can easily be compared to the starting materials. The spectrum displayed 3 peaks; 2 singlets and 1 quartet, as does $V(Ntol)(S_2CN(CH_3)_2)Cl_2$. The peak due to the tolyl-methyl group is observed to shift from 2.4317 ppm to 2.2745 ppm indicating higher electron density and thus greater shielding around the methyl protons. This effect is also noticed for the methyl groups of the $S_2CN(CH_3)_2$ moiety as the ^1H signal shifts downfield from 3.4407 ppm to 3.3064 pm. These shifts would indicate a larger electron donation to the vanadium metal center by the $S_2Fe_2(CO)_6$, when compared with the chloride ligands. This should be true as chlorine is a strong electron withdrawing group. The remaining proton signal arises from the AB pattern of the tolyl group. The pair of doublets is expected to be shifted downfield from the parent compound and the spectrum confirms this prediction. The doublets shift from being centered at 7.2360 ppm to 6.9422 ppm. This indicates greater electron density around the tolyl ring protons. The coupling constants are also shifted from J_{AB} = 8.00 Hz to J_{AB} = 7.08 Hz in the product.

The final spectral analysis of $V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$ was ^{13}C NMR spectroscopy. In the uncoordinated $S_2Fe(CO)_6$, the carbonyl signal is found at 208.312 ppm and in the product the signal appears at 207.333 pm. Three of the four carbons in the tolyl-ring appear in the ^{13}C NMR spectrum. In the parent compound the signals are found at 140.722 ppm, 128.638 ppm and 126.738 ppm and an increase in electron density would shift these signals downfield. This is observed in the

product spectrum, as peaks appear at 129.722 ppm, 128.384 ppm and 125.535 ppm. The carbons of the carbamate methyl groups exhibits a signal in the parent compound at 39.750 ppm and in the product at 39.602 ppm, indicating a slight increase in electron density around the carbon atoms. The tolyl-methyl carbon exhibited a signal in the parent compound at 21.721 ppm, but in the product, this signal was extremely faint and almost nondetectable. The largest peak in this area was located at -8.00 ppm, which shows quite a shift and remains to be confirmed.

The only remaining carbon in the compounds are those found in the carbamate ligands, bridging the sulfur and nitrogen atoms. Signals for these carbons were not found in either ^{13}C NMR spectrum.

Table 3-A

Proton NMR Chemical Shift Assignments
for $V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$

	Chemical Shifts (ppm)	Coupling Constants J(Hz)
$S_2CN(CH_3)_2$	2.2745, s	
$NC_6H_4CH_3$	6.9422, q	J_{AB} = 7.08
$NC_6H_4CH_3$	3.3064, s	

The spectrum was taken in $CDCl_3$ at ambient temperature.

Table 3-B

Carbon 13 Chemical Shift Assignments

Compound		Chemical Shifts (ppm)
$S_2Fe_2(CO)_6$	$\underline{C}O$	208.312
$V(Ntol)(dmdtc)Cl_2$	$NC_{\underline{6}}H_4CH_3$	140.722
		128.638
		126.738
	$S_2CN(\underline{C}H_3)_2$	39.750
	$NC_6H_4\underline{C}H_3$	21.721
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_6)$	$\underline{C}O$	207.333
	$N\underline{C}_6H_4CH_3$	129.722
		128.384
		125.535
	$S_2CN(\underline{C}H_3)_2$	39.602
	$NC_6H_4\underline{C}H_3$	-8.00

All samples were run in $CDCl_3$ at ambient temperatures.

Table 3-C

Mass Spectral Data for
$V(Ntol)(S_2CNMe_2)(S_2Fe_2(CO)_6)$

Fragment	Calculated Mass	Observed Mass
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_6)$	619.97	619.60
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_5)$	591.97	591.46
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_4)$	563.97	563.40
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_3)$	535.97	535.66
$V(Ntol)(dmdtc)(S_2Fe_2(CO)_2)$	507.97	507.62
$V(Ntol)(dmdtc)(S_2Fe_2(CO))$	479.97	479.66
$V(Ntol)(dmdtc)(S_2Fe_2)$	451.97	451.58
$V(Ntol)(SCNMe_2)(S_2Fe_2)$	419.97	419.68
$(S_2CNMe_2)(S_2Fe_2)$	296.02	295.72
$(SCNMe_2)(S_2Fe_2)$	263.96	264.78
$(SCNMe)(S_2Fe_2)$	248.93	248.94
$V(S_2Fe(CO)_2)$	226.91	227.78
$V(S_2Fe_2)$	226.76	227.78
$V(S_2Fe(CO)$	198.91	199.74
$V(SFe_2)$	194.70	195.66
S_2Fe_2	175.81	176.06
$V(S_2CNMe_2)$	171.14	171.80
$V(S_2Fe)$	170.91	171.80
SFe_2CO	171.75	171.80
S_2FeCO	147.97	148.32
SFe_2	143.75	143.86
S_2CNMe_2	120.21	121.02
Fe_2	111.69	111.96

Ntol	105.14	105.42
SFe	87.91	88.20
$SCNMe_2$	88.14	88.20
VS	83.00	84.04
SCNMe	73.11	73.16

TABLE 3-D

Infrared Spectral Data of

$V(Ntol)(S_2CN(CH_3)_2)(S_2Fe_2(CO)_6)$

(in cm^{-1})

2061 s, 2037 s, 2007 vs, 1989 vs, 1967 vs, 1510 m, 1498 m, 1287 s, 1128 m, 1089 m, 1038 w, 1006 w, 968 s, 883 m, 804 s, 758 vw, 741 w, 733 m, 717 vs, 605 vs, 591 s, 573 vs, 555 vs, 493 s, 487 s, 426 s, 398 s, 368 w, 345 w, 319 w.

Abbreviations:

vw - very weak

w - weak

m - moderate

s - strong

vs - very strong

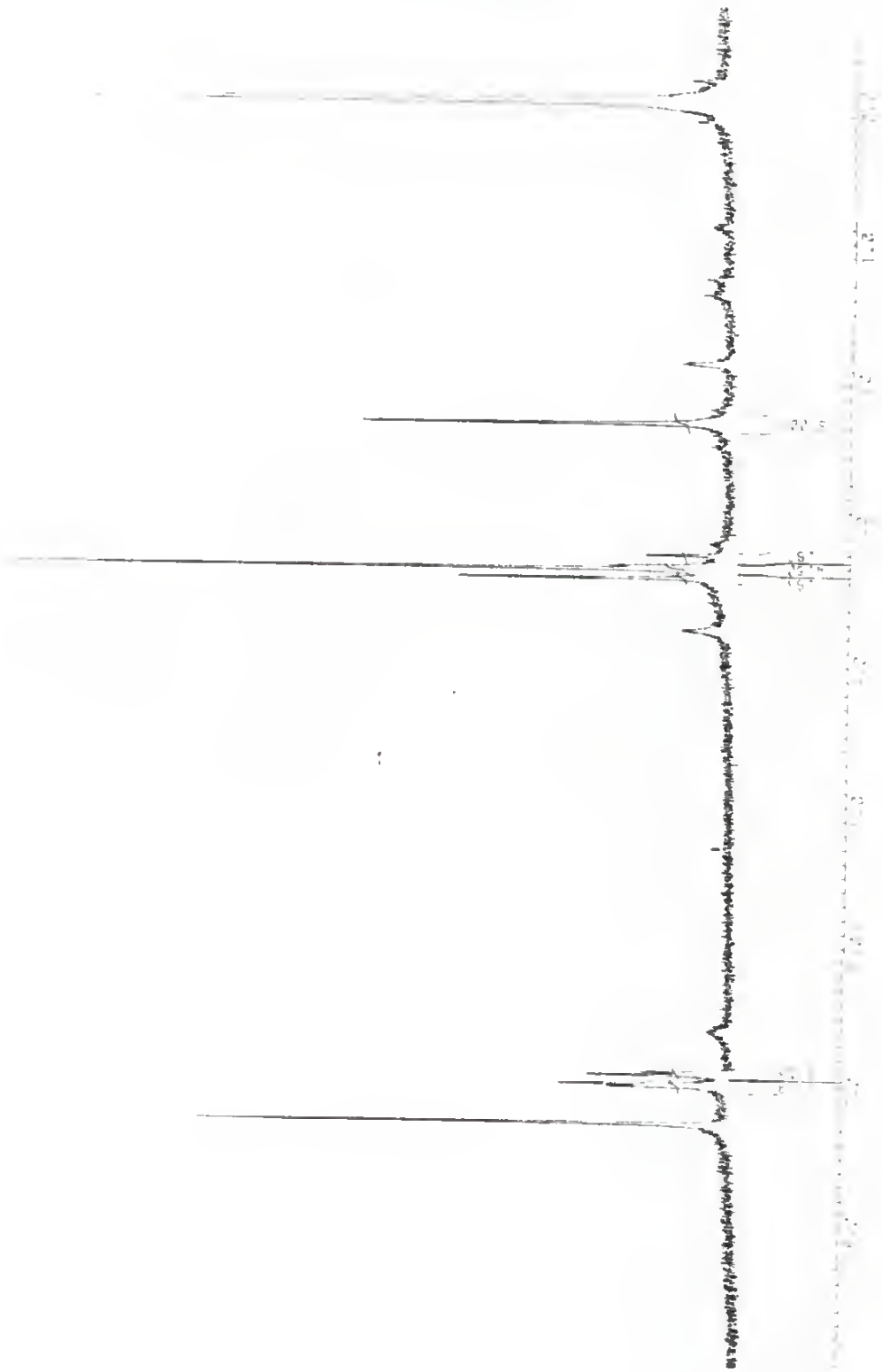

Fig. 3-A ^{1}H NMR Spectrum of N,N-Dimethyldithiocarbamato μ-dithio-bistricarbonyliron para-tolylimido vanadium (V), ($CDCl_3$)

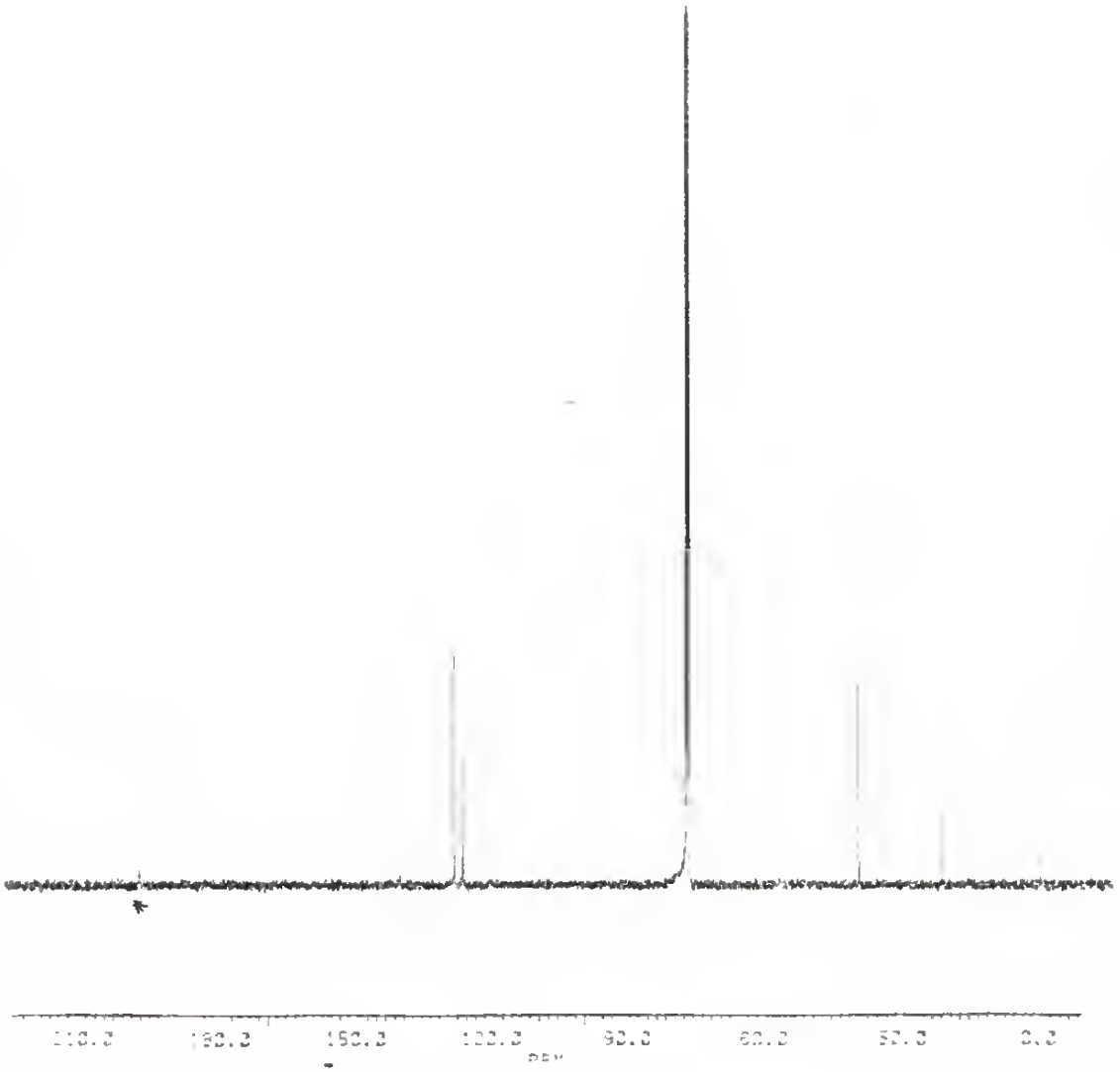

Fig. 3-B ^{13}C NMR Spectrum of (N,N-Dimethyldithiocarbamato para-tolylimido vanadium V dichloride), ($CDCl_3$)

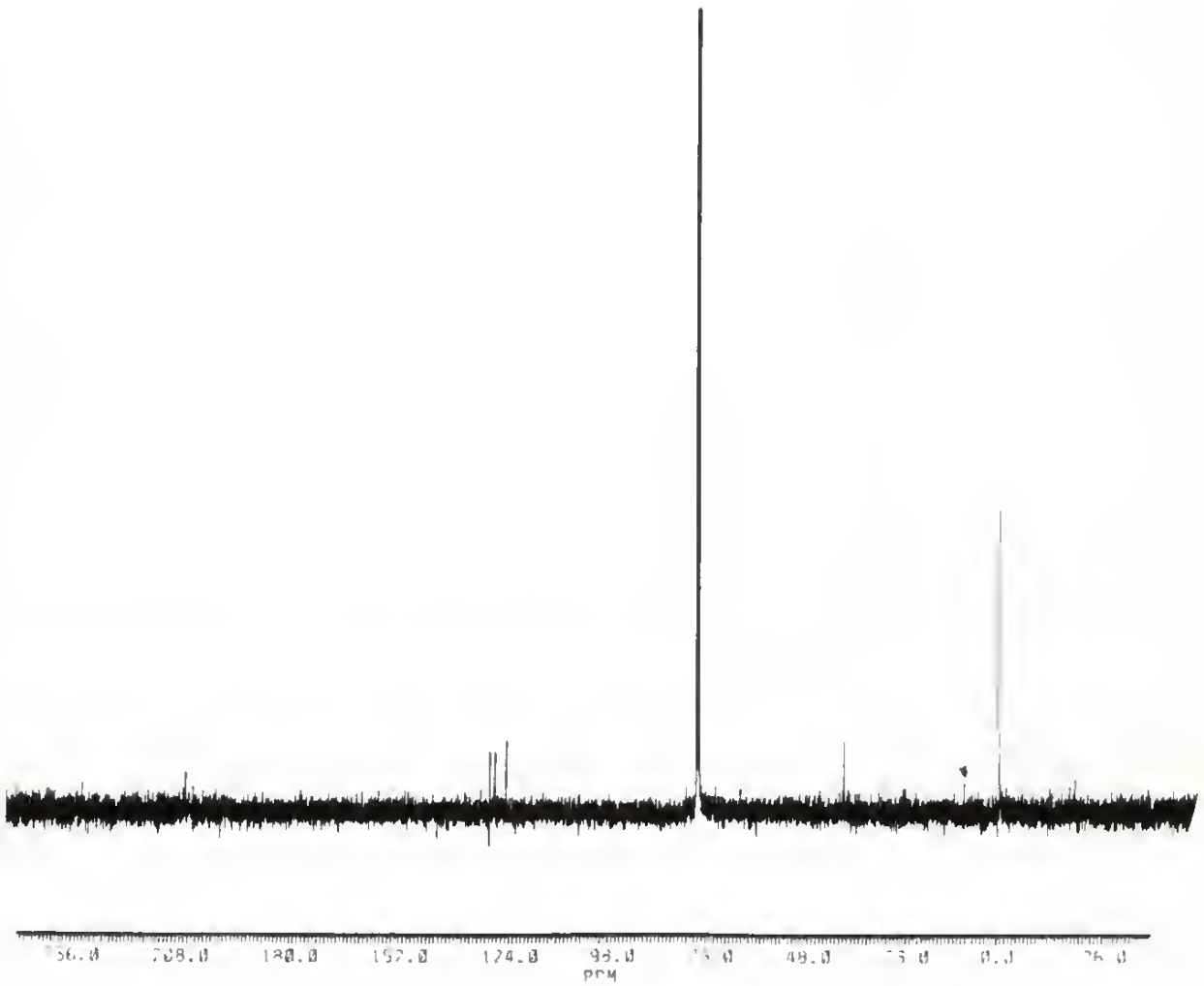

Fig. 3-C ^{13}C NMR Spectrum of N,N-Dimethyldithiocarbamato μ-dithiobistricarbonyliron para-tolylimido vanadium (V), ($CDCl_3$)

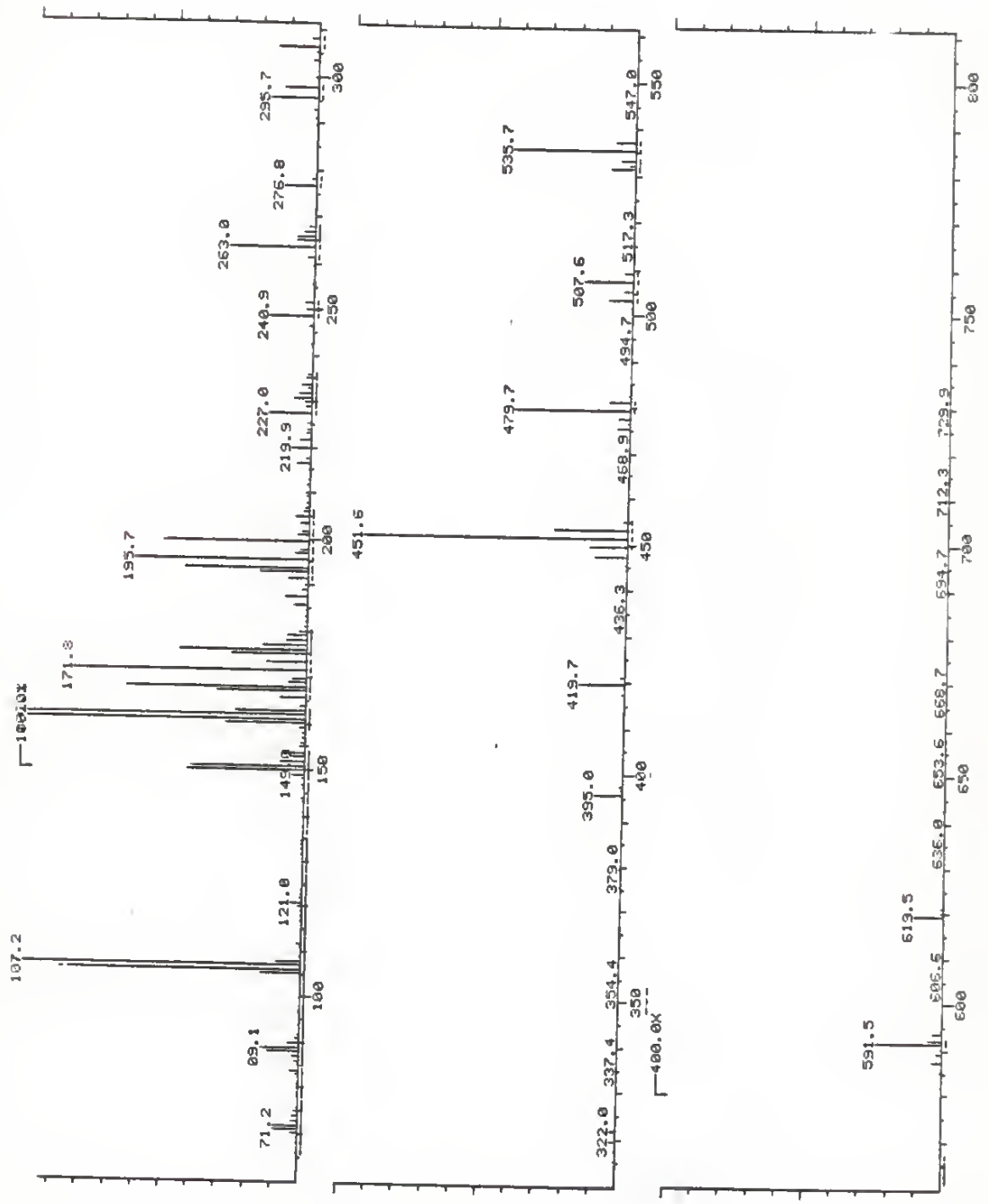

Fig. 3-D Mass Spectrum of N,N-Dimethyldithiocarbamato μ-dithiobistricarbonyliron para-tolylimido vanadium (V), ($CDCl_3$)

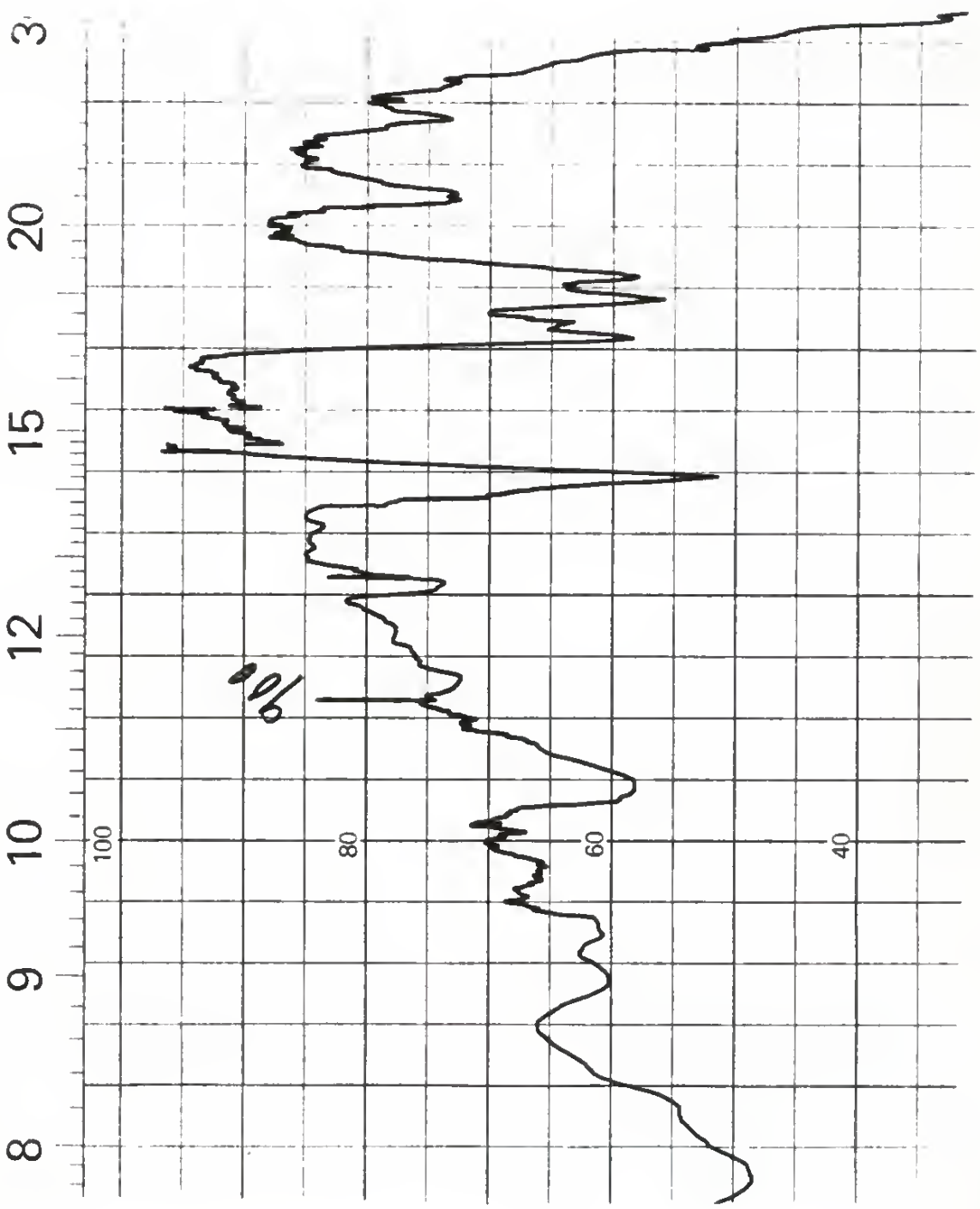

Fig. 3-E Infrared Spectrum of N,N-Dimethyldithiocarbamato μ-dithiobistricarbonyliron para-tolylimido vanadium (V), ($CDCl_3$) 1400 cm^{-1} to 350 $cm.^{-1}$ in Nujol

Chapter IV

Experimental Section

Synthesis of $V(Ntol)(acac)_2Cl$

$V(Ntol)Cl_3$, (0.525 g, 2.00 mmoles), was placed in a 2-necked reaction flask equipped with a septum along with a stir bar and ca. 5 grams of Celite in the N_2-filled dry box. CH_2Cl_2, (ca. 40 ml), was vacuum distilled into the reaction flask and the solution was allowed to warm to room temperature with stirring. During the warm-up, the solution changed from purple to a dark green color. acacH, (0.43 mL, 4.0 mmoles), was added to the stirring $V(Ntol)Cl_3$ solution via syringe and the green solution turned to a red-orange color. Immediately, $(CH_3CH_2)_3N$, (0.56 mL, 4.0 mmoles), was added to the reaction mixture via syringe. As the triethylamine combined with the reaction mixture, a white cloud appeared and then quickly dissipated. The reaction mixture appeared as a dark orange solution and stirring continued for 20 minutes at room temperature. The solution was then filtered and the filtrate was a dark red-orange CH_2Cl_2 solution. The solvent was removed by vacuum and the product dried for 2 hours. n-Pentane was vacuum distilled into the flask containing the crude product and the product was washed and triturated with stirring. The product was slightly soluble in pentane and after stirring for 15 minutes, the wash solution was filtered leaving a microcrystalline solid on the filter frit and a slightly orange pentane filtrate that turned brown upon exposure to the air. The product, $V(Ntol)(acac)_2Cl$, was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The product was analyzed for

identity by ^{1}H NMR Spectroscopy. Data for this analysis are found in Table 4-A.

Synthesis of $V(Ntol)(S_2P\emptyset_2)_2Cl$

$V(Ntol)Cl_3$, (0.525 g, 2.00 mmoles), was placed in the bottom of a 3-necked flask with Celite, (ca. 5 grams), and a stir bar in the N_2-filled dry box. The reaction flask was equipped with a septum, a filter frit and a side arm containing $HS_2P\emptyset_2$, (1.05 g, 4.00 mmoles). CH_2Cl_2, (ca. 50 ml), was vacuum distilled into the reaction flask and the $V(Ntol)Cl_3$ solution was stirred and warmed to room temperature. The $HS_2P\emptyset_2$ was added to the reaction solution and immediately the green solution turned to a dark red color. $(CH_3CH_2)_3N$, (0.56 ml, 4.0 mmoles), was quickly added by syringe to the solution turned to an orange-red color and was allowed to stir. During the 30 minute reaction time, the solution turned dark orange and was then filtered. The Celite and $(CH_3CH_2)_3N{\cdot}HCl$ was collected on the filter frit and the CH_2Cl_2 filtrate appeared as a dark orange solution. The solvent was removed by vacuum and the product solid dried for 2 hours. The dark orange solid was washed and triturated using n-Pentane and stirring followed by filtration leaving a dark crystalline solid on the filter frit. The pentane filtrate appeared slightly lavender colored. The product was dried in vacuo for 2 hours and then rewashed with n-Pentane. The wash solution was allowed to stir at room temperature overnight and then was filtered leaving a brown powder on the filter frit. The filtrate appeared as a dark orange-brown solution. The pentane was removed by vacuum and the products dried in vacuo for 2 hours. The pentane soluble dark orange-brown solid was removed from the sides of the filtration

flask and stored in the N_2-filled dry box. The product $V(Ntol)(S_2P\emptyset_2)_2Cl$ was analyzed for identification and purity by ^1H NMR spectroscopy. Data for this analysis are found in Table 4-B.

Results and Discussion

$V(Ntol)(acac)_2Cl$

Analysis by ^1H NMR Spectroscopy.

The two major peaks found in this spectrum are contaminants from $(CH_3CH_2)_3N \cdot HCl$ which showed up at 1.4253 ppm due to the methyl protons and at 3.1167 ppm due to the methylene protons. These peaks are not listed in Table 4-A.

An interesting aspect of the spectrum, is that the two acetylacetonate ligands are non-equivalent. This is substantiated by the occurrence of the 2 equal intensity peaks at 5.7498 ppm and 5.5841 ppm, which are due to the single central acetylacetonate protons. Non-equivalence also appears in the methyl region of the spectrum as four peaks are exhibited. If all five of the methyl groups occurring within this molecule are non-equivalent, then one would expect five peaks to occur. One peak must be due to the p-tolyl methyl protons and the signal at 2.4523 ppm is designated as occurring due to that moiety. This leaves the four acetylacetonate methyl groups and three signals. The conclusion reached is that two of the methyl groups are equivalent giving rise to the largest peak at 2.1850 ppm. The other two methyl moieties represent non-equivalent methyl groups, coordinating out of the equatorial plane, and these peaks appear at 2.0017 ppm and 2.3445 ppm. The remaining peaks are the AB pattern of the tolyl-ring, of which only one pattern appears. This indicates only one type of V(Ntol) compound

and since the peaks are shifted from the original values, reaction must have occurred.

$V(Ntol)(S_2P\emptyset_2)_2Cl$

Analysis by ^1H NMR Spectroscopy

The spectrum produced from the analysis of the product shows two distinct broad singlets not found in Table 4-B, due to contamination of $(CH_3CH_2)_3N \cdot HCl$. The methyl protons exhibit a peak at 1.4215 ppm and the methylene protons at 3.0916 ppm. The only other peak found in this region is a singlet at 2.4227 ppm due to the p-tolyl methyl protons. The remaining spectral data is observed in the aromatic region as expected. The AB pattern of the Ntol moiety shows one doublet centered at 6.9693 ppm. The other doublet, however, is partially concealed within a complex multiplet. There are two possible positions for this other doublet upon close examination. A doublet does appear centered at 7.4867 ppm and could be of the AB pattern, however two things rule this out. One, the coupling constant of the first doublet is 7.92 Hz which is reasonable, however the coupling constant of the possible doublet partner is only 6.24 Hz and is therefore not coupled with the first signal. Secondly, if this possible doublet were of the AB pattern the chemical shift would equal 206.9 Hz which is much larger than detected in other similar compounds. For these two reasons, this doublet is not considered part of the AB pattern. Another signal appears on the downfield edge of the multiplet, which upon examination, could be half of the missing doublet. An overlapping peak appears to intensify the upfield portion of the doublet, therefore masking the true signal appearance. Since the signal exhibits a coupling constant of 8.16 Hz

and a chemical shift of 150.6 Hz with respect to the downfield doublet of the AB pattern, therefore the plausibilty of this being the upfield doublet is good. The integration for the entire multiplet was 12 protons of the twenty phenyl protons in the product.

The remaining eight protons exhibit a very distinct and interesting quartet pattern centered at 7.7866 ppm. It appears to be four peaks of equal intensity having a coupling constant of 7.36 Hz. Because of the presence of only one sharp tolyl-methyl peak, one AB pattern, and good integration throughout the spectrum, the conclusion can be reached that this is the correct spectrum of the product.

TABLE 4-A

Proton NMR Spectral Data for

$V(Ntol)(acac)_2Cl$

Acetylacetone	Chemical Shift (ppm)	
$CH(COCH_3)_2$	2.08 s	
$CH(COCH_3)_2$	5.50 s	
$V(Ntol)Cl_3$		
	Chemical Shift (ppm)	Coupling Constant (Hz)
$NC_6H_4CH_3$	2.5372 s	
$NC_6H_4CH_3$	7.3405 q	J_{AB} = 7.80
$V(Ntol)(acac)_2Cl$		
	Chemical Shift (ppm)	Coupling Constant (Hz)
$CH(COCH_3)_2$	2.0017 s	
	2.1850 s	
	2.3445 s	
$CH(COCH_3)_2$	5.5841 s	
	5.7498 s	
$NC_6H_4CH_3$	2.4523 s	
$NC_6H_4CH_3$	7.1316 q	J_{AB} = 8.00

TABLE 4-B

Proton NMR Spectral Data for

$V(Ntol)(S_2P\emptyset_2)_2Cl$

$V(Ntol)Cl_3$

	Chemical Shift (ppm)	Coupling Constant (Hz)
$NC_6H_4CH_3$	2.5372 s	
$NC_6H_4CH_3$	7.3405 q	J_{AB} = 7.80

$V(Ntol)(S_2P\emptyset_2)_2Cl$

	Chemical Shift (ppm)	Coupling Constant (Hz)
$NC_6H_4CH_3$	2.4227 s	
$NC_6H_4CH_3$	7.1527 q	J_{AB} = 8.04
$S_2P(C_6H_5)_2$	7.3658 m	
	7.4281 bs	
	7.4865 d	
	7.7866 q	

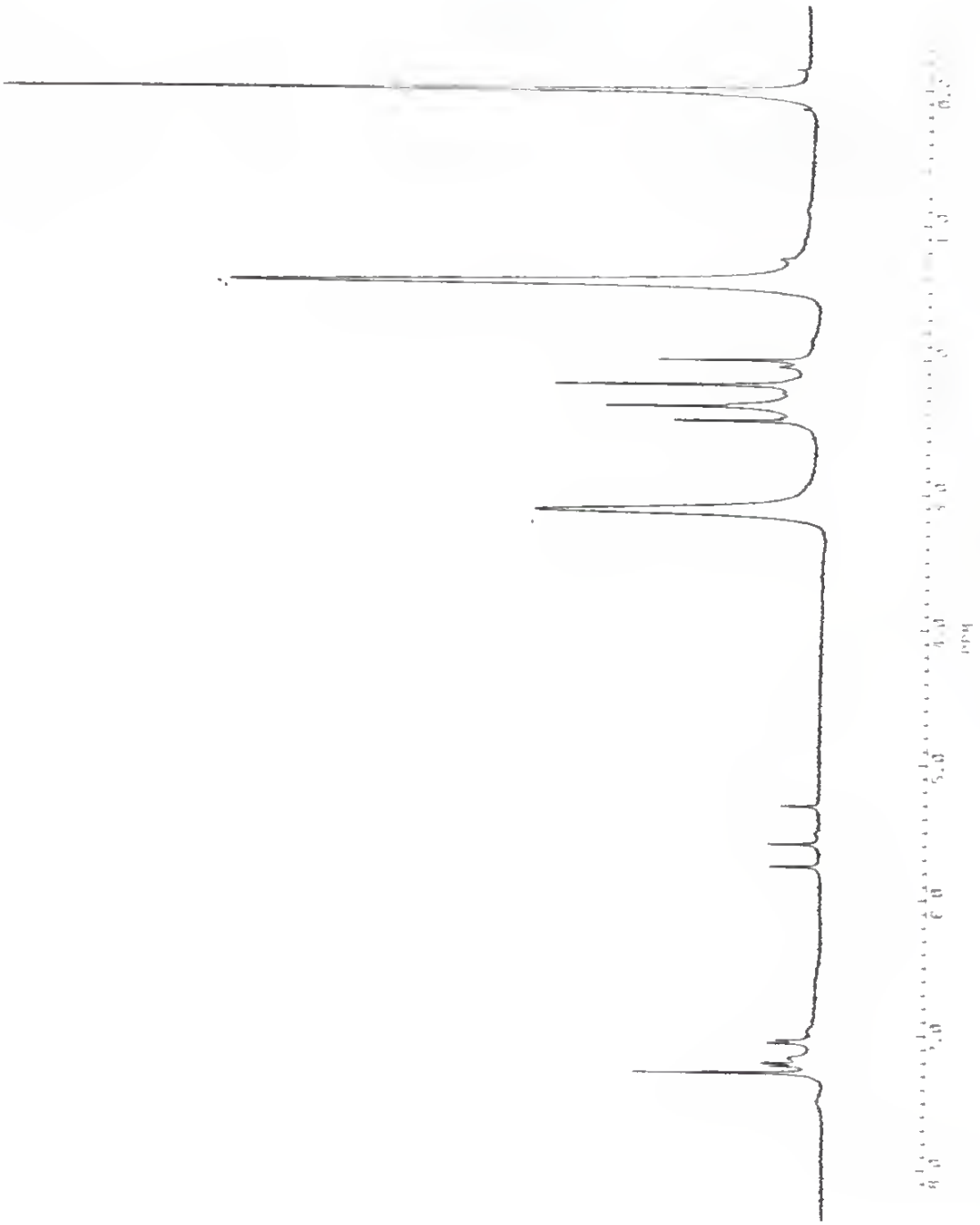

Fig. 4-A ^{1}H NMR Spectrum of Bis(acetylacetonato)para-tolylimido vanadium V chloride in $CDCl_3$

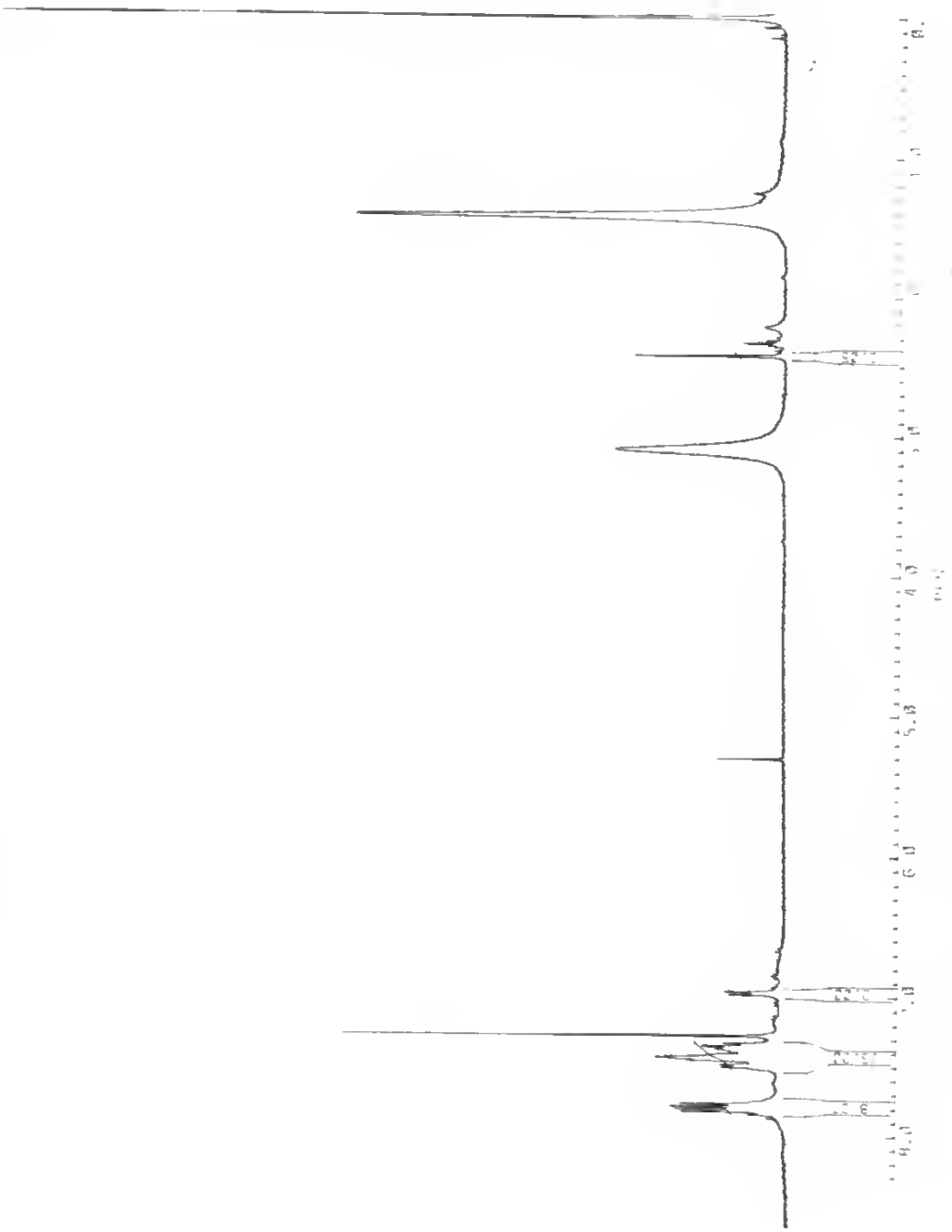

Fig. 4-B ^{1}H NMR Spectrum of Bis(diphenyldithiophosphino) para-tolylimido vanadium V chloride in $CDCl_3$

Chapter V

Experimental Section

Synthesis of $V(Ntol)(P(CH_3)_3)_2Cl_2$

$P(CH_3)_3$ was transferred to a tared side arm bearing a valve in the N_2-filled dry box and found to weigh 0.296 g (3.89 mmoles). $V(Ntol)Cl_3$, (0.511 g, 1.94 mmoles), was combined with Zn, (1.96 g, 30.0 mmoles), in a reaction flask with a stir bar in the N_2-filled dry box. CH_2Cl_2, (ca. 40 ml), was vacuum distilled into the reaction flask and the solution was allowed to warm to room temperature with stirring. The $P(CH_3)_3$ was then vacuum transferred into the reaction solution and immediately the green solution turned dark red. During the 3 hour reaction time, the solution slowly changed to a dark yellow-brown color. The solution was then filtered leaving $ZnCl_2$ and excess Zn on the filter frit. The filtrate appeared as a dark yellow-brown CH_2Cl_2 solution and the solvent was then removed from the product solution leaving a dark-yellow-brown solid, which dried for 2 hours. The product was then washed and triturated using n-Pentane with stirring for 15 minutes. The wash solution was then filtered leaving a dark yellow-brown powder on the filter frit and the pentane filtrate appeared colorless. The product was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. Analysis for identification and purity was completed by Mass, IR, and ESR spectroscopy and molecular weight determination. Data for these analyses are found in Table 5-E, Table 5-F, and Table 5-A.

Synthesis of $V(Ntol)(P\emptyset_2(CH_2CH_3))_2Cl_2$

$P\emptyset_2(CH_2CH_3)$, (1.0541 g, 4.93 mmoles), was added to a sidearm and attached to a typical reaction flask in the N_2-filled dry box. In the reaction flask, $V(Ntol)Cl_3$, (0.65 g, 2.46 mmoles), was combined with Zn, (1.96 g, 30.0 mmoles), and a stir bar. CH_2Cl_2, (ca. 50 ml), was vacuum distilled into the reaction vessel and the $V(Ntol)Cl_3$ solution was allowed to stir and slowly warm to room temperature. After 15 minutes, the $P\emptyset_2(CH_2CH_3)$ was added to the green solution and instantaneously the solution turned red. During the 2 hour reaction time, the solution slowly changed from red to a dark yellow color. The reaction mixture was filtered leaving $ZnCl_2$ and excess Zn on the filter frit. The filtrate appeared as a dark yellow CH_2Cl_2 solution, the solvent was then removed by vacuum, and the product dried for 2 hours. The dark yellow-brown solid product was washed and triturated using n-Pentane with stirring for 15 minutes. The wash solution was filtered leaving a dark powdered solid on the frit and a very pale yellow pentane filtrate. The product $V(Ntol)(P\emptyset_2(CH_2CH_3))_2Cl_2$ was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The product was analyzed for identification and purity by IR, ESR, and Mass spectroscopy, and molecular weight determination. Data for this analysis are found in Table 5-F, Table 5-B, and Table 5-E.

Synthesis of $V(Ntol)(P\emptyset_3)_2Cl_2$

$V(Ntol)Cl_3$, (0.525 g, 2.00 mmoles), was placed in a reaction flask with Zn, (1.96 g, 30.0 mmoles), and a stir bar in the N_2-filled dry box. $P\emptyset_3$, (1.048 g, 4.00 mmoles), was placed in a sidearm and attached to the reaction flask. CH_2Cl_2, (ca. 40 ml), was vacuum distilled into the

reaction flask and the $V(Ntol)Cl_3$ solution was allowed to warm to room temperature with stirring. The $P\emptyset_3$ was then added to the solution and immediately the color changed from green to red and then to a red-orange color. During the 8 hour reaction time, the solution slowly turned to a yellow-brown color. The reaction mixture was then filtered leaving $ZnCl_2$ and excess Zn on the filter frit. The filtrate was a dark yellow CH_2Cl_2 solution of $V(Ntol)(P\emptyset_3)_2Cl_2$. The solvent was removed by vacuum leaving a yellow-brown solid which was dried for 2 hours. The product was washed and triturated with n-Pentane with stirring for 15 minutes. (NOTE: If oxygen is allowed to come into contact with the solution at this time, the product will turn purple indicating oxidation and must be discarded). The pentane wash solution was filtered leaving a dark yellow powder on the frit and a colorless pentane filtrate. The product was dried on the frit in vacuo for 2 hours and upon drying, turned to pumpkin-orange colored powder. The product was stored in the N_2-filled dry box. Analyzation for identification and purity was done by Mass, ESR, and IR spectroscopy and molecular weight determination. Data for these analyses are found in Table 5-E, Table 5-C, and Table 5-F.

Synthesis of $V(Ntol)(diphos)Cl_2$

$V(Ntol)Cl_3$, (0.525 g, 2.00 mmoles), was placed with Zn, (1.96 g, 30.0 mmoles), and a stir bar in a reaction flask in the N_2-filled dry box. Bis(diphenylphosphino)ethane, (diphos), (0.796 g, 2.00 mmoles), was placed in a side arm and attached to the reaction flask. CH_2Cl_2, (ca. 40 ml), was vacuum distilled into the reaction flask and allowed to warm to room temperature with stirring. The diphos was then added to the $V(Ntol)Cl_3$ solution and the green solution immediately turn to a

dark orange. During the 3 hour reaction time, the solution gradually changed to a dark yellow color. The reaction mixture was filtered leaving $ZnCl_2$ and excess Zn on the filter frit. The filtrate appeared as a dark yellow CH_2Cl_2 solution and the solvent was removed by vacuum. The product was dried for 4 hours leaving a dark yellow solid which seemed to mass-crystallize upon drying. The solid was washed and triturated using n-Pentane with stirring for 15 minutes and the wash solution was then filtered. A dark orange-brown crystalline solid collected upon the frit and the pentane filtrate appeared colorless. The product was dried in vacuo for 2 hours and upon drying became a free flowing dark orange crystalline solid which was stored in the N_2-filled dry box. The product was analyzed for identification and purity by Mass, ESR, and IR spectroscopy and molecular weight determination. Data for these analyses are found in Table 5-E, Table 5-D, and Table 5-F.

Results and Discussion

Organophosphine Derivatives of $V(Ntol)Cl_2$

Analyses and Discussion

The small family of four vanadium-phosphine complexes $V(Ntol)Cl_2 \cdot 2(PR_3)$, with varying bulkiness of the substituents R, have been analyzed by electron spin resonance studies. The factors of a single d-electron outside of a closed (argon) shell, predominance of the vanadium-51 isotope, and the high nuclear spin (I = 7/2), combine to make the imidovanadium(IV) species attractive for experimental studies. Since much investigation has been accomplished with the oxovanadium(IV) species, correlations between the corresponding compounds aids in explaining the chemical nature of these compounds. The spectra

collected show the interaction of the unpaired electron of V^{IV} with the ^{51}V nucleus. Each of the eight vanadium lines is further split into a 1:2:1 triplet attributed unambiguously to the two equivalent phosphorus nuclei.

The ESR experiment was carried out at a fixed frequency in the X-band frequency range (about 9.5 GHz), where a field strength of about 3500 gauss was employed. The g value was calculated for each spectrum using the equation

$$g = \frac{h\nu}{BH}$$

where h is Planck's constant, 6.6262×10^{-27} erg s, B is the Bohr magneton, 9.2741×10^{-21} erg G^{-1}, v is the fixed frequency of the probe, and H (which is being swept) is obtained from the spectrum. The g value for a free electron has a value of 2.0023193. The g values obtained for the organophosphines $V(Ntol)Cl_2 \cdot 2(PR_3)$, range in values from 1.9544 to 1.9788 in the order $PEtPh_2$ < diphos < $P(CH_3)_3$ < PPh_3.

The energy separation of two peaks within a spectrum is A. $A(^{51}V)$ was calculated for each spectrum by taking the average separation value between the center of the eight triplets. Values of $A(^{51}V)$ were obtained and reported as 83.4 Hz, $P(CH_3)_3$; 92.4 Hz, $PEt\emptyset_2$; 99.6 Hz, $P\emptyset_3$; and 102.0 Hz, diphos. Values of $A(^{31}P)$ were obtained and reported as 24.5 Hz, $P\emptyset_3$; 26.1 Hz, $PEt\emptyset_2$; 27.3 Hz, diphos; and 29.2 Hz, PMe_3.

Henrici-Olive' and Olive'[25] reported in 1971, ESR spectra along with g and A values for several vanadyl-phosphine complexes $VOCl_2 \cdot 2(PR_3)$. Their findings were that the g factor was independent of the phosphine ligand, $g_o = 1.981$. They also state that given the close

similarity of the magnetic parameters, it is tempting to relate the peak separation to increasing molecular volume, making use of the theory for the line width of paramagnetic species by Kivelson et al[26]. It can be shown by the data collected that as the molecular volume of the ligand increases, so do the peak separation values.

The organophosphine complexes $V(Ntol)Cl_2 \cdot 2(PR_3)$ were also analyzed by mass spectroscopy. The data exhibited clearly shows the lability of the phosphine ligands. Two mass unit signals were detected for the trimethyl phosphine derivative, 105.0 daltons for the Ntol moiety and 77.08 daltons for the $P(CH_3)_3$ moiety. These signals were so dominant that no other peaks were detected. Only two peaks were exhibited in the diphos derivative spectrum, the diphos signal at 398.64 daltons without further fragmentation and the signal attributed to the Ntol moiety. Again these signals were so dominant that no other peaks were detected. Three peaks appeared in the spectrum for the ethyldiphenyl complex. The phosphine dissociated giving a signal at 214.20 daltons followed by fragmentation to $P\emptyset_2$, indicated by the peak at 186.24 daltons. The final peak was once again associated with the Ntol moiety. The mass spectrum for the triphenylphosphine complex, exhibited four peaks. The dissociated phosphine exhibited a signal at 252.84 daltons, followed by fragmentation to $P\emptyset_2$ at 185.61 daltons and C_6H_5 at 77.19 daltons. The final peak was again the Ntol moiety, which was present in all four spectra. The conclusion must be made that the lability of the organic phosphines produce signals that overpower any other fragments present in the detection chamber. No parent ion peaks were detected for any of the organophosphine complexes.

The infrared spectral data is consistent with the predicted values. There were no stretching frequencies found above 1317 cm^{-1}, but several were detected between 1317 cm^{-1} and 467 cm^{-1}. The majority of these stretching bands can be attributed to C-H vibrational modes. One band was found consistent throughout the spectral data occurring 1028 cm^{-1} to 1022 cm^{-1} which may be the vanadium-nitrogen stretch.

Molecular weight determination was calculated by using the isopiestic method, which relies on the fact that solutions of equal molarity have equal vapor pressures. Known weights, and therefore known moles of triphenylphosphine were put into solution in one chamber of the apparatus. Then, a known weight of the organophosphine complex was put into solution in the other calibrated chamber. The solutions were sealed off from the atmosphere and the vapor pressures were allowed to equilibrate. Daily measurements were taken until there was no further change in the molecular weight value calculated from the volumes of the solutions. Good results were obtained for the four organophosphine complexes as follows: $V(Ntol)(PMe_3)_2Cl_2$, Actual 379.1 grams/mole, Found 371 grams/mole; $V(Ntol)(P\emptyset_3)_2Cl_2$, Actual 750.8 grams/mole, Found 751 grams/mole, $V(Ntol)(diphos)Cl_2$, Actual 625.0 grams/mole, Found 627 grams/mole; $V(Ntol)(PEt\emptyset_2)_2Cl_2$, Actual 655.2 grams/mole, Found 651 grams/mole.

Table 5-A

Electron Paramagnetic Resonance
Spectrum Peak Assignments for $V(Ntol)(P(CH_3)_3)_2Cl_2$

Peak	Value (G)
1	3252.2
2	3320.0
3	3393.0
4	3471.3
5	3554.8
6	3643.5
7	3737.4
8	3836.5

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.773 GHz.

$$A(^{51}V) = 83.4$$

$$A(^{31}P) = 29.2$$

$$g = 1.9701$$

NOTE: The spectrum occurred as a 24 line spectrum; an octet of triplets.

Table 5-B

Electron Paramagnetic Resonance Spectrum
Peak Assignments for $V(Ntol)(PEt\emptyset_2)_2Cl_2$

Peak	Value (G)
1	3204.6
2	3286.8
3	3370.4
4	3458.2
5	3550.2
6	3646.4
7	3746.7
8	3851.2

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.650 GHz.

$$A(^{51}V) = 92.4$$

$$A(^{31}P) = 27.3$$

$$g = 1.9544$$

NOTE: The spectrum occurred as a 24 line spectrum; an octet of triplets.

Table 5-C

Electron Paramagnetic Resonance
Spectrum Peak Assignments for
$V(Ntol)(P\emptyset_3)_2Cl_2$

Peak	Value (G)
1	3180.7
2	3272.6
3	3364.9
4	3455.8
5	3557.5
6	3662.1
7	3762.8
8	3878.2

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.775 GHz.

$$A(^{51}V) = 99.6$$

$$A(^{31}P) = 26.1$$

$$g = 1.9788$$

NOTE: The spectrum occurred as a 24 line spectrum; an octet of triplets.

Table 5-D

Electron Paramagnetic Resonance
Spectrum Peak Assignments for
V(Ntol)(diphos)Cl_2

Peak	Value (G)
1	3191.2
2	3277.1
3	3369.8
4	3468.3
5	3572.2
6	3675.6
7	3790.2
8	3904.9

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.775 GHz.

$$A(^{51}V) = 102.0$$

$$A(^{31}P) = 24.5$$

$$g = 1.9684$$

NOTE: The spectrum occurred as a 24 line spectrum; an octet of triplets.

Table 5-E

Mass Spectral Data for the
Organic Phosphine Complexes
$V(Ntol)(PR_3)_2Cl_2$

Compound	Observed Mass	Fragment
$V(Ntol)(P(CH_3)_3)_2Cl_2$	106.0	Ntol
	77.08	$(P(CH_3)_3$
$V(Ntol)(P\emptyset_3)_2Cl_2$	252.84	$P\emptyset_3$
	185.61	$P\emptyset_2$
	105.04	Ntol
	77.19	C_6H_5
$V(Ntol)(P\emptyset_2(CH_2CH_3))_2Cl_2$	214.20	$P\emptyset_2(CH_2CH_3)$
	186.24	$P\emptyset_2$
	107.08	Ntol
$V(Ntol)(diphos)Cl_2$	398.64	diphos
	108.08	Ntol

TABLE 5-F

Infrared Spectra of Bisorganophosphine Derivatives (in cm^{-1})

$V(Ntol)(P\emptyset_3)_2Cl_2$

1157,m, 1096 vs, 1028 m, 909 m, 834 m, 752 vs, 732 s, 712 m, 701 s, 527 m, 517 m, 498 s.

$V(Ntol)(P\emptyset_2(CH_2CH_3))_2Cl_2$

1317 s, 1307 s, 1267 s, 1157 m, 1102 s, 1022 s, 822 m, 742 s, 728 vs, 697 m, 522 w, 482 w.

$V(Ntol)(diphos)_2Cl_2$

1154 w, 1096 m, 1025 w, 892 vw, 865 vw, 816 m, 737 vs, 720 vs, 691 s. 652 vw, 515 vs, 485 s, 467 m.

$V(Ntol)(P(CH_3)_3)_2Cl_2$

1296 w, 1263 m, 1095 s, 1022 s, 960 s, 848 vw, 820 m, 803 m, 743 w.

Abbreviations:

vw - very weak
w - weak
m - moderate
s - strong
vs - very strong

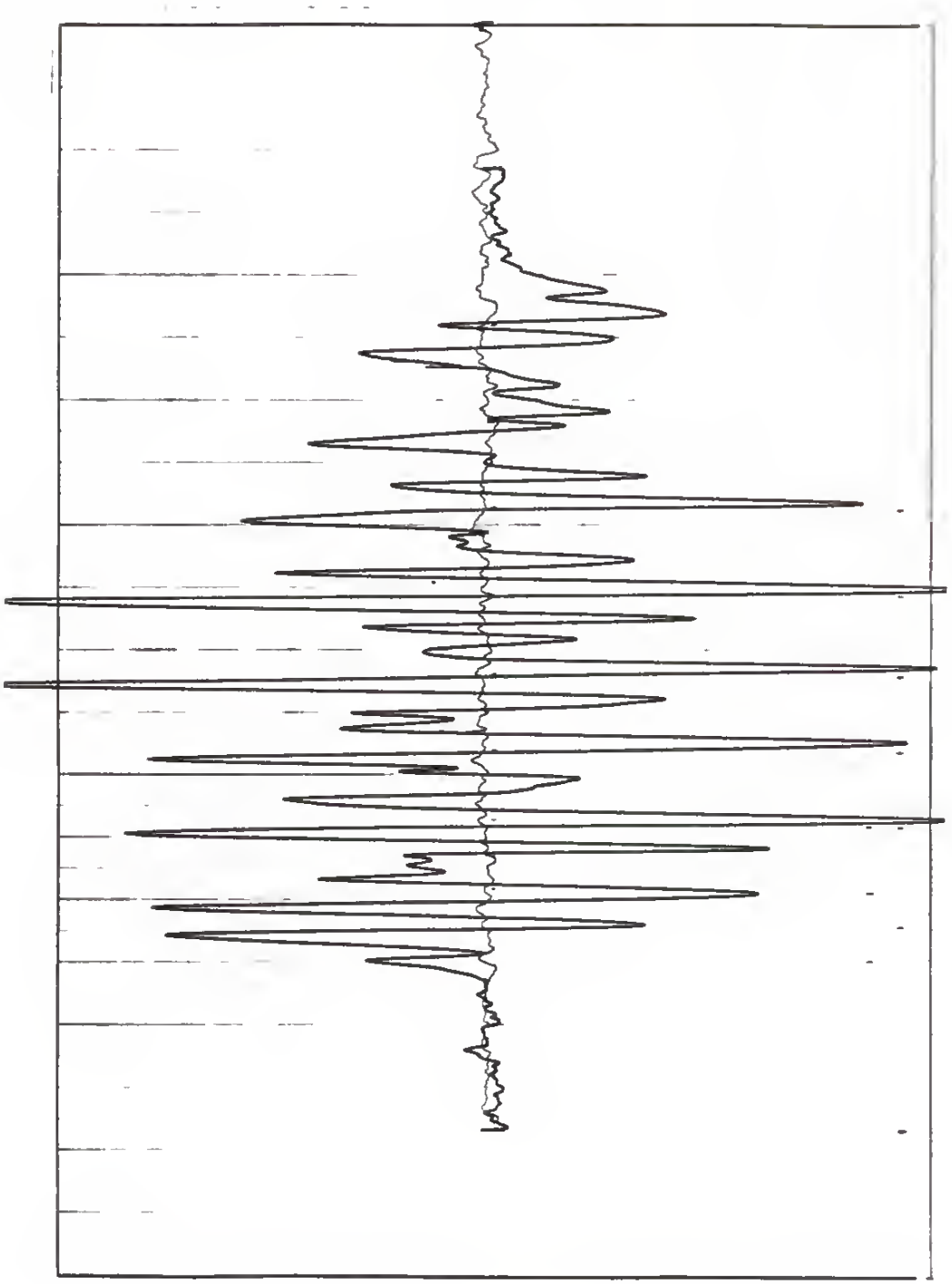

Fig. 5-A ESR Spectrum of Bis(trimethylphosphino) para-tolylimido vanadium IV dichloride in $CDCl_3$

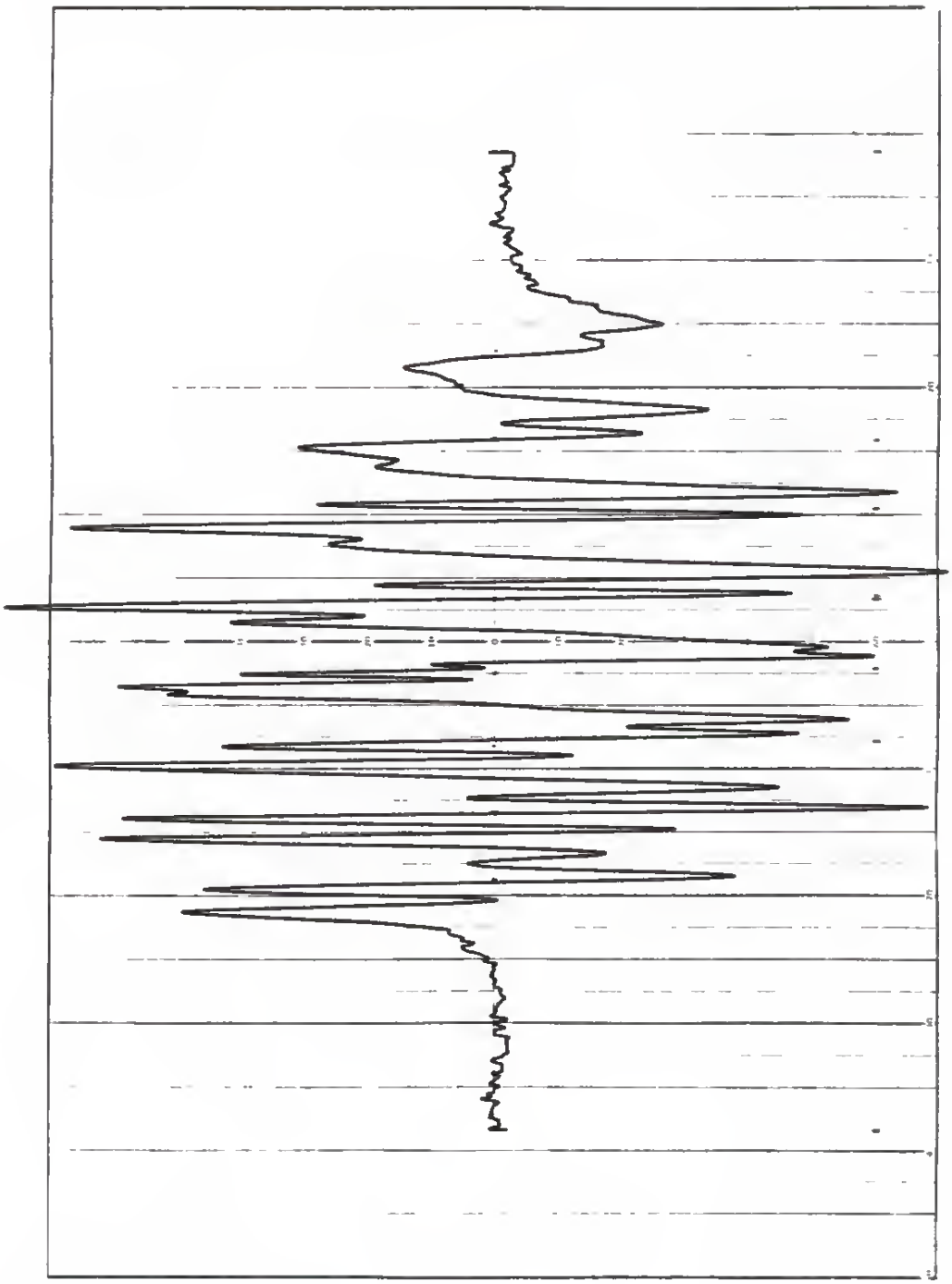

Fig. 5-B ESR Spectrum of Bis(ethyldiphenylphosphino)para-tolylimido vanadium IV dichloride in $CDCl_3$

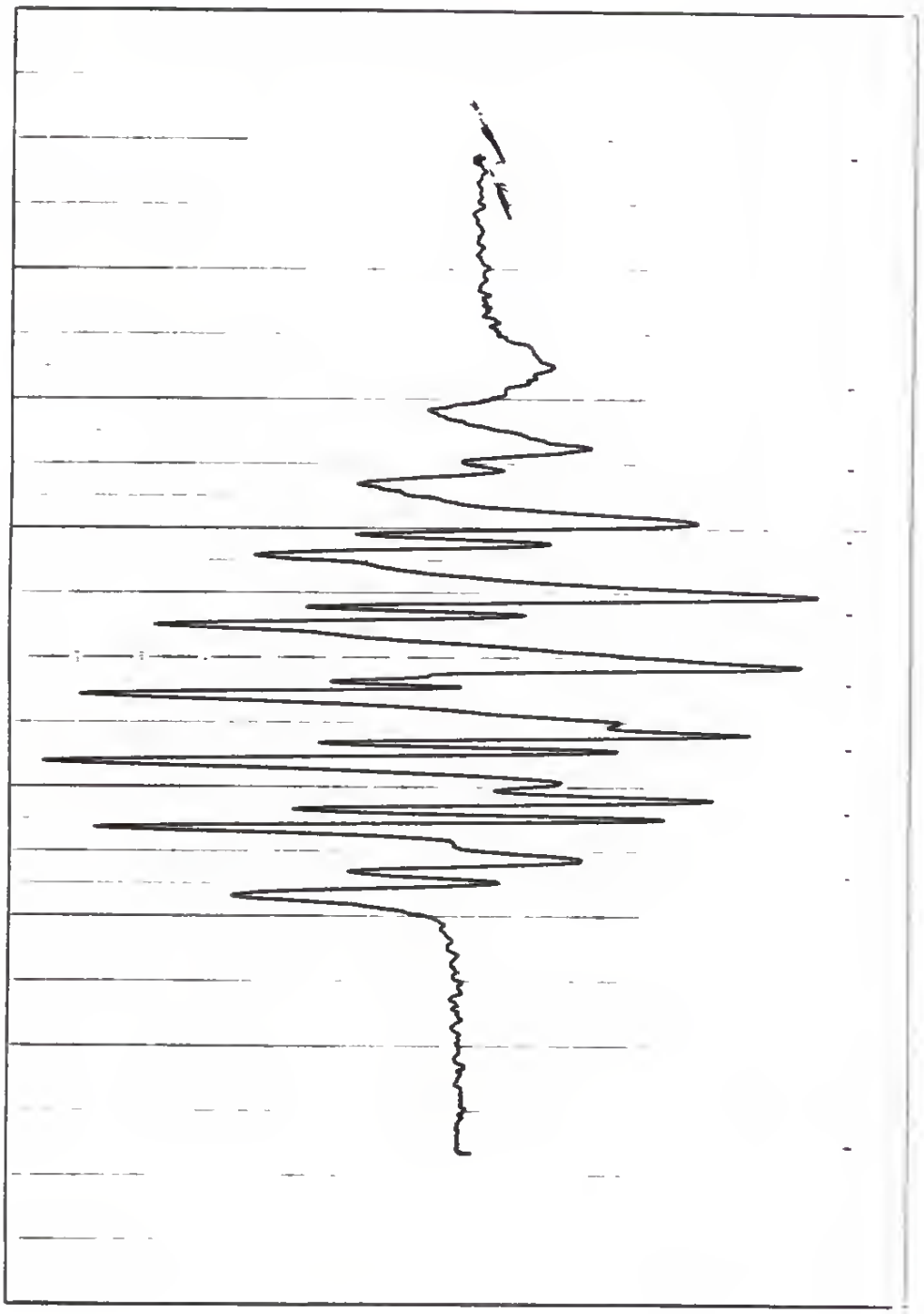

Fig. 5-C ESR Spectrum of Bis(triphenylphosphino)para-tolylimido vanadium IV dichloride in $CDCl_3$

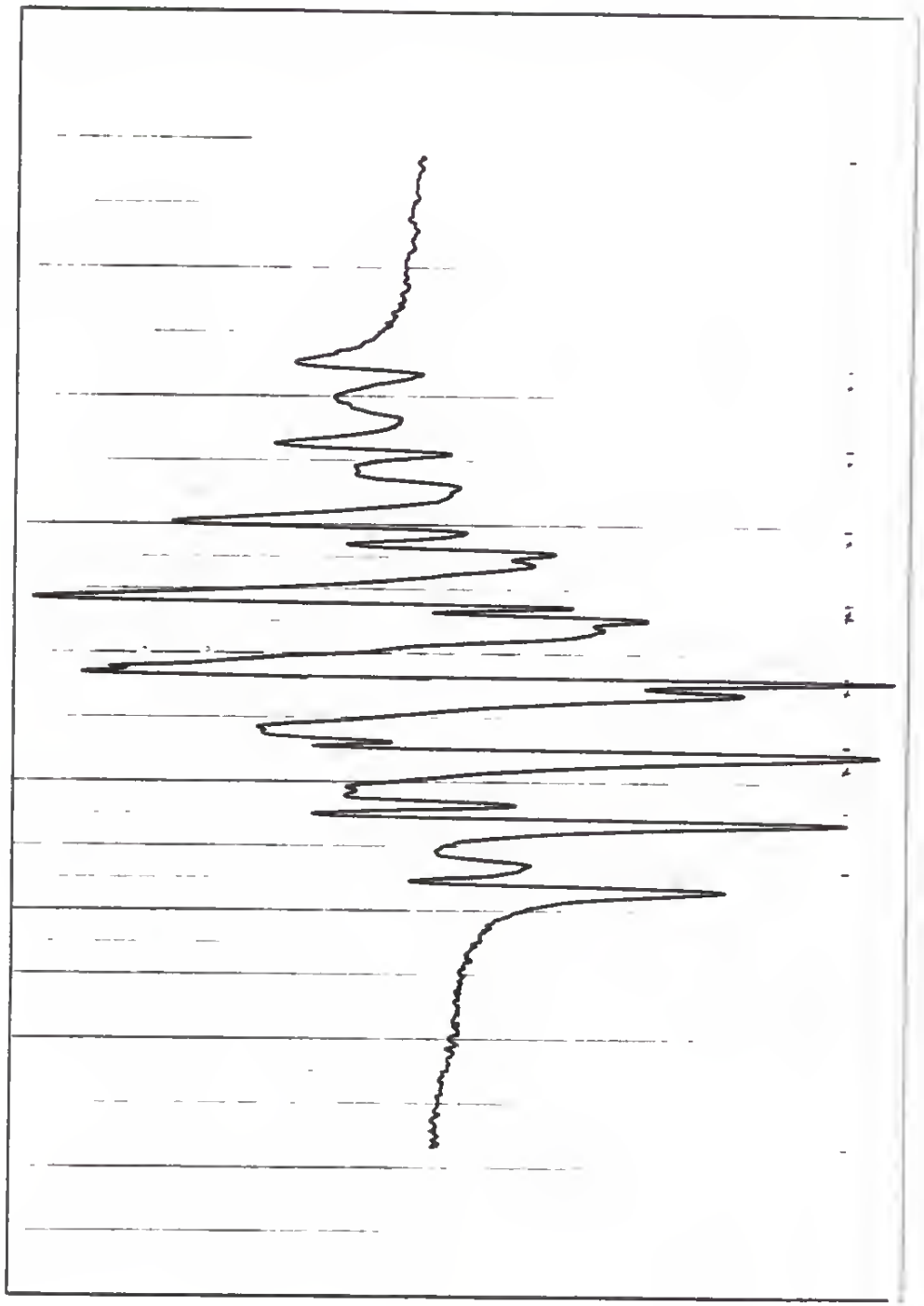

Fig. 5-D ESR Spectrum of Bis(diphenylphosphino)ethane para-tolylimido vanadium IV dichloride in $CDCl_3$

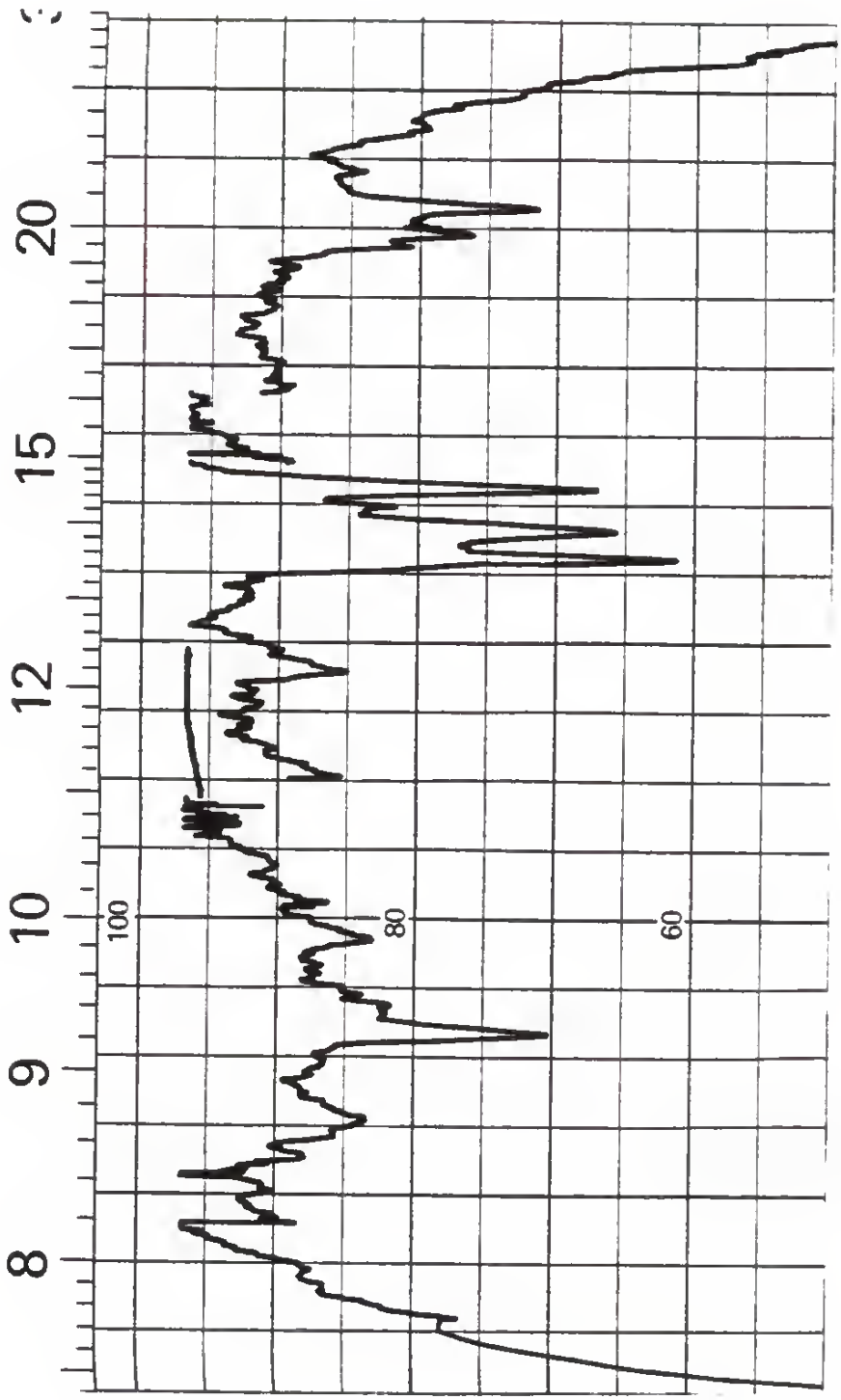

Fig. 5-E Infrared Spectrum of Bis(triphenylphosphino)para-tolylimido vanadium IV dichloride

Chapter VI

Experimental Section

Synthesis of $V(Ntol)(S_2CN(CH_3)_2)_2$

$V(Ntol)(S_2CN(CH_3)_2Cl_2$, (0.30 g, 0.695 mmoles), was combined with Zn, (1.36 g, 20.8 mmoles), and a stir bar in a reaction flask in the N_2-filled dry box. CH_2Cl_2, (ca. 50 ml), was vacuum distilled into the reaction flask and the reaction mixture was allowed to stir at room temperature. The orange-red colored solution slowly changed to a yellow-brown solution during 18 hours of reaction time. The reaction mixture was filtered leaving the excess Zn and $ZnCl_2$ on the filter frit. The filtrate was yellow-brown CH_2Cl_2 solution, the solvent was removed by vacuum, and the product dried for 2 hours. The dark solid product was then washed and triturated with n-Pentane and stirred for 30 minutes. The wash mixture was filtered leaving a dark powder on the filter frit and a colorless pentane filtrate. The product was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The product was analyzed for identification by ESR. Data are found in Table 6-A.

Synthesis of $V(Ntol)(S_2CN(CH_2CH_3)_2)_2$

$V(Ntol)(S_2CN(CH_2CH_3)_2)Cl$, (0.30 g, 0.616 mmoles), was combined in a reaction flask with Zn, (1.45 g, 22.2 mmoles), and a stir bar in the N_2-filled dry box. CH_2Cl_2, (ca. 50 ml), was vacuum distilled into the reaction flask and the reaction mixture was allowed to stir at room temperature. The orange-red colored solution changed to yellow-brown during 24 hours of reaction time. The reaction mixture was then filtered leaving the excess Zn and $ZnCl_2$ on the filter frit. The

filtrate was a yellow-brown colored CH_2Cl_2 solution and the solvent was removed by vacuum. The product was dried for 2 hours and then n-Pentane was vacuum distilled into the flask containing the product. The solid was washed and triturated with stirring for 30 minutes and then filtered leaving a dark powder on the filter frit and a colorless pentane filtrate. The product was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The product was analyzed for identification by ESR. Data are found in Table 6-B.

Synthesis of $V(Ntol)(acac)_2$

$V(Ntol)(acac)_2Cl$, (0.20 g, 0.51 mmoles), was placed in a reaction flask along with Zn, (0.333 g, 5.1 mmoles), and ca. 5 grams of Celite in the N_2-filled dry box. CH_2Cl_2, (ca. 40 ml), was vacuum distilled into the reaction flask and the orange-red solution was allowed to stir and warm to room temperature. After 45 minutes, the solution had turned to a clear green color. The solution was allowed to stir for an additional 20 minutes and the appearance was only slightly darker green. The reaction mixture was then filtered to remove the $ZnCl_2$ and excess Zn. The clear green CH_2Cl_2 filtrate was placed under vacuum, the solvent was removed, and the product dried for 2 hours leaving a yellow-green-turquoise colored solid. The product was washed and triturated using n-Pentane with stirring for 15 minutes. The solution was filtered leaving a green powder on the frit and a colorless pentane filtrate. The product, $V(Ntol)(acac)_2$, was dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The product was analyzed for identity by ESR Spectroscopy. Data for this analysis are found in Table 6-C.

Synthesis of $V(Ntol)(S_2P\emptyset_2)_2$

$V(Ntol)(S_2P\emptyset_2)_2Cl$, (0.35 g, 0.51 mmoles), was placed in a reaction flask in N_2-filled dry box and Zn, (0.35 g, 5.4 mmoles), was placed in a sidearm. CH_2Cl_2, (ca. 50 ml), was vacuum distilled into the reaction flask and the solution was allowed to warm to room temperature with stirring. The Zn was then added and the reaction proceeded for 2 hours until the orange solution had turned to a milky lavender color. The reaction mixture was filtered leaving $ZnCl_2$, excess Zn, and a lavender colored powder on the filter frit. The CH_2Cl_2 filtrate was clear green and the solvent was removed under vacuum leaving a green-yellow solid. Both the insoluble lavender solid and the soluble green-yellow solid were dried in vacuo for 2 hours and then stored in the N_2-filled dry box. The lavender solid was found to be insoluble in all common solvents which made analysis by ^1H NMR or ESR spectroscopy unavailable. The solid was slightly soluble in d6-benzene, but no product peaks were detected. The green-yellow solid product was analyzed for identification and purity by ^1H NMR and ESR spectroscopy, but no useful information was gained.

Results and Discussion

$V(Ntol)(dtc)_2$

Analyses by ESR Spectroscopy

Both $V(Ntol)(S_2CN(CH_3)_2)_2$ and $V(Ntol)(S_2CN(CH_2CH_3)_2)_2$, were analyzed by ESR spectroscopy and were found to exhibit very similar characteristics. These properties are also similar to those found in the related vanadyl compound $VO(S_2CN(CH_2CH_3)_2)_2$. It was reported in

1973[4] that the ESR spectrum of the vanadyl bisdiethyldithiocarbamate, analyzed in toluene at 298K, exhibited a g value of 1.9794 and an A(^{51}V) value equal to 83.5 G. The two spectra collected for the imidovanadium carbamate complexes displayed simple eight line spectra arising from the interaction of the unpaired electron with the ^{51}V nucleus. For the $V(Ntol)(S_2CN(CH_3)_2)_2$ analysis, a solution was prepared at ambient temperature in $CDCl_3$ and the spectral data collected. It was found to have a g value equalling 1.9912 and an A(^{51}V) value of 89.9 G. $V(Ntol)(S_2CN(CH_2CH_3)_2)_2$ was analyzed as a $CDCl_3$ solution at ambient temperature and also displayed a simple eight line spectrum. The g value was found to equal 1.9756 and had an A(^{51}V) value of 89.1 G. The values obtained for these compounds are in close agreement with those found in the vanadyl compounds and can therefore be considered valid. Since the spectra were characterized by having g values < 2 and similar to the vanadyl compounds, it can be surmised that the unpaired d^1 electron would also reside largely in the d_{xy} orbital.

$V(Ntol)(acac)_2$

Analysis by ESR Spectroscopy

An eight line spectrum was obtained by ESR as predicted and the values are found in Table 6-C. The g value was calculated and found to be 1.9823 in $CDCl_3$ at ambient temperature. In 1963, Bernal and Rieger[27] reported the ESR spectral data for vanadyl acetylacetonate and found it to be very sensitive to changes in the solvent. The composition and structure are well established.[28] The two acetylacetone ligands lie flat in the equatorial plane and the vanadyl oxygen lies in the axial position. The sixth position, trans to the vanadyl oxygen, is thus open

and may coordinate solvent molecules leading to changes in magnetic properties due to different solvents. Reported are g values from 1.968 to 1.972 and although chloroform was not used as an experimental solvent, the g value calculated for $V(Ntol)(acac)_2$ was 1.9823. Also reported were $A(^{51}V)$ values ranging from 102.3 t 108.0 while reported here, the $A(^{51}V)$ value was found to equal 106.9.

$V(Ntol)(S_2P\emptyset_2)_2$

Analysis by ^1H NMR and ESR Spectroscopy

Reduction of $V(Ntol)(S_2P\emptyset_2)_2Cl$ with zinc produced two products separated by CH_2Cl_2 and filtration. The soluble product was a green-yellow solid that showed no p-tolyl methyl peak in the ^1H NMR spectrum, but did exhibit a complex signal in the aromatic region. Because the product appeared pure and produced an NMR signal, an ESR spectral analysis was not performed. The other product was a lavender solid which was found to be insoluble in CH_2Cl_2, pentane, toluene, $CDCl_3$, THF, diethylether, and was only very slightly soluble in d_6-benzene. A proton NMR spectrum was taken of the solution but only signal exhibited was due to the solvent. An ESR spectral analysis was also attempted, but the solution proved too dilute for any signal to be detected.

TABLE 6-A

Electron Paramagnetic Resonance

Spectrum Peak Assignments for

$V(Ntol)(dmdtc)_2$

Peak	Value (G)
1	3209.0
2	3291.6
3	3376.6
4	3463.7
5	3553.6
6	3645.4
7	3739.9
8	3836.1

$$A(^{51}V) = 89.9$$

$$g = 1.9912$$

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.780 GHz.

Table 6-B

Electron Paramagnetic Resonance

Spectrum Peak Assignments for

$V(Ntol)(dedtc)_2$

Peak	Value (G)
1	3209.8
2	3291.6
3	3376.3
4	3463.2
5	3552.3
6	3643.4
7	3737.2
8	3833.4

$A(^{51}V) = 89.1$

$g = 1.9756$

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.700 GHz.

Table 6-C

Electron Paramagnetic Resonance

Spectrum Peak Assignments for

$V(Ntol)(acac)_2$

Peak	Value (G)
1	3165.5
2	3262.5
3	3363.0
4	3466.6
5	3573.5
6	3683.8
7	3797.2
8	3914.5

$$A(^{51}V) = 106.9$$
$$g = 1.9823$$

The spectrum was taken as a $CDCl_3$ solution at 25°C with a frequency of 9.775 GHz.

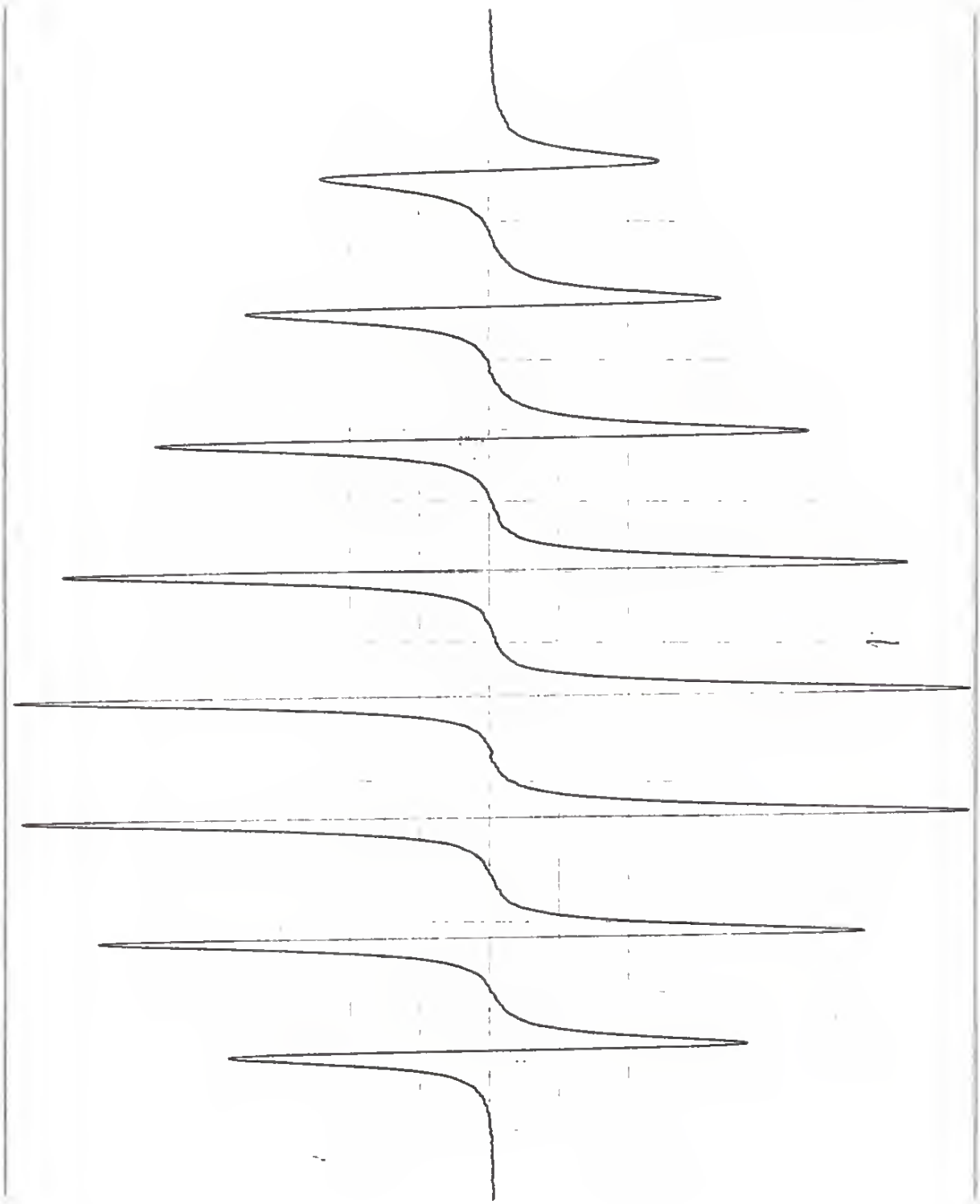

Fig. 6-A ESR Spectrum of Bis(N,N-dimethyldithiocarbamato) para-tolylimido vanadium IV

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THE CHEMISTRY OF PARA-TOLYLIMIDOVANADIUM V TRICHLORIDE: SYNTHESIS AND CHARACTERIZATION OF DIALKYLDITHIOCARBAMATE AND RELATED DERIVATIVES AND OF BIS(ORGANOPHOSPHINE)VANADIUM IV COMPLEXES

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ABSTRACT

The chemistry of para-tolylimidovanadium (V) trichloride has been explored. Metathesis reactions using sodium dialkyldithiocarbamates successfully replaced each chlorine atom forming a series of compounds that were fully characterized. Reduction reactions using zinc with the monochloride derivatives yielded the bis(dialkyldithiocarbamate)vanadium (IV) derivatives. Replacement of the chlorine atoms was also completed using acetylacetone and diphenyldithiophosphonic acid. These compounds were also reduced using zinc.

$(\mu\text{-LiS})_2Fe_2(CO)_6$ was found to react with dimethyldithiocarbamate-para-tolylimidovanadium (V) dichloride forming a heterotrimetallic compound. The product was well characterized.

Reduction reactions using zinc and organophosphines produced a series of bis(organophosphine)para-tolylimidovanadium (IV) dichlorides. The electron spin resonance spectra exhibited splitting by the coordinated phosphines, therefore displaying twenty-four line signals.