Master's Theses   Theses and Dissertations

1993

Correlation of 17O Chemical Shifts of Chromium Carbene Complexes with Moss' Mxy Reacitvity Parameter

Shuyuan Liao
Loyola University Chicago

Follow this and additional works at: https://ecommons.luc.edu/luc_theses

Part of the Chemistry Commons

Recommended Citation

Correlation of ^{17}O Chemical Shifts of Chromium Carbene

Complexes with Moss' m_{xy} Reactivity Parameter

by

SHUYUAN LIAO

A Dissertation Submitted to the Faculty of the Graduate

School of Loyola University of Chicago in Partial

Fulfillment of the Requirements of the Degree of

Master of Science

May

1993

ACKNOWLEDGEMENTS

VITA

Shuyuan Liao is the daughter of Yue Ai Lei and Jun Chao Liao. She was born December 6, 1962 in Guangzhou, Guangdong, the People's Republic of China.

In September, 1980, she was enrolled into Zhongshan University, Guangzhou, Guangdong, China, where she received a Bachelor of Science with a major in physical chemistry in 1984.

In July, 1984, she was employed as an analytical chemist at the Environmental Protection Research Institute of Guangzhou for more than two years.

In December, 1986, she entered the United States to pursue further education. She studied English at Roosevelt University and the University of Illinios at Chicago.

In 1989, she joined E. J. Brach & Sons, Inc., Chicago, Illinois, as an analytical chemist and studied graduate chemistry courses at Roosevelt University.

In 1990, she transfered to Loyola University of Chicago. In Spring, 1991, She was granted an assistantship to support her study. She joined David S. Crumrine's group. Under the direction of Dr. Crumrine, she synthesized some chromium carbene complexes and studied the reactivities of the organometallic carbene complexes using ^{17}O Nuclear

Magnetic Resonance spectroscopy. She also served as a teaching assistant in general chemistry, nursing class and organic chemistry.

In April, 1992, she participated in the 22nd annual Loyola Sigma Xi Graduate Student Forum and got the second place award. In May, she was employed as an organic chemist by Medi Chem Research, Inc. In June, she gave a talk entitled "^{17}O NMR of Chromium Pentacarbonyl Carbene Complexes." at the 25th ACS Great Lakes Regional Meeting in Milwaukee, Wisconsin. She will complete her studies in May, 1993.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

STATEMENT OF THE PROBLEM

The general procedure for recording relative carbene reactivities involves measuring product ratios from carbene attack on several alkenes and comparing the m_{xy} parameters. However, it is very difficult to measure the reactivities of the unreactive nucleophilic carbenes which usually do not cyclopropanate alkenes well. Metal carbonyl compounds of chromium are an example of such reactive species, which, until recently, have found little data to compare their reactivities. ^{17}O NMR chemical shift data of the carbonyl group is a parameter to understand the metal-to-ligand bonding. They might provide some information toward the understanding of reactivities of carbene complexes in relation to the m_{xy} parameter. Our preliminary observations of a correlation of ^{17}O chemical shift with calculated m_{xy} suggested that a series of chromium carbene complexes should be made and studied, especially complexes of the unreactive nucleophilic carbenes.

A) Carbenes

1) Synthesis

Originally, a dichlorocarbene intermediate was postulated by Hine's group to explain the basic hydrolysis of chloroform[1] (Equation 1).

$$CHCl_3 + HO^- \longrightarrow Cl_3C^- + H_2O \longrightarrow :CCl_2 + Cl^- \qquad (1)$$
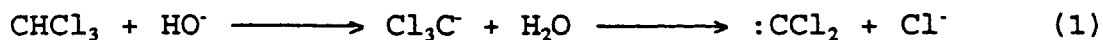
Carbenes can also be generated by the photolysis of diazoalkanes[2] (Equation 2).

$$\underset{Ph}{\overset{Ph}{>}}C{=}N_2 \xrightarrow{\ h\nu\ } \underset{Ph}{\overset{Ph}{>}}C: \ + \ N_2 \uparrow \qquad (2)$$
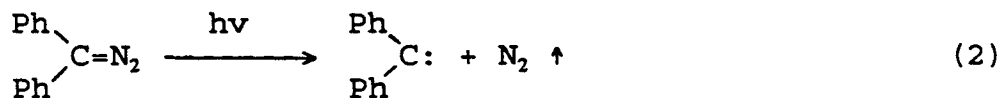
Photolysis of diazirines also gives carbenes[3] (Equation 3).

$$\underset{N=N}{\overset{Ph\ \ H}{C}} \xrightarrow{\ h\nu\ } \underset{H}{\overset{Ph}{>}}C: \ + \ N_2 \uparrow \qquad (3)$$
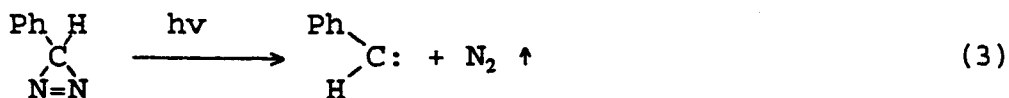
2) Reactivities

It is well known that carbenes are short-lived reactive intermediates[4] which are electron deficient. Many carbene sources such as diazo and diazene compounds, are carcinogenic substances, so they should be handled with extreme care.

Carbenes can undergo addition to alkenes. For example, Under the action of heat, methylenes react with alkenes to produce cyclopropanes[5,6] (Equation 4).

$$:CCl_2 \; + \; CH_2=CH_2 \; \longrightarrow \; \underset{H_2C-CH_2}{\overset{Cl\diagdown \underset{C}{}\diagup Cl}{}} \qquad (4)$$
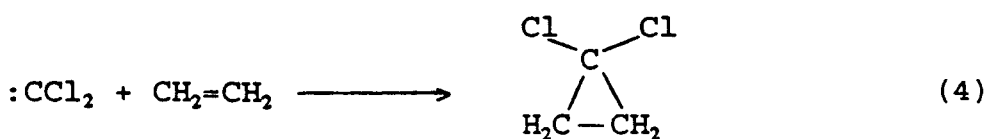
Decomposition of arydiazomethanes with zinc halide-catalysis[7] gives a better yield of cyclopropane when reacted with olefins (Equation 5).

$$\underset{H}{\overset{Ph}{\diagdown}}C=N_2 \; \xrightarrow{\; ZnCl_2 \;} \; \underset{H}{\overset{Ph}{\diagdown}}\underset{Cl}{\overset{ZnCl}{\diagup}}C \; \xrightarrow{\; CH_3CH=CH_2 \;} \; \underset{H_3C}{\overset{Ph\diagdown \underset{C}{}\diagup H}{HC-CH_2}} \qquad (5)$$
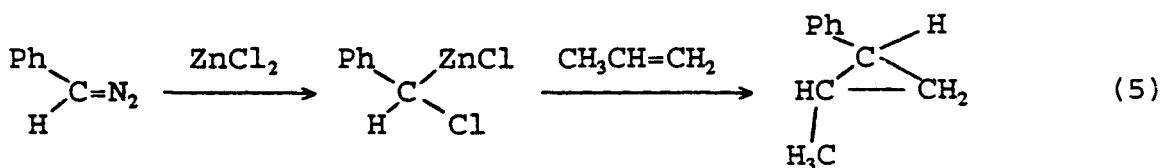
Carbenes react with alkynes[8] to produce cyclopropenes and side products (Equation 6).

$$CH_3-C\equiv C-C_2H_5 \; + \; CH_2N_2 \; \longrightarrow \; \underset{CH_2}{\overset{H_3C}{\diagdown}}C=C\overset{C_2H_5}{\diagup} \qquad + \text{ side product} \quad (6)$$

3
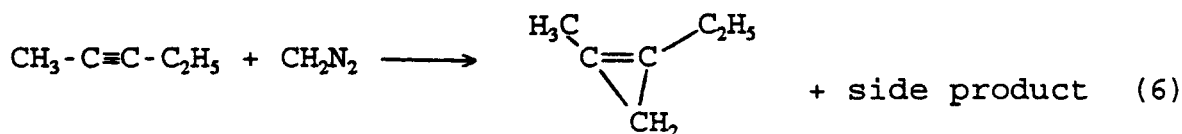
Arylcarbenes can also undergo rearrangement[9], or insert into C-H bonds[10], and dimerize.

$$ \text{(diagram of arylcarbene rearrangement)} \tag{7} $$
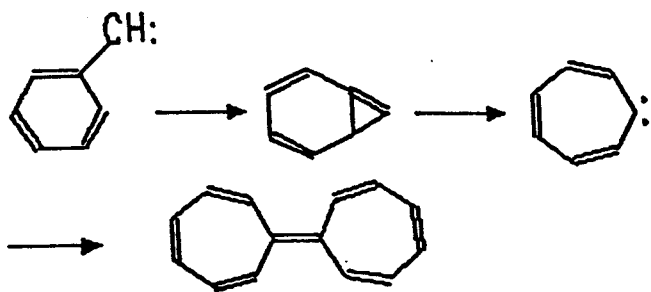
It was also found that carbenes can exist in both singlet and triplet electronic states. They are pictured in this way:
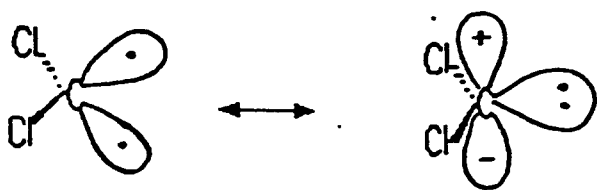
The two carbene states have completely different mechanisms when they react. For this reason, singlet carbenes produces both cis and trans alkenes when they react with alkynes.

3) Physical Studies

Many physical studies have been made on carbenes. However, it was very difficult to isolate and characterize such species, so spectroscopic techniques were applied at low temperatures. Herzberg and Shoosmith[11] observed a spectrum of methylene on flash photolysis of diazomethane in the vaccuum ultraviolet region. Twenty years ago,

4

Jones'[12] group successfully studied triplet carbenes in solution through electron paramagnetic resonance (EPR) spectroscopy. In 1970, Wasserman's[13] group observed the EPR spectra of $:CD_2$ and $:CHD$ in a solid matrix. The spectra were different from the spectrum of $:CH_2$[14]. They observed the X-band EPR spectra of methylene that was:

Signal/noise increases from a) to c) and is associated with increased concentration.
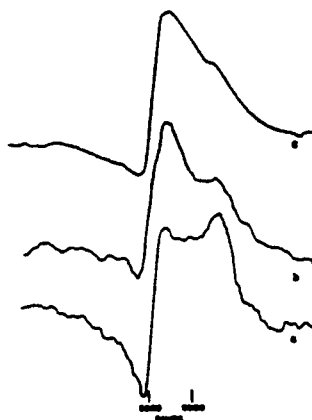
They observed an ESR signal for the triplet was:
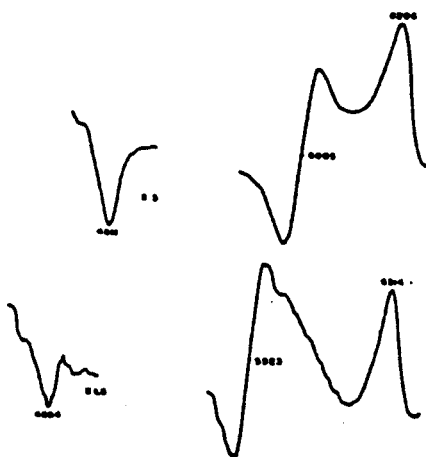
Spectra of $:CD_2$ (top) and $:CHD$ (bottom) with $hv/g\beta$ = 3279.2 and 3277.4 G, respectively.

People have studied the kinetics of carbenes. For example, the decay of some triplet carbenes were

5

monitored[15] by EPR. Based on EPR and laser flash photolysis (LFP) results, Platz[16] explained atom-transfer of aromatic carbenes by using quantum mechanical tunneling (QMT) theories.

B) Fischer Carbene Complexes

1) Synthesis

Metal carbene complexes are very special carbenes. Although singlet, triplet reactivity differences are important for carbenes, they don't occur in metal carbene complexes which are closed shell ground state-singlets. The synthesis of carbene complexes has a twenty year history.

Since the pioneering work of Fischer *et. al.*,[17] a large number of synthetic studies on amino chromium-carbene complexes have appeared. The earliest of these was the use of lithium reagents on $Cr(CO)_6$ followed by alkylation[18] (Equation 8).

$$Cr(CO)_6 + MeLi \longrightarrow (CO)_5CrC \begin{array}{c} OLi \\ Me \end{array}$$

$$\xrightarrow{[Me_3O]^+[BF_4]^-} (CO)_5CrC \begin{array}{c} OMe \\ Me \end{array} \qquad (8)$$
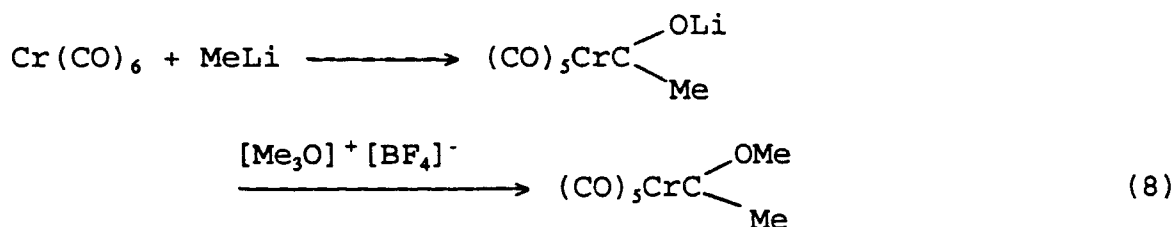
The substitution reactions of alkylamines on pentacarbonylchromium [methoxy(methyl)carbene][19] produced amino chromium carbene complexes (Equation 9).

$$MeNH_2 + (CO)_5CrC \begin{array}{c} OMe \\ Me \end{array} \longrightarrow (CO)_5CrC \begin{array}{c} Me \\ NHMe \end{array} + MeOH \qquad (9)$$

6
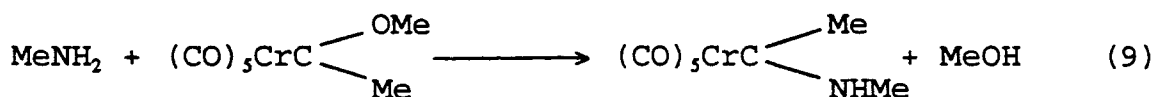
Potassium intercalated graphite complex reacted with $Cr(CO)_6$ to produce the chromium pentacarbonyl dianion which then can be reacted with amides[20] to give chromium amino carbene complexes (Equation 10).

$$C_8K + Cr(CO)_6 \longrightarrow K_2Cr(CO)_5$$

$$\xrightarrow{\text{Me-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-N(Me)}_2} (CO)_5CrC \overset{N(Me)_2}{\underset{Me}{\diagdown}} \qquad (10)$$
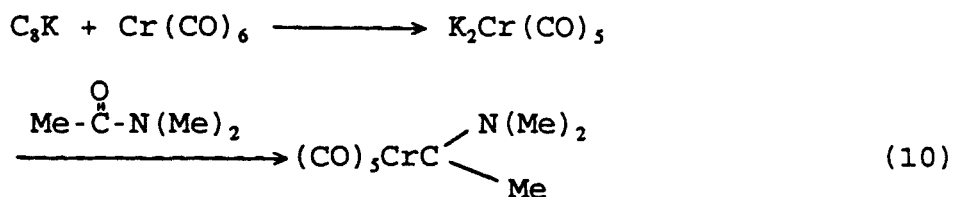
A similar reaction with sodium naphthalenide on $Cr(CO)_6$ produces the chromium pentacarbonyl dianion which can react with acid halides to make chromium pentacarbonyl acyl anions which can then be alkylated[21] (Equation 11).

$$2Na^+ \left[\right]^- + (CO)_6Cr \longrightarrow Na_2Cr(CO)_5$$

$$\xrightarrow{\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-Cl}} Na^+[R-\overset{\overset{\text{O}}{\|}}{\text{C}}-Cr(CO)_5]^-$$

$$\xrightarrow{[Me_3O]^+[BF_4]^-} \overset{MeO}{\underset{R}{\diagup}}CCr(CO)_5 \qquad (11)$$
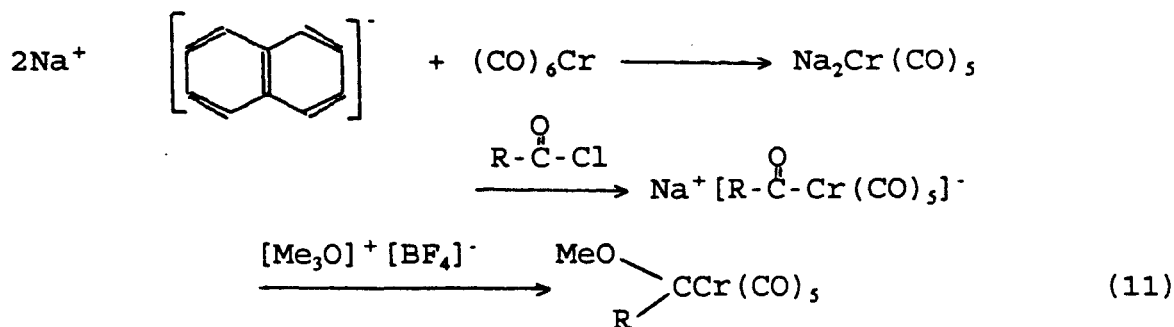
2) Physical studies

Metal carbonyl carbene complexes have been studied extensively using spectroscopy. In Connor's work,[22] infrared spectroscopy (IR) was employed to identify the isomeric effects and the steric effects of the substituents

7

in amino carbene complexes of the type $(CO)_5CrC(Me)NHR$. They observed the N-H stretching frequency and the vibrational frequency of the carbonyl ligand trans to the carbene. The electron density at the nitrogen atom could be correlated with the N-H stretching frequency and then the trans carbonyl stretching frequency.

Another study of metal carbonyl carbene complexes was undertaken by ^{13}C NMR. For example, a correlation was observed between the carbonyl chemical shifts and the stretching force constants for a series of tungsten-carbonyl complexes[23] and π-$(C_5H_5)Fe(CO)_2X$ derivatives[24].

Todd and Bodner[25], studied the ^{13}C NMR spectra of a series of (π-arene)tricarbonyl chromium complexes and found a correlation between the ^{13}C NMR carbonyl chemical shifts and the carbonyl stretching frequencies.

Organometallic carbene complexes have also been studied by [17]O Nuclear Magnetic Resonance spectroscopy (NMR). Todd's group[26], studied a group of transition metal carbonyl complexes and found the [17]O chemical shifts range 400-300 ppm downfield from $H_2^{17}O$. Due to a very long correlation time, they found the trans carbonyl resonance

is broader than the cis carbonyl resonance.

Iwamura[27] et. al., studied the chemical bonding in some tungsten carbonyls $LW(CO)_5$ by ^{17}O NMR and found that the ^{17}O chemical shift of the trans carbonyl was more shielded when L was a strong σ-donor/π-acceptor.

3) Reaction

Although metal carbene complexes also react with a variety of unsaturated substrates[28], they often react differently from free carbenes. For example:[29]

C) Relative Reactivities

Carbenes can add to double bonds to form cyclopropanes and insert in C-H bonds. Numerous investigations have compared carbene reactivites[30]. Moss developed the m_{xy} parameter[31] to compare reactivites of various carbenes through cyclopropanation reaction on certain alkenes. For X-$\ddot{C}$-Y,

$$m = -1.11\sum_{xy}\sigma_r^+ + 0.53\sum_{xy}\sigma_l - 0.31. \qquad (12)$$

In this empirical equation, σ_r^+ and σ_l depend on the nature of the carbene substituents, X and Y. Moss' reactivity parameter m_{xy} for carbenes has become the parameter used to measure the reactivity of electrophilic and ambiphilic, but not nucleophilic carbenes which usually do not cyclopropanate alkenes well.

Compared to carbenes, there are not many reactivity studies on metal carbonyl complexes. This is of particular interest because preliminary work carried out by Crumrine and Iwamura[32] on ^{17}O NMR spectroscopy of some complexes, indicated that such ^{17}O NMR data could provide insights into the reactivity of the parent nucleophilic carbenes.

CHAPTER III

RESULTS AND DISCUSSION

1. Synthesis of Chromium Carbene Complexes:

In our study, seven chromium pentacarbonyl carbenes were synthesized. The syntheses are discussed below and the results are summarized in Table I.

The phenyl ethoxy chromium carbene complex **4** was synthesized by adding phenyl lithium **(1)** to chromium hexacarbonyl **(2)** in ether. The intermediate anion **3** was then alkylated with triethyloxonium tetrafluoroborate at 0°C to give **4** as an orange red oil in 20% yield.

Scheme I: Synthesis by Lithium Reagent Generated Anions

$$\text{PhLi} + \text{Cr(CO)}_6 \xrightarrow[\text{ether}]{25°C} (\text{CO})_5\text{CrC} \overset{\text{OLi}}{\underset{\text{Ph}}{\diagdown}}$$

$$\begin{array}{ccc} \mathbf{1} & \mathbf{2} & \mathbf{3} \end{array}$$

$$\xrightarrow[0°C]{[\text{Et}_3\text{O}]^+[\text{BF}_4]^-} (\text{CO})_5\text{CrC} \overset{\text{OEt}}{\underset{\text{Ph}}{\diagdown}}$$

$$\mathbf{4}$$
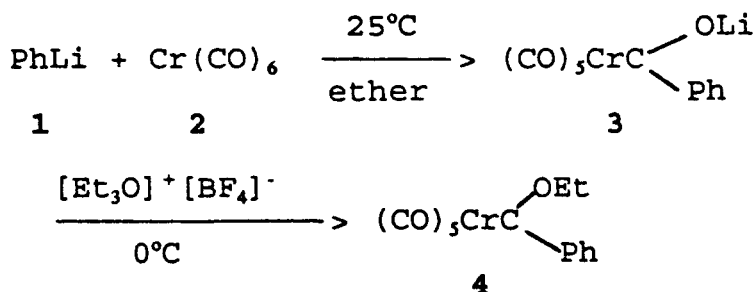
The phenyl amino chromium carbene complex **5** was prepared in 66% yield by substituting ammonia on complex **4**. (Equation 13.)

$$\text{NH}_3 + (\text{CO})_5\text{CrC} \overset{\text{OEt}}{\underset{\text{Ph}}{\diagdown}} \xrightarrow[0°C]{\text{ether}} (\text{CO})_5\text{CrC} \overset{\text{Ph}}{\underset{\text{NH}_2}{\diagdown}} + \text{EtOH} \qquad (13)$$

$$\mathbf{5}$$
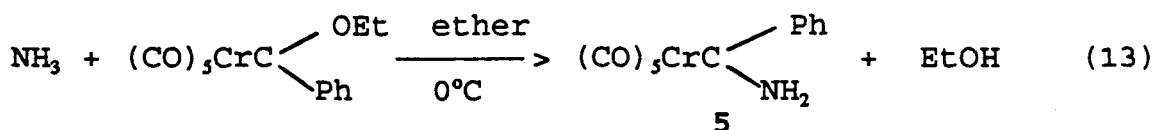
Synthesis of the hydrogen dimethyl amino chromium carbene complexe **9** in 43% yield involved potassium intercalated graphite **6** with chromium hexacarbonyl **(2)** to make the dipotassium chromium pentacarbonyl **(7)** which then was reacted with dimethylformamide **(8)** (R=H; R'=Me).

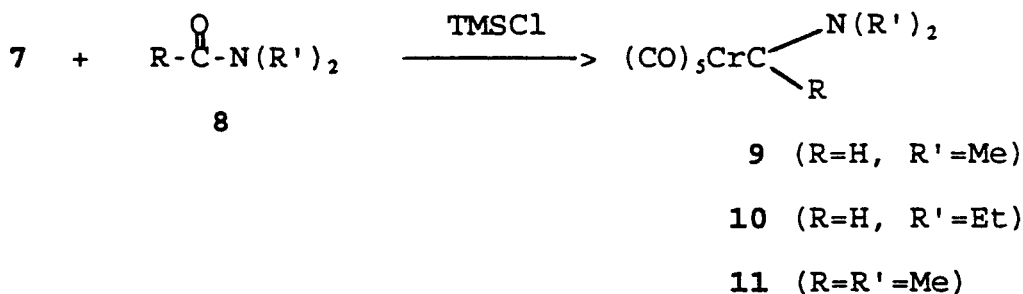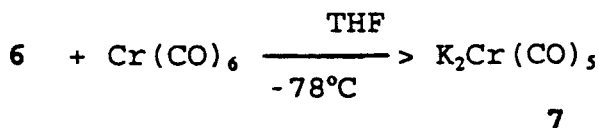**Scheme II: Synthesis by C$_8$K Generated (CO)$_5$Cr^{2-}, Followed by Amides**

$$8C + K \xrightarrow{\quad 160\text{-}180°C \quad} C_8K$$

6

$$6 + Cr(CO)_6 \xrightarrow[-78°C]{THF} K_2Cr(CO)_5$$

7

$$7 + \underset{\textbf{8}}{R-\overset{\overset{O}{\|}}{C}-N(R')_2} \xrightarrow{\quad TMSCl \quad} (CO)_5CrC\overset{N(R')_2}{\underset{R}{\big\langle}}$$

9 (R=H, R'=Me)

10 (R=H, R'=Et)

11 (R=R'=Me)
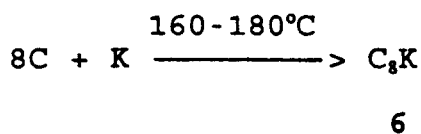
In a similar manner, **10** was obtained in 50% yield from dianion **7** and diethylformamide **(8)** (R=H; R'=Et) and **11** was obtained in 52% yield from dianion **7** and dimethyl acetamide **(8)** (R=R'=Me).

The reaction of **7** with N,N-dimethyl carbamayl chloride **(8)** (R=Cl; R'=Me) produced the chromium acyl salt **12** which was alkylated by trimethyloxonium tetrafluoroborate **(13)**

(R"=Me) to give **14** in 1.3% yield.

Scheme III: Synthesis by C_8K Generated $(CO)_5Cr^{2-}$, Followed by Acid Halides
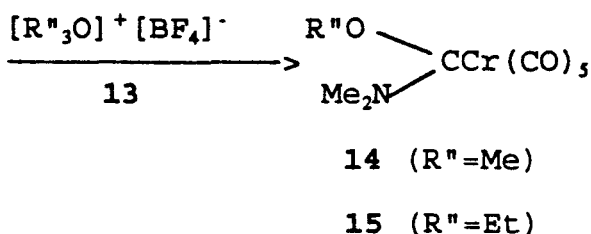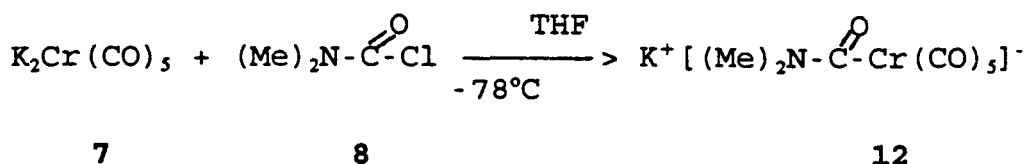
$$K_2Cr(CO)_5 + (Me)_2N-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-78°C]{THF} K^+[(Me)_2N-\overset{O}{\overset{\|}{C}}-Cr(CO)_5]^-$$

$$\text{7} \qquad\qquad \text{8} \qquad\qquad\qquad\qquad \text{12}$$

$$\xrightarrow[13]{[R"_3O]^+[BF_4]^-} \quad \underset{Me_2N}{\overset{R"O}{>}}CCr(CO)_5$$

$$\text{14} \ (R"=Me)$$
$$\text{15} \ (R"=Et)$$

In the same way, alkylating the salt **12** with triethyloxonium tetrafluoroborate **(13)** (R"=Et) gave **15** in 14.3% yield.

In preliminary experiments, it was thought that complex **14** could be synthesized by Scheme I, which used a phenyl lithium generated anion, followed by the alkylation with trimethyloxonium tetrafluoroborate in water, nitromethane in hexane, or other alkylating reagents. However, the result was negative. It seemed that a good solvent had not been found for the alkylation step.

One attempt to synthesize **14** involved some work similar to Scheme II using 10 mmol of diethylcarbamate to

react with the C_8K-generated $Cr(CO)_5^{2-}$, but it was not successful. It seemed that carbamates decomposed the $K_2Cr(CO)_5$, or the starting materials were recovered unchanged. Further experiments confirmed that the carbamates, in fact, failed to convert the $K_2Cr(CO)_5$ into the corresponding alkoxyaminocarbene complexes.

It was reported[20] that methoxy carbene complexes could be synthesized by reacting sodium naphthalenide with $Cr(CO)_6$ followed by reaction with acid halides and alkylating agents. Therefore, the potassium graphite intercalated complex reaction with $Cr(CO)_6$ was sustituted for the sodium naphthalenide reaction with $Cr(CO)_6$. Then dimethylcarbamyl chloride was used as one of the acid halides. New chromium carbene complexes **14** and **15** were sucessfully prepared in this manner as shown in Scheme III. The structures proposed for the two complexes are consistent with data obtained from ^1H, ^{13}C, ^{17}O NMR, MS and IR spectra.

The physical properties and yields of the complexes prepared for this study are summarized in Table I. The ^1H NMR chemical shifts for this series of $(CO)_5CrCRR'$ derivatives were given in Table II. Solutions of the complexes in $CDCl_3$ and C_6D_6 were placed in 10 mm (OD) NMR tubes and the ^{13}C and ^{17}O spectra were obtained on the 7.0 T Varian NMR at 20°C using the parameters listed in the experimental section. The ^{17}O NMR spectra were referenced to

14

TABLE I. PHYSICAL PROPERTIES AND YIELD FOR CHROMIUM CARBENE COMPLEXES

#	$(CO)_5CrCRR'$ R	R'	physical state	mp °C	yield (%)
4	Ph	OEt	oil (orange red)		20
5	Ph	NH_2	crystals (orange)	78.5-79.5	66
9	NMe_2	H	crystals (light yellow)	66-68	43
10	NEt_2	H	crystals (yellow)		50
11	NMe_2	Me	crystals (pale green)	54-55	52
14	NMe_2	OMe	liquid (light green)		1.3
15	NMe_2	OEt	crystals (pale yellow)	44-46	14.3

TABLE II. ^{1}H NMR DATA FOR CHROMIUM CARBENE COMPLEXES

			δ ^{1}H NMR			
(CO)$_5$CrCRR'			---------- R ----------		---------- R' ----------	
#	R	R'				
1	Ph	OEt	7.50~7.38(5H m)		4.95(2H q)	1.65(3H t)
2	NMe$_2$	OEt	3.56(3H s)	3.05(3H s)	4.61(2H q)	1.40(3H t)
3	NMe$_2$	OMe	3.57(3H s)	3.04(3H s)	4.23(3H s)	
4	NEt$_2$	H	4.05(2H q)	3.57(2H q)	10.8(1H s)	
			1.41(3H t)	1.29(3H t)		
5	NMe$_2$	H*	2.59(3H s)	1.81(3H s)	9.89(1H s)	
6	NMe$_2$	Me	3.29(3H s)	3.86(3H s)	2.68(3H s)	
7	Ph	NH$_2$	7.42~7.35(3H m)		8.85(1H s)	8.29(1H s)
			7.18~7.15(2H m)			

* = Spectra were recorded in C$_6$D$_6$.

external D_2O. The results of an analysis of the ^{17}O NMR spectra of a series of chromium pentacarbonyl carbene complexes are presented in Table III along with a tabulation of the ^{13}C NMR spectra.

2. The Correlation of NMR of the Complexes with Moss' m_{xy} Reactivity Parameter

The ^{17}O NMR chemical shift values are listed in Table III. The ^{17}O NMR chemical shifts of the carbonyl ligands for this group of chromium carbene complexes occur between $\delta 365$-400 ppm downfield relative to external and naturally abundant $D_2^{17}O$. The ^{17}O NMR chemical shifts of the trans carbonyl ligands follow the trend:
PhCOEt > PhCNH$_2$ > HCN(Et)$_2$ > HCN(Me)$_2$ > MeN(Me)$_2$ > N(Me)$_2$COMe > N(Me)$_2$COEt.

Following the Moss reactivity equation, the m_{xy} parameters of a series of chromium pentacarbonyl carbene complexes were calculated and are shown in Table IV.

A plot of the ^{17}O chemical shifts of the trans C=O vs m_{xy} parameters along with the Lotus 1-2-3 regression analysis data are shown in Figure I and Table V respectively. There is not a simple relationship between ^{17}O NMR data and m_{xy}. They don't have good linear or quadratic correlation. However, ^{17}O NMR data on the trans C=O of this series of unreactive nuclephilic chromium pentacarbonyl carbene complexes show a non linear cubic

17

TABLE III. ^{17}O and ^{13}C NMR DATA FOR CHROMIUM CARBENE COMPLEXES

$(CO)_5CrCRR'$			δ(CO) ^{17}O NMR		δ ^{13}C NMR			
#	R	R'	trans	cis	trans(CO)	cis(CO)	C:	other
1	Ph	OEt	397.5	373.9	223.7	215.8		153.71 129.8 128.1 122.5
2	NMe$_2$	OEt	367.3	371.8	220.9	216.8	242.1	70.4 45.4 38.7 15.7
2a		*	369.7	372.5				
3	NMe$_2$	OMe	368.4	372.3	220.8	216.8	243.8	61.5 45.7 38.6
3a		*	370.5	373.2				
4	NEt$_2$	H	379.0	369.0	223.5	217.1	259.3	57.6 52.0 15.0 14.2
5	NMe$_2$	H	378.2	368.0				
5a		*			224.1	218.2	263.0	53.7 45.5
6	NMe$_2$	Me	375.2	369.1	223.0	217.4	272.8	53.2 42.5 40.4
6a		*	377.0	369.6				
7	Ph	NH$_2$	385.0	370.2	222.6	216.6	290.6	152.5 129.3 128.5 121.8

* = Spectra were recorded in C$_6$D$_6$.

Table IV. Calculation of m_{xy} by Taft Constants[33]

Func.grp.	σ_p^+	σ_I	$\sigma_R^+ = \sigma_p - \sigma_I$	Structure	m_{xy}
MeO	-0.78	0.27	-1.05	C(OMe)(NMe$_2$)	2.9507
NMe$_2$	-1.67	0.06	-1.73	C(OEt)(NMe$_2$)	2.9174
NH$_2$	-1.3	0.12	-1.42	C(Ph)(NH$_2$)	1.6936
Ph	-0.18	0.1	-0.28	C(Ph)(OEt)	1.3291
H	0	0	0	C(H)(NMe$_2$)	1.6421
Me	-0.31	-0.05	-0.26	C(Me)(NMe$_2$)	1.9042
OEt	-0.75	0.27	-1.02	C(H)(NEt$_2$)	2.0861
NEt$_2$	-2.07	0.06	-2.13		
F	-0.07	0.5	-0.57	CF$_2$	1.4854

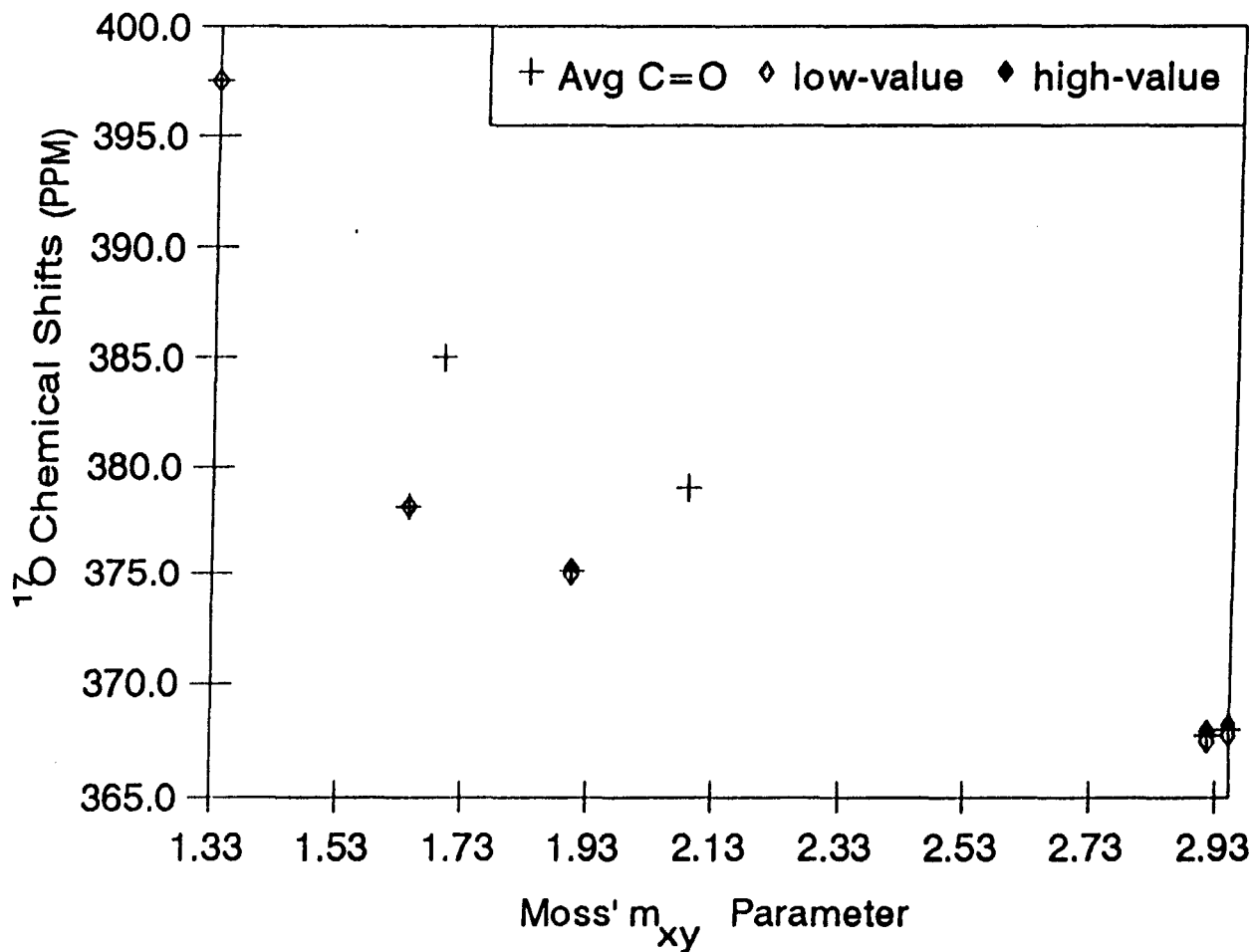Figure I. ^{17}O Chemical Shifts of the Trans C=O vs Moss' m$_{xy}$ Parameter

Table V. ^{17}O NMR DATA FOR THE TRANS CARBONYL OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.						
------ $(CO)_5CrCRR'$ -----			-----δ-----	---------Regression----------		
R	R'	m_{xy}	trans C=O	linear	quadratic	cubic
Ph	OEt	1.3291	397.57±0.04	389.33	394.97	397.49
H	NMe$_2$	1.6421	378.18±0.02	384.84	384.51	381.57
Ph	NH$_2$	1.6936	385.00	384.10	383.03	380.27
Me	NMe$_2$	1.9042	375.07±0.15	381.08	377.70	377.66
H	NEt$_2$	2.0861	379.04	378.48	374.01	377.77
OEt	NMe$_2$	2.9174	367.67±0.21	366.55	368.06	368.75
OMe	NMe$_2$	2.9507	367.94±0.22	366.08	368.19	366.97

Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	408.3893	0.761426	5.555330	3.5855		
Quadratic	467.5855	0.871486	4.558557	-71.8099	12.92087	
Cubic	752.4492	0.931356	3.847010	-521.318	239.5684	-36.3190

correlation of 0.93 with Moss' m_{xy} parameter. A plot of the ^{17}O chemical shifts of the cis C=O chemical shifts vs m_{xy} parameters along with the Lotus 1-2-3 regression analysis data are shown in Figure II and Table VI respectively. Clearly, there is no correlation of the ^{17}O chemical shifts of the cis C=O of the carbene complexes with Moss' m_{xy} parameter. However, a plot of the ^{17}O chemical shifts of the difference of the trans and cis C=O chemical shifts vs m_{xy} parameters (Figure III) along with the Lotus 1-2-3 regression data analysis (Table VII) were made. ^{17}O NMR data of the overall effect have a non linear cubic correlation of 0.95 with Moss' reactivity m_{xy} parameters. A plot of ^{13}C chemical shifts of the carbene carbon vs m_{xy} parameters (Figure IV) along with the Lotus 1-2-3 regression data analysis (Table VIII) were made. An interesting aspect of the plot is the lack of correlation with Moss' reactivity m_{xy} parameters. It is possible that the carbene carbon experiences different electronic effects due to its being directly bonded to the metal. A plot of ^{13}C chemical shifts of the trans carbonyl vs m_{xy} parameters (Figure V) along with the Lotus 1-2-3 regression data analysis (Table IX) were made. Also, a plot of ^{13}C chemical shifts of the cis carbonyl vs m_{xy} parameters (Figure VI) along with the Lotus 1-2-3 regression data analysis (Table X) were made. Linear, quadratic and cubic plots lack correlation with Moss'

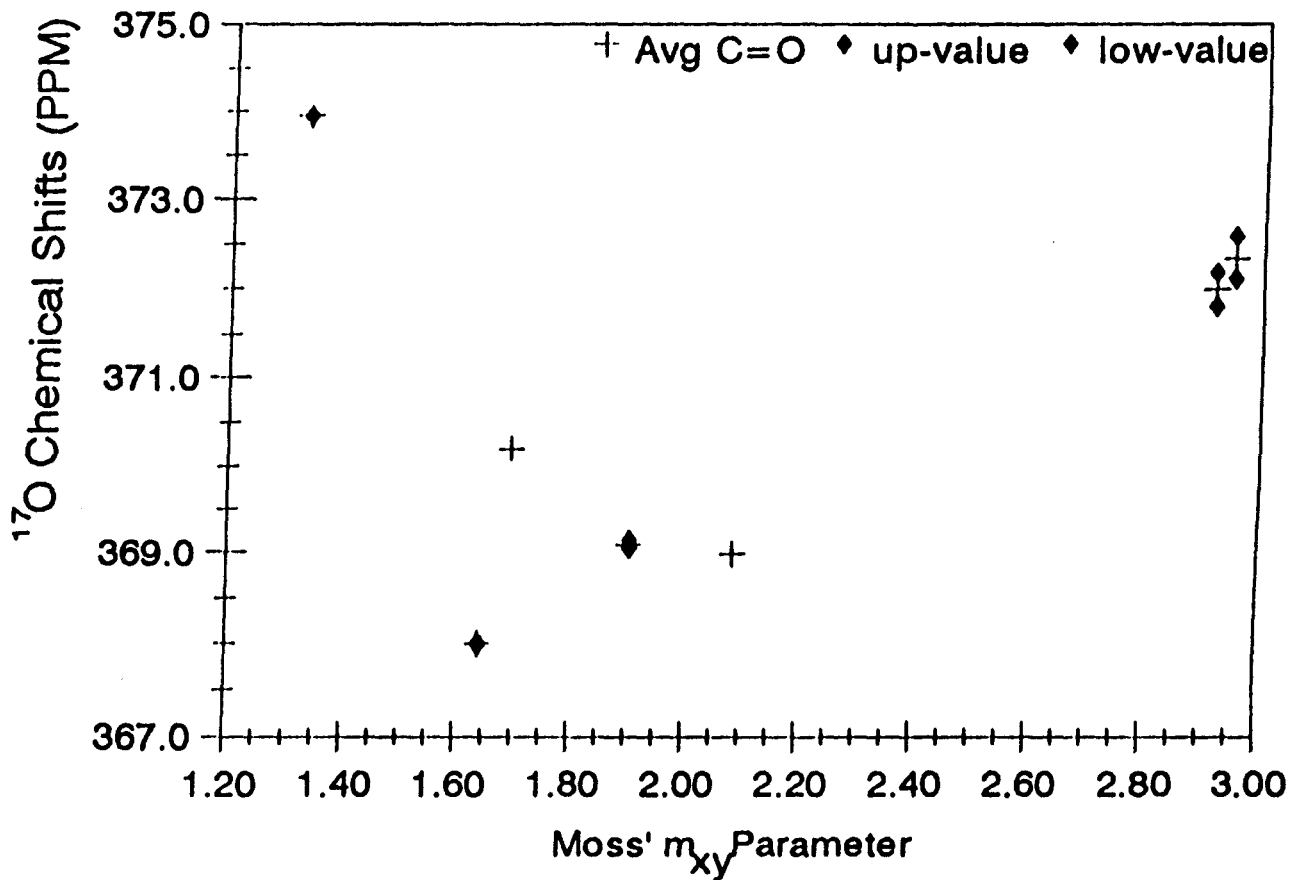Figure II. ^{17}O Chemical Shifts of the Cis C=O vs Moss' m_{xy} Parameter

Table VI. ^{17}O NMR DATA FOR THE CIS CARBONYL OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.						
------ (CO)$_5$CrCRR' -----			-----δ-----	----------Regression----------		
R	R'	m_{xy}	cis C=O	linear	quadratic	cubic
Ph	OEt	1.3291	373.94±0	370.12	373.14	373.79
H	NMe$_2$	1.6421	368.00± 0.01	370.34	370.16	369.41
Ph	NH$_2$	1.6936	370.24	370.38	369.80	369.10
Me	NMe$_2$	1.9042	369.09± 0.05	370.53	368.71	368.70
H	NEt$_2$	2.0861	368.98	370.66	368.27	369.23
OEt	NMe$_2$	2.9174	372.00± 0.18	371.26	372.07	372.25
OMe	NMe$_2$	2.9507	372.34± 0.24	371.29	372.42	372.11

Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	369.1600	0.044566	2.310827	0.721109		
Quadratic	400.9441	0.778952	1.242696	-30.1361	6.937562	
Cubic	473.6684	0.869266	1.103533	-144.893	64.79959	-9.27207

Figure III. ^{17}O Chemical Shifts of the Difference of Trans-Cis C=O vs Moss' m_{xy} Parameter
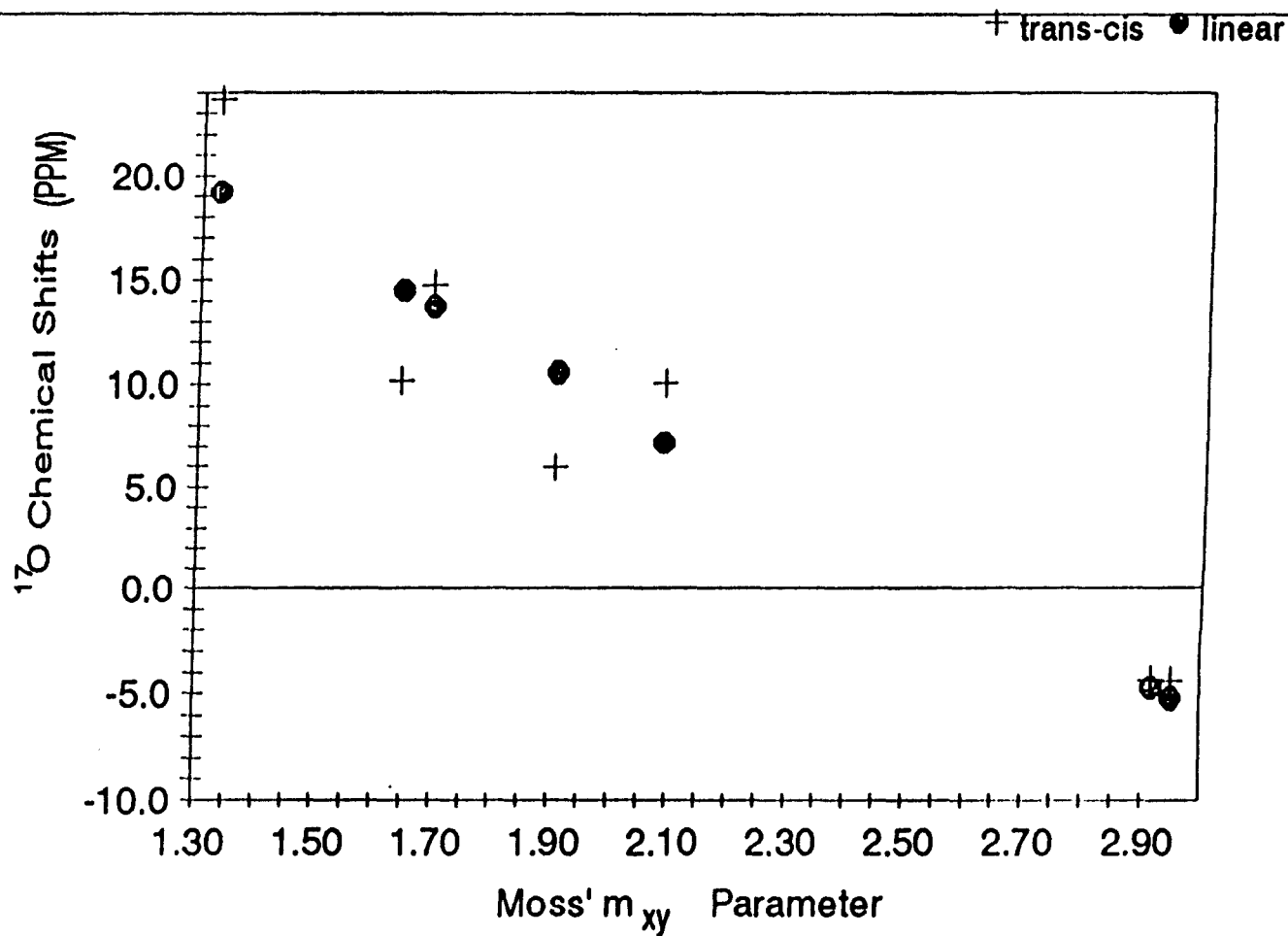
+ trans-cis ● linear

Table VII. ^{17}O NMR DATA FOR THE DIFFERENCE OF THE TRANS AND CIS CARBONYL OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.						
------(CO)$_5$CrCRR'-----			-----δ-----	----------Regression----------		
R	R'	m_{xy}	trans-cis	linear	quadratic	cubic
Ph	OEt	1.3291	23.63	19.21	21.82	23.70
H	NMe$_2$	1.6421	10.18	14.50	14.34	12.15
Ph	NH$_2$	1.6936	14.77	13.72	13.22	11.17
Me	NMe$_2$	1.9042	5.97	10.55	8.98	8.95
H	NEt$_2$	2.0861	10.06	7.81	5.74	8.54
OEt	NMe$_2$	2.9174	-4.33	-4.71	-4.01	-3.50
OMe	NMe$_2$	2.9507	-4.41	-5.21	-4.23	-5.14
Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	39.22923	0.891644	3.633719	-15.0609		
Quadratic	66.64144	0.916698	3.562111	-41.6737	5.983308	
Cubic	278.7807	0.951945	3.124054	-376.425	174.7688	-27.0469

Figure IV. ^{13}C Chemical Shifts of the Carbene Carbons C=O vs Moss' m_{xy} Parameter
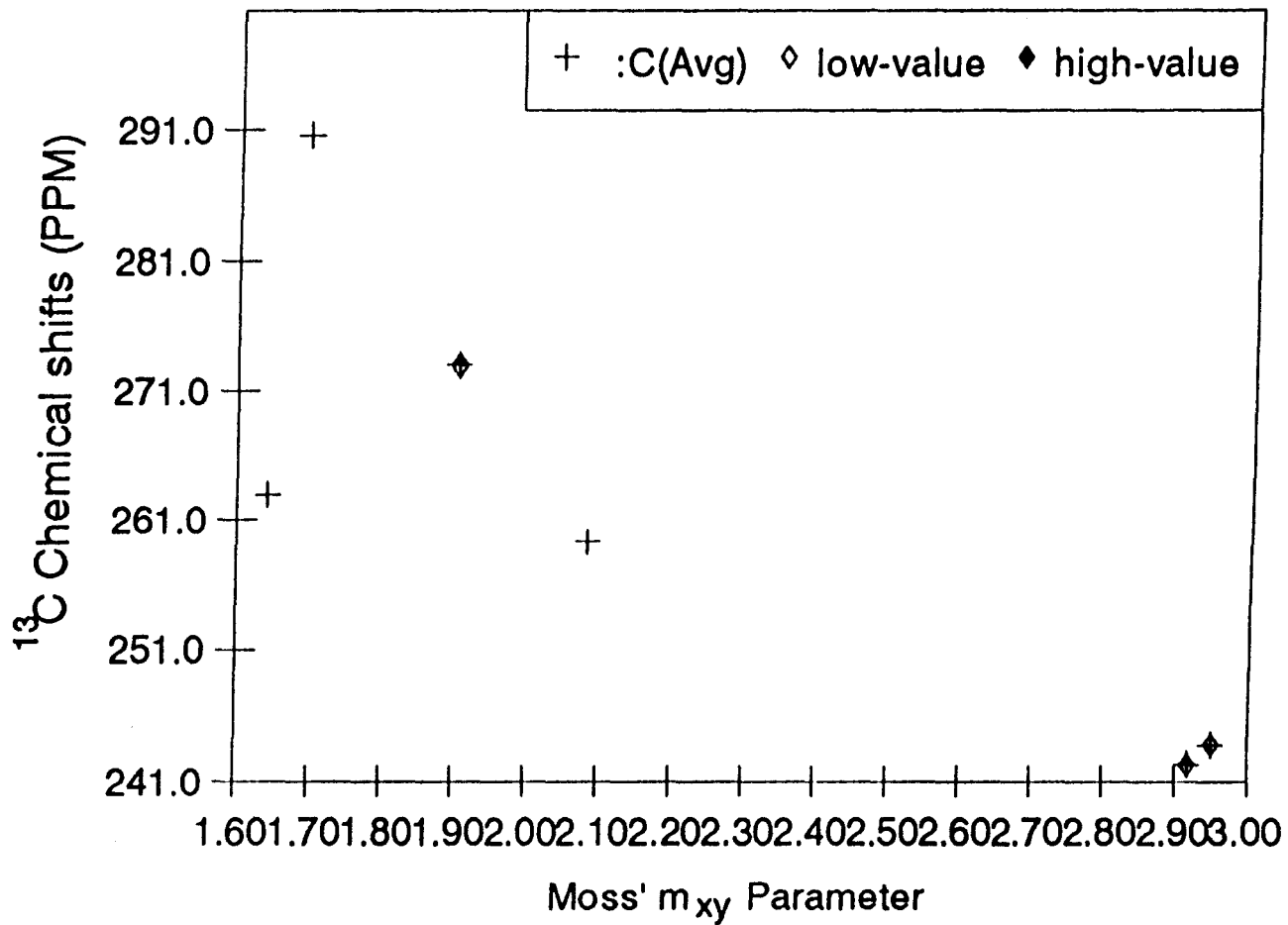
Table VIII. ^{13}C NMR DATA FOR THE CARBENE CARBON OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.						
------(CO)$_5$CrCRR'-----			-----δ-----	----------Regression----------		
R	R'	m_{xy}	:C=	linear	quadratic	cubic
PhO	OEt	1.3291				
H	NMe$_2$	1.6421	*262.97	264.94	277.02	272.69
Ph	NH$_2$	1.6936	290.59	275.23	275.49	277.41
Me	NMe$_2$	1.9042	272.99±0.13	269.71	269.38	276.93
H	NEt$_2$	2.0861	259.28	276.58	264.29	259.12
OEt	NMe$_2$	2.9174	242.29±0.09	243.16	243.24	228.37
OMe	NMe$_2$	2.9507	243.79±0.02	242.28	242.48	247.39

Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	319.6159	0.719727	10.80620	-26.2076		
Quadratic	333.0580	0.720228	12.46676	-38.4268	2.619218	
Cubic	-2240.96	0.812707	12.49274	3643.740	-1710.50	258.0518

* = Spectra were recorded in C_6D_6.

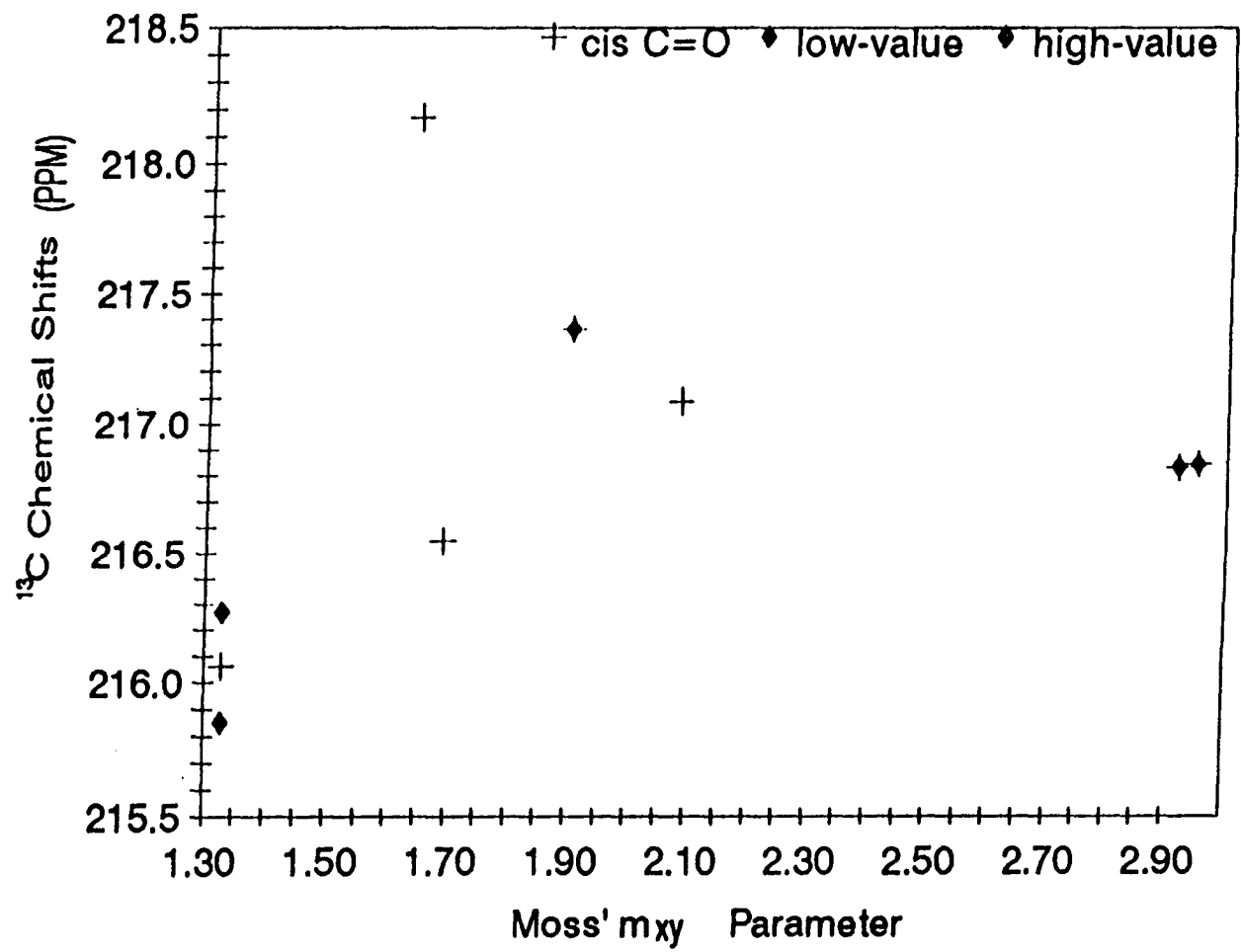Figure V. ^{13}C Chemical Shifts of the Trans C=O vs Moss' m $_{xy}$ Parameter
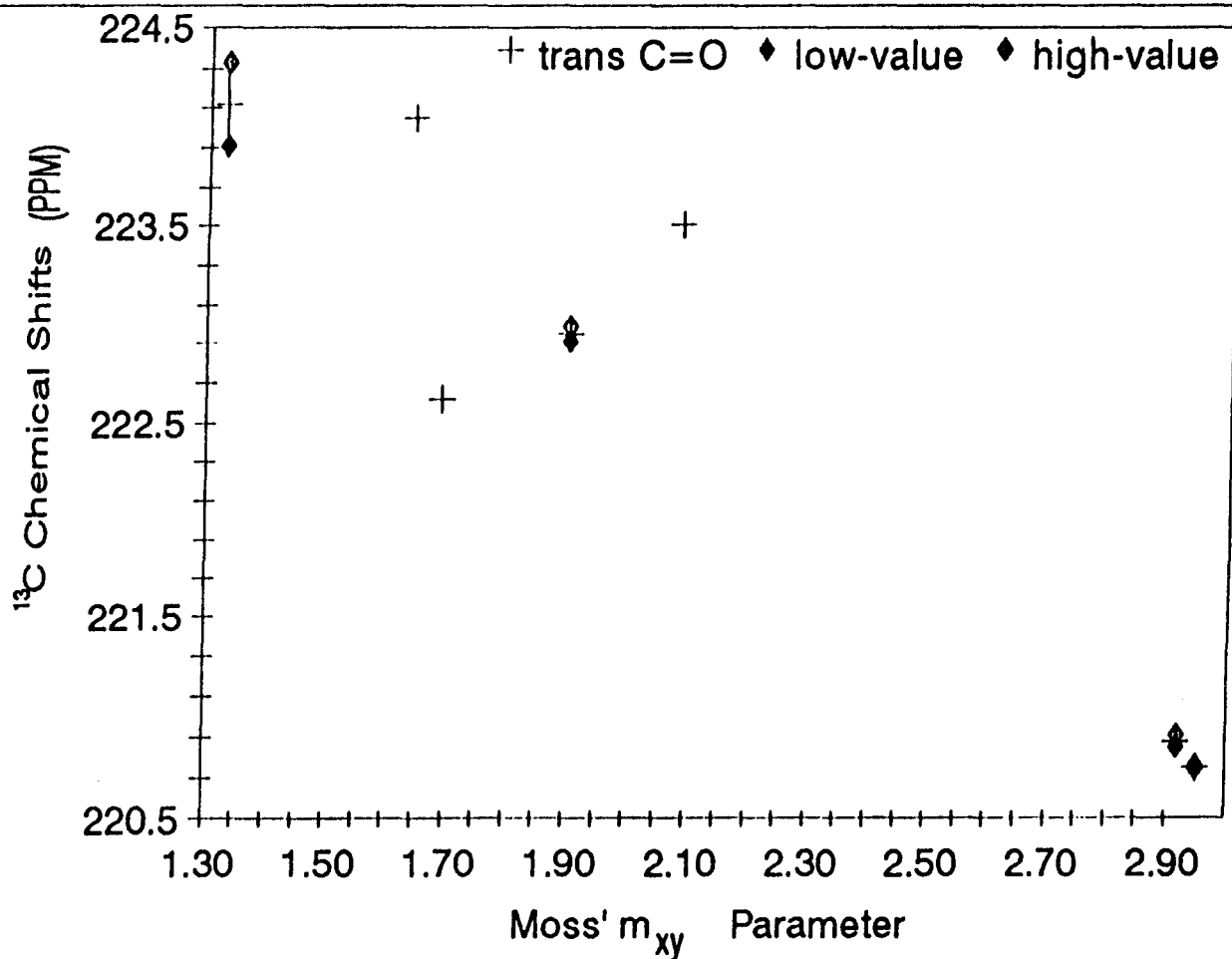
Table IX. ^{13}C NMR DATA FOR THE TRANS CARBONYL CARBON OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.

------ (CO)$_5$CrCRR' -----			----- δ -----	---------- Regression ----------		
R	R'	m_{xy}	trans C=O	linear	quadratic	cubic
PhO	OEt	1.3291	224.19± 0.21	224.22	223.92	224.19
H	NMe$_2$	1.6421	*224.05	223.58	223.60	223.29
Ph	NH$_2$	1.6936	222.62	223.47	223.53	223.24
Me	NMe$_2$	1.9042	222.95± 0.04	223.04	223.22	223.22
H	NEt$_2$	2.0861	223.51	222.67	222.90	223.29
OEt	NMe$_2$	2.9174	220.88± 0.03	220.98	220.90	220.97
OMe	NMe$_2$	2.9507	220.75± 0.01	220.91	220.80	220.67

Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	226.9277	0.853324	0.585267	-2.03968		
Quadratic	223.8633	0.869662	0.616830	0.935404	-0.66888	
Cubic	253.2887	0.905047	0.607928	-45.4973	22.74305	-3.75163

* = Spectra were recorded in C_6D_6.

Figure VI. ^{13}C Chemical Shifts of the Cis C=O vs Moss' m_{xy} Parameter

Table X. ^{13}C NMR DATA FOR THE CIS CARBONYL CARBON OF CHROMIUM CARBENE COMPLEXES VS MOSS' m_{xy} PARAMETER.						
------ (CO)$_5$CrCRR' -----			-----δ-----	----------Regression----------		
R	R'	m_{xy}	cis C=O	linear	quadratic	cubic
PhO	OEt	1.3291	216.06± 0.21	216.98	216.39	216.12
H	NMe$_2$	1.6421	*218.17	216.98	217.02	217.33
Ph	NH$_2$	1.6936	216.55	216.98	217.09	217.39
Me	NMe$_2$	1.9042	217.36± 0	216.98	217.34	217.34
H	NEt$_2$	2.0861	217.09	216.99	217.45	217.04
OEt	NMe$_2$	2.9174	216.83± 0	216.99	216.84	216.76
OMe	NMe$_2$	2.9507	216.84± 0	216.99	216.77	216.90
Regression Output						
	Constant	R Squared	Std Err of Y Est	X Coefficient(s)		
Linear	216.9669	0.000074	0.728783	0.009067		
Quadratic	210.7795	0.292909	0.685184	6.016021	-1.35052	
Cubic	180.0602	0.462467	0.689829	54.49031	-25.7918	3.916583

* = Spectra were recorded in C$_6$D$_6$.

reactivity m_{xy} parameters.

Thus, the ^{17}O NMR data versus Moss' m_{xy} parameter shows cubic correlation. The higher order correlations here are not simple curved lines. We conclude that there is a similar trend between the [17]O chemical shifts and the m_{xy} parameters. However the simple correlation does not have a high correlation coefficient because here the two carbon groups are both conjugated to the same lobe. This usually destroys any additivity for substituent effects. We believe that ^{17}O NMR is a good spectroscopic technique which provides direct information about the relation between physical properties of the chromium carbene complexes and the reactivity of the corresponding free carbene.

CHAPTER IV

CONCLUSION

In conclusion, the ^{17}O NMR chemical shifts of seven chromium carbene complexes have been correlated with Moss' m_{xy} parameters. Measuring the ^{17}O NMR chemical shifts on the carbonyl systems of the unreactive nucleophilic pentacarbonyl chromium carbene complexes provides a direct method to assess the carbene reactivity of the complexes. The poor correlation coefficients are caused by having two groups conjugated to the only one carbene lobe in the chromium complexes. The other carbene lobe is now involved in bring to the chromium. Our ^{17}O NMR chemical shift data confirm the m_{xy} parameters predicted by Moss' equation for these nucleophilic carbenes. This is the first experimental confirmation of these results.

CHAPTER V

EXPERIMENTAL

(1) General Information.

Solvents. THF was predried over CaH_2 and distilled under
argon from sodium benzophenone ketyl before use. Diethyl
ether and hexane were distilled from powdered CaH_2, while
dichloromethane was distilled from anhydrous $MgSO_4$. The
solvents were degassed by rapidly bubbling nitrogen through
them for 10 min.

Reagents. Phenyl lithium, n-butyl lithium, trimethyloxonium
tetrafluoroborate, triethyloxonium tetrafluoroborate, N,N-
dimethylformamide, N,N-dimethylacetamide, N,N-diethyl-
formamide, potassium, graphite, trimethylsilyl chloride,
and dimethylcarbamyl chloride were purchased from the
Aldrich Chemical Company and used as received. Chromium
hexacarbonyl was from Aldrich or Spectrum Chemical Company.

Measurements. Melting points were taken in a capillary tube
on a Mel-Temp apparatus and are uncorrected. ^1H NMR spectra
were recorded on either a Varian EM360A (60 MHz) or a
Varian VXR 300 (300 MHz) spectrometer. ^{13}C (75 MHz) and ^{17}O
(43 MHz) were obtained in a 10 mm broadband probe in $CDCl_3$
or C_6D_6. On the VXR 300 ^1H and ^{13}C chemical shifts were given

in parts per million (ppm) relative to Me$_4$Si, whereas [17]O chemical shifts were given in ppm relative to external and naturally abundant D$_2$[17]O. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica Gel 60, or polyester backed Silica Gel 60 (PF-254 with CaSO$_4$). Developed plates were visualized under UV light. Column chromatographic separations used hexane and ether eluant on Florisil. Mass spectra for **14** and **15** were run on a VG mass spectrometer by direct injection at Northwestern University.

(2) Synthesis by the lithium reagent-generated anion. Preparation of (CO)$_5$Cr=C(OEt)Ph (4). In a 250 mL round bottom flask fitted with a side arm for nitrogen introduction and provided with a stirrer, were placed 100 mL of dry ether and 625 mg (2.84 mmol) of Cr(CO)$_6$. Phenyl lithium in hexane, 1.2 mL (2.8 mmol), was added without allowing the temperature to rise above room temperature. After stirring for 5 min, solvent was removed with a rotary evaporator. Then 10 mL of degassed H$_2$O was added, and a sample of [Et$_3$O]$^+$[BF$_4$]$^-$ in CH$_2$Cl$_2$ was added via syringe until the solution became acidic to pH paper. The solution was extracted with three 30 mL portions of degassed hexane. The combined extracts were dried over anhydrous Na$_2$SO$_4$ (1.5 g). Column chromatography (10 g Florisil, hexane eluant)

afforded an orange-red fraction which deposited 179 mg (20 %) of **4** as a bright orange-red crystallizing oil upon removal of solvent on a rotary evaporator. IR(hexane) 2050, 1982, 1940 (C=O) cm^{-1}; (Lit[34] 2050, 1982, 1960, 1940 (C=O) cm^{-1}). ^{1}H NMR (CDCl$_3$) 7.50-7.38 (5H m, ArH], 4.92 (2H q, CH$_2$O), 1.65 (3H t, CH$_3$). ^{13}C (CDCl$_3$) 215.8 (CO, cis), 223.7 (CO, trans), (C:, not observed), (Ar): 153.7, 129.8, 128.1, 122.5; ^{17}O NMR spectra were obtained from the combined products of three different syntheses. ^{17}O NMR (CDCl$_3$) 373.9 (4CO, cis), 397.5 (CO, trans).

Preparation of (CO)$_5$Cr=C(NH$_2$)Ph (5). A sample of 359 mg (1.10 mmol) of pentacarbonylphenylethoxycarbenechromium complex **(4)** was dissolved in 200 mL of dry ether. Excess dry ammonia, which was generated by dropping aqueous NH$_4$Cl solution onto solid NaOH, was passed through a glass frit into the ether solution of **4**. When the red ether solution had turned to yellow, the solvent was removed by vaccum pump. Column chromatography (10 g Florisil, hexane eluant) afforded a yellow fraction which deposited 216 mg (66.0%) of yellow crystals upon removal of solvent by a vacuum pump. Chromatography on a 1 cm by 10 cm Florisil column, with hexane eluant provided a pure sample of yellow crystals of **5**. mp 78.5-79.5°C; (lit[35] mp 79°C). IR(neat) 2059, 1980, 1930 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.42-7.35 (3H m, ArH), 7.18-7.15 (2H m, ArH), 8.85 (1H s, NH), 8.29 (1H s,

NH); ^{13}C NMR (CDCl$_3$) 216.6 (CO, cis), 222.6 (CO, trans), 290.6 (C:), (Ar): 152.5, 129.3, 128.5, 121.8; ^{17}O NMR (CDCl$_3$) 370.2 (4CO, cis), 385.0 (CO, trans).

(b) Synthesis by C_8K-generated $Cr(CO)_5^{2-}$.

Preparation of Potassium Intercalated Graphite (C_8K) (6).
In a 100 mL three-neck airless flask, provided with a stirrer and heated by a sand bath, was placed 2.30 g (195 mmol) of graphite. When the stirred graphite had heated to 150-160°C for 15 min, 0.74 g (19 mmol) of potassium was added under argon without allowing the temperature to drop below 160°C. When the potassium was gone and a bronze color had appeared, the potassium intercalated graphite had formed.[36] If stirring was inadequate, the bronze color was weak and the flask could be carefully shaken by hand with leather gloves-CAUTION.

Preparation of C_8K-generated $Cr(CO)_5^{2-}$ (7). Continuing with the above complex, the flask was cooled with dry ice in acetone. Then THF, 15 mL, was added and 1.8 g (8.2 mmol) of $Cr(CO)_6$ was added under a positive pressure of argon (balloon). The reaction mixture was stirred for 30 min at -78°C and placed in an ice bath at 0°C until the solution turned to a thick slurry of silvery green solid in a yellow-green solution[23] which indicated the presence of $Cr(CO)_5^{2-}$.

Preparation of (CO)₅Cr=C(H)NMe₂ (9). A 8.18 mmol sample of
C_8K-generated $K_2Cr(CO)_5$ contained in a flask was cooled by
dry ice in acetone and 0.60 mL (7.7 mmol) of N,N-
dimethylformamide **(8)** (R=H, R'=Me) was added via syringe.
After the stirred mixture had cooled at -78°C for 30 min
and then warmed to 0°C for 1 h, a 2.9 mL sample of TMSCl
(trimethylchlorosilane) was added via syringe. This
solution was stirred for 0.5 h and warmed to 25°C. Then 22
g of neutral Al_2O_3 was added to absorb the product. The
solvent was stripped on a rotary evaporator employing water
aspiration. The Al_2O_3 was placed at the top of a column. The
column was eluted with hexane to give 0.87 g (43%) of pale
yellow crystals of **9**. mp 66-68°C; (Lit[37] mp 64-66°C)
IR(hexane) 2059, 1930 (C=O), 1545 (C-N) cm⁻¹ in good
agreement with the literature. ¹H NMR (C_6D_6) 9.89 (1H s H),
2.59 (3H s N-CH₃), 1.81 (3H s, N-CH₃); ¹³C NMR (C_6D_6) 263.0
[=CH-N], 218.2 (CO, cis), 224.0 (CO, trans), 53.7, 45.5 (N-
CH₃); ¹⁷O NMR (CDCl₃) 368.0 (4CO, cis), 378.2 (CO, trans).

Preparation of (CO)₅Cr=C(H)NEt₂ (10). A flask, which
contained 6.98 mmol of $K_2Cr(CO)_5$, was cooled in dry ice-
acetone and 0.78 mL (7.7 mmol) of N,N-diethylformamide **(8)** .
(R=H, R'=Et) was added via syringe. After the stirred
mixture had cooled at -78°C for 30 min and warmed to 0°C for
1 h, 3.5 mL of TMSCl was added via syringe. This solution
was stirred for 0.5 h and warmed to 25°C. Then neutral Al_2O_3

was added to absorb the product. The alumina was placed at the top of a chromatography column and eluted with hexane. The solvent was stripped on a vacuum pump to give 0.96 g (50%) of pale yellow crystals of **10**. IR(CDCl$_3$) 2059, 1975, 1900-1940. (C=O), 1520 (C-N) cm^{-1}; ^{1}H (CDCl$_3$) 3.94 (2H q, NCH$_2$), 3.51 (2H q, NCH$_2$), 1.33 (3H t, CH$_3$), 1.20 (3H t, CH$_3$), 10.8 (1H s, H); ^{13}C (CDCl$_3$) 217.1 (CO, cis), 223.5 (CO, trans), 259.3 (C:), 57.6, 52.0 (N-CH$_2$), 15.0, 14.2 (CH$_3$); ^{17}O (CDCl$_3$) 369.0 (4CO, cis), 379.0 (CO, trans).

Preparation of (CO)$_5$Cr=C(Me)NMe$_2$ (11). A flask, which contained 10.6 mmol of K$_2$Cr(CO)$_5$, was cooled by dry ice and 0.95 mL (10.2 mmol) of N,N-dimethylacetamide **(8)** (R=R'=Me) in 5 mL of THF was added via syringe. After the stirred mixture had cooled at -78°C for 30 min and then warmed to 0°C for 1 hr, 3.8 mL of TMSCl was added via syringe. This solution was stirred for 1/2 hr. and warmed to 25°C. Then 25 g of neutral Al$_2$O$_3$ was added to absorb the product. The alumina was placed at the top of a chromatography column and eluted with hexane. The solvent was stripped on a vacuum pump to give 1.44 g (52%) of pale green crystals of **11**. mp 54-55°C; IR(neat) 2030, 1975, 1930. (C=O) cm^{-1}; (Lit[38] IR(net) 2055, 1967, 1933, 1930). ^{1}H NMR 3.29 (3H s, NCH$_3$), 3.86 (3H s, NCH$_3$), 2.68 (3H s, CH$_3$); ^{13}C NMR (CDCl$_3$) 217.4 (CO,cis), 223.0 (CO, trans), 272.8 (C:), 53.2, 42.5 (NCH$_3$), 40.4 (CH$_3$); ^{17}O NMR (CDCl$_3$) 369.1 (4CO, cis), 375.2

(CO, trans), (C_6D_6) 369.6 (4CO, cis), 377.0 (CO, trans).

Preparation of $(CO)_5Cr=C(OMe)NMe_2$ (14). In a 100 mL three-neck airless flask, provided with a stirrer and heated by a sand bath, was placed 2.50 g. of graphite. When the stirred graphite had heated to 150-160°C under vacuum for 25 min, Potassium, 1.01 g (25.3 mmol), was added under an argon balloon without allowing the temperature to drop below 160°C. When the bronze color had formed and the potassium was gone, the flask was cooled by dry ice. THF, 25 mL, was added and 1.57g (7.14 mmol) of $Cr(CO)_6$ was added under a positive flow of argon. The reaction mixture was stirred 30 min at -78°C and placed in an ice bath at 0°C until the solution turned to a thick slurry of silvery green solid in a yellow-green solution. The flask was cooled by dry ice-acetone again and 0.78 mL (8.47 mmol) of dimethylcarbamyl chloride **(8)** (R=Cl; R'=Me) in 5 mL of THF was added via syringe. The mixture was warmed to 4°C for 5 min then cooled by the dry ice. The above mixture was stirred for 10 min, then $[Me_3O]^+[BF_4]^-$, 0.95 g, was added all at once to this solution. The mixture was stirred for 1 h and then was put in the refrigerator at 4°C over night. The reaction mixture was warmed to 25°C. After 15 min, solvent was stripped *in vacuo*, then 15 g of Florisil was added to absorb the product. The combined mixtures eluted with hexane from a 10 g Florisil column. The eluate was

concentrated under vacuum to give a 1.16 g of pale yellow-green crystals which contained $Cr(CO)_6$. Further purification by column chromatography gave 26 mg (1.3%) of the pure compound **14** as a pale yellow-green liquid. IR(neat) 2020, 1960, 1930. (C=O) cm^{-1}; ^1H NMR 3.57 (3H s, NCH_3), 3.04 (3H s, NCH_3), 4.23 (3H s, OCH_3); ^{13}C NMR ($CDCl_3$) 216.8 (CO, cis), 220.8 (CO, trans), 243.8 (C:), 61.5 (OCH_3): 54.7, 38.6 (NCH_3); ^{17}O NMR ($CDCl_3$) 372.3 (4CO, cis), 368.4 (CO, trans), (C_6D_6) 373.2 (4CO, cis), 370.5 (CO, trans); MS m/z (% of base)[39] 279 (14.9, M^+), 251 (15.1, -CO), 223 (16.1, -CO), 195 (9,-CO), 167 (15.8, -CO), 139 (100,-CO), 124 (34, $-CH_3$), 109 (7.4, $-CH_3$), 94 (26,$-CH_3$), 80 (12.1,-N), 52 (25.9,-CO). Mass Calcd. for $C_9H_9NO_6Cr$: 278.9835. Found: 278.9821.

Preparation of $(CO)_5Cr=C(OEt)NMe_2$ (15). A sample of $K_2Cr(CO)_5$ (9.05mmol) was prepared similarly. The flask was cooled with dry ice-acetone and 0.90 mL (9.77 mmol) of dimethylcarbamyl chloride **(8)** (R=Cl; R'=Me) in 5 mL of THF was added via syringe. The mixture was warmed to 4°C for 5 min then cooled by the dry ice. The mixture was stirred for 10 min, then 11 mL of $[Et_3O]^+[BF_4]^-$ in CH_2Cl_2 was added into the mixture. After stirring for 1 h, solvent was stripped *in vacuo*. Florisil, 15 g, was added to absorb the product. The combined mixtures eluted with hexane from a 10 g Florisil column. The eluate was evaporated under vacuum to

give pale yellow-green crystals, 1.18g (44% crude). The product was loaded into a 1 cm by 20 cm Florisil column. The pure fractions of **15** were dried under vacuum pump (0.38g, 14.3%). mp 44-45°C; IR(neat) 2040, 1963, 1930. (C=O) cm^{-1}; ^{1}H NMR 2.87 (3H s, NCH$_3$), 2.10 (3H s, NCH$_3$), 4.34 (2H q, OCH$_2$), 0.91 (3H t, OCH$_3$); ^{13}C NMR (CDCl$_3$) 216.8 (CO, cis), 220.9 (CO, trans), 242.1 (C:), 70.4 (OCH$_2$), 45.4, 38.7 (NCH$_3$), 15.7 (CH$_3$); ^{17}O NMR (CDCl$_3$) 371.8 (4CO, cis), 367.3 (CO, trans), (C$_6$D$_6$) 372.5 (4CO, cis), 369.7 (CO, trans); MS m/z (% of base)[36] 293 (7.4, M$^+$), 265 (11.7, -CO), 237 (12.6, -CO), 209 (5.4, -CO), 181 (21, -CO), 153 (100, -CO), 124 (40.7, -CH$_2$CH$_3$), 109 (5.3, -CH$_3$), 94 (17.6, -CH$_3$), 80 (7.6, -N), 52 (21.2, -CO). Mass Calcd. for C$_{10}$H$_{11}$NO$_6$Cr: 292.9991.[40]

APPENDIX

44

1a. $(CO)_5CrC(Ph)(OEt)$ in $CDCl_3 - ^{17}O$ at $20\pm1°C$.
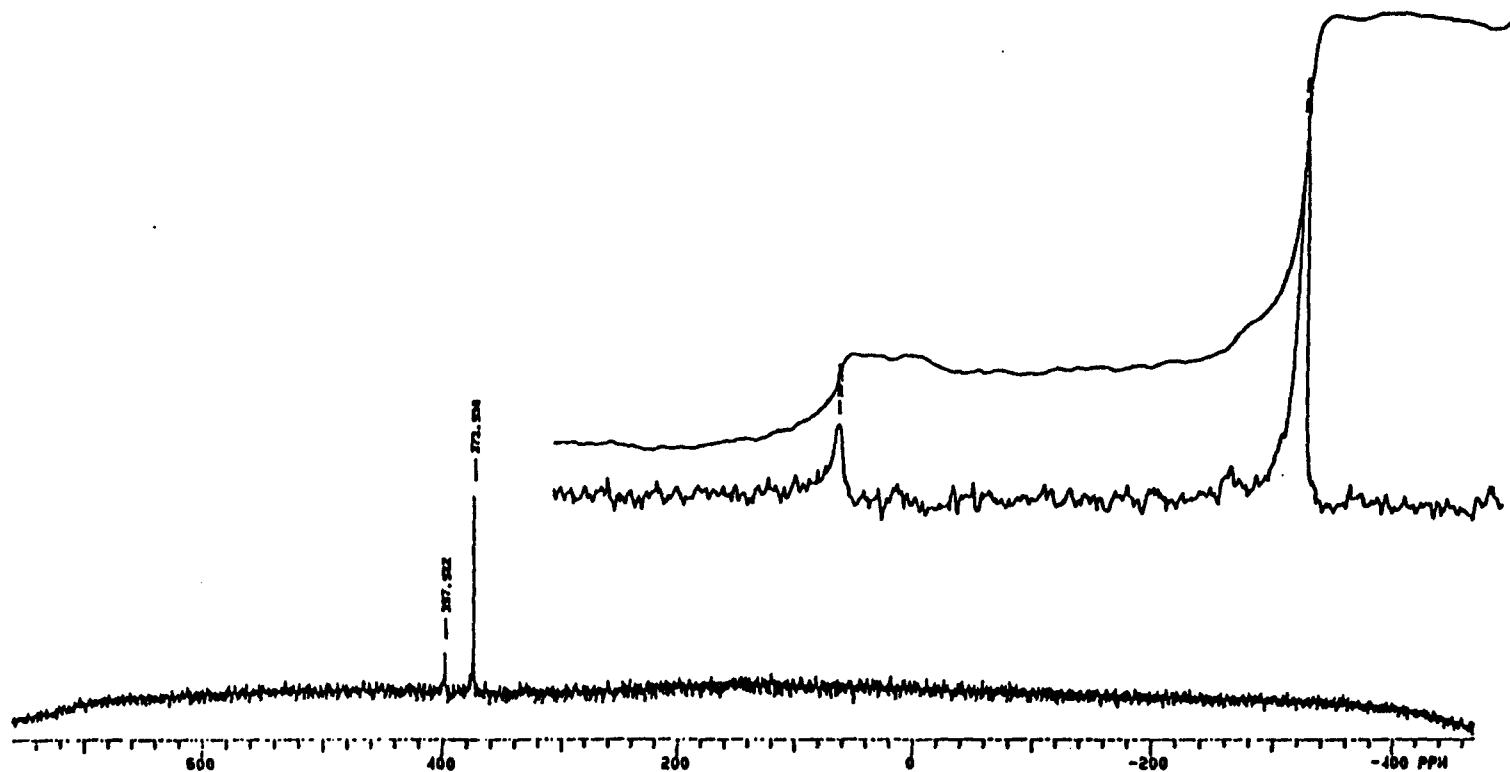
2a. (CO)$_5$CrC(NMe$_2$)(OEt) in CDCl$_3$ - ^{17}O at 20±1°C.
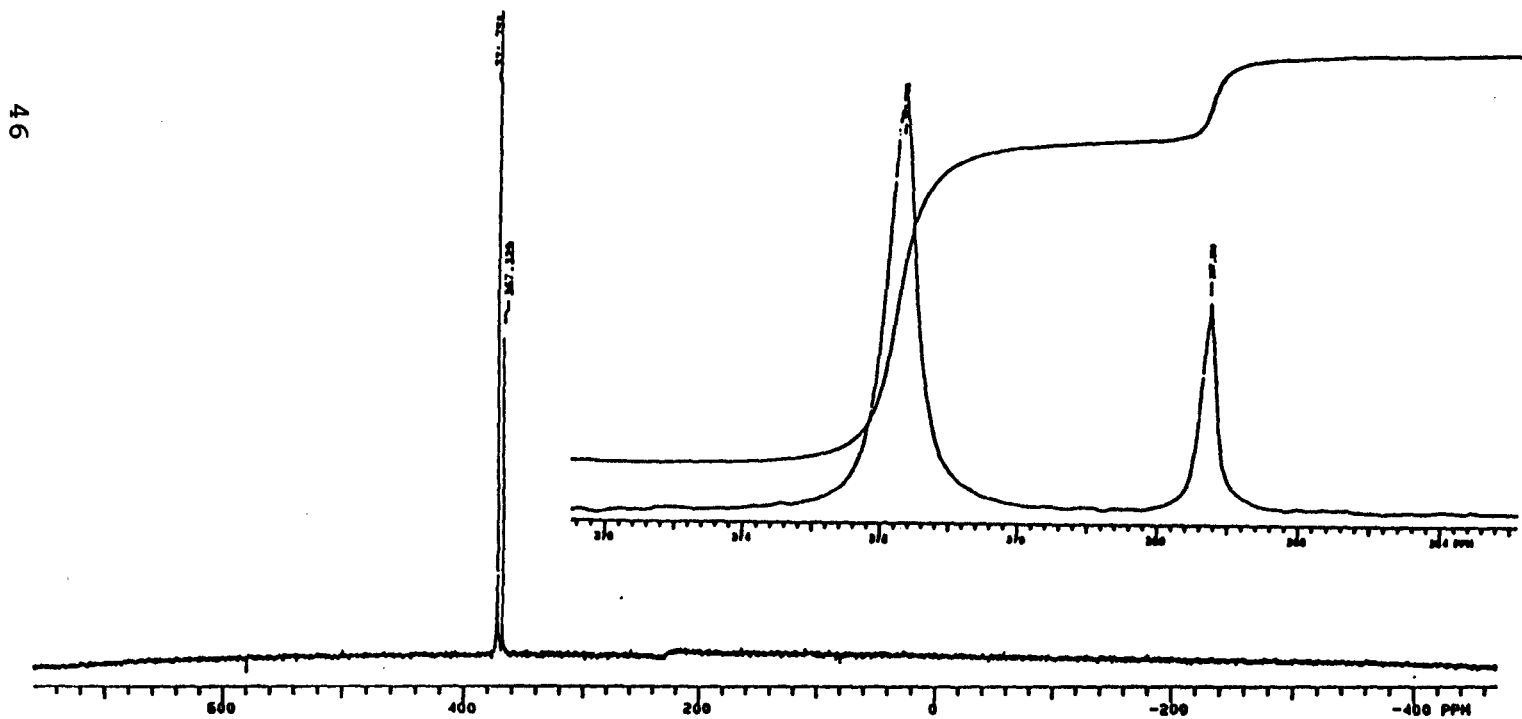
2a'. $(CO)_5CrC(NMe_2)(OEt)$ in C_6D_6 - ^{17}O at $20\pm1°C$.
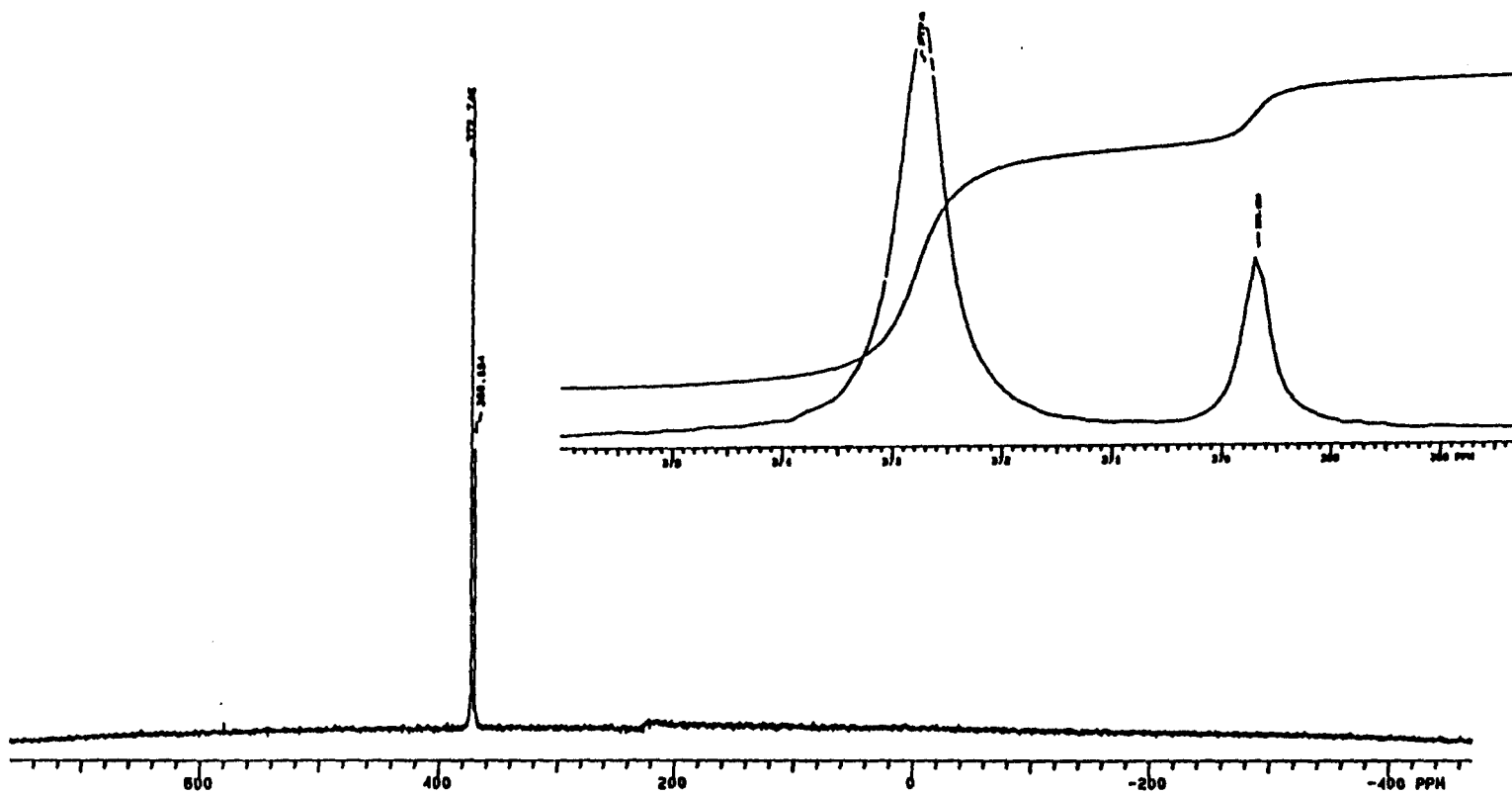
3a. $(CO)_5CrC(NMe_2)(OMe)$ in $CDCl_3$ - ^{17}O at $20\pm1°C$.
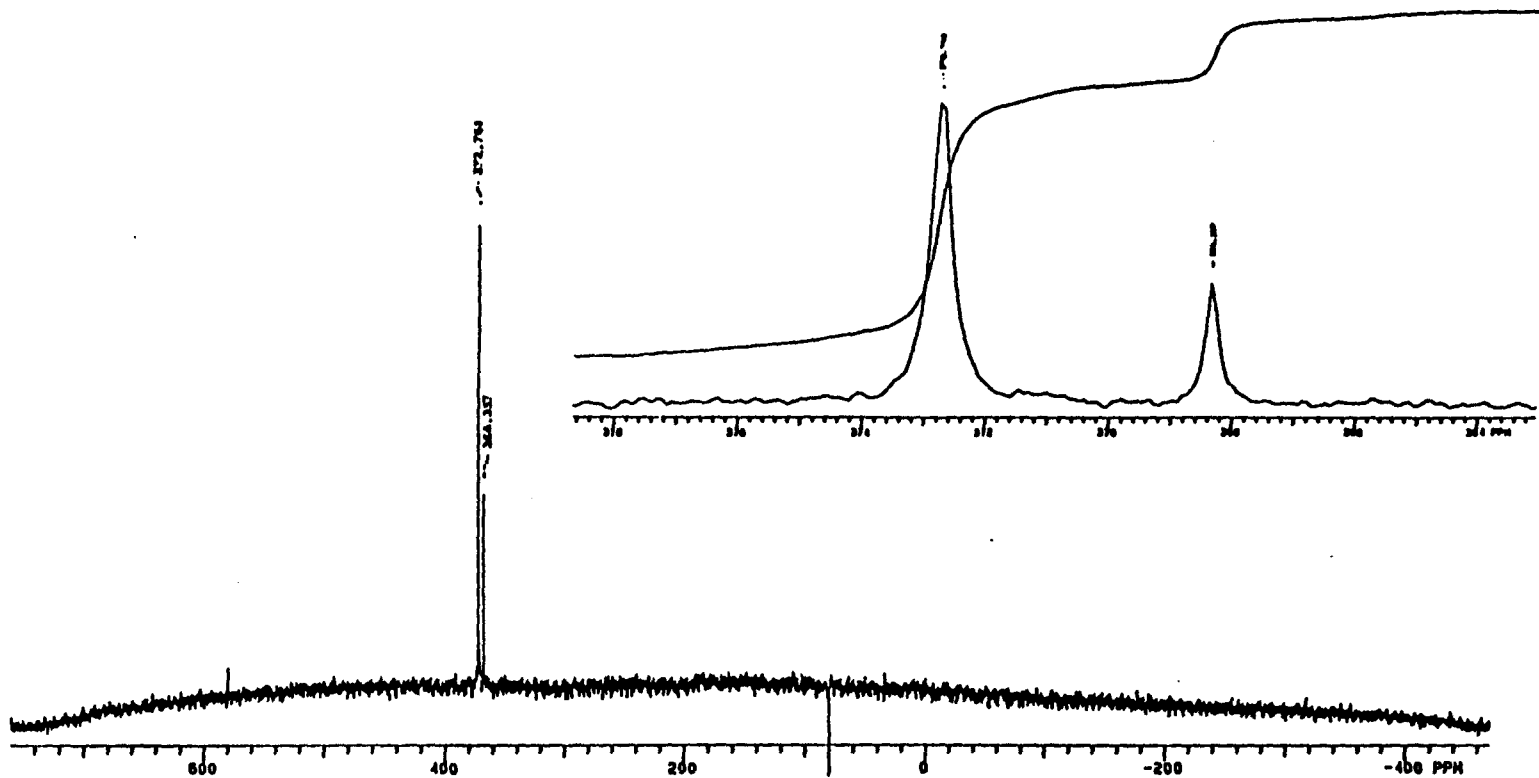
3a'. (CO)$_5$CrC(NMe$_2$)(OMe) in C$_6$D$_6$ - ^{17}O at 20±1°C.
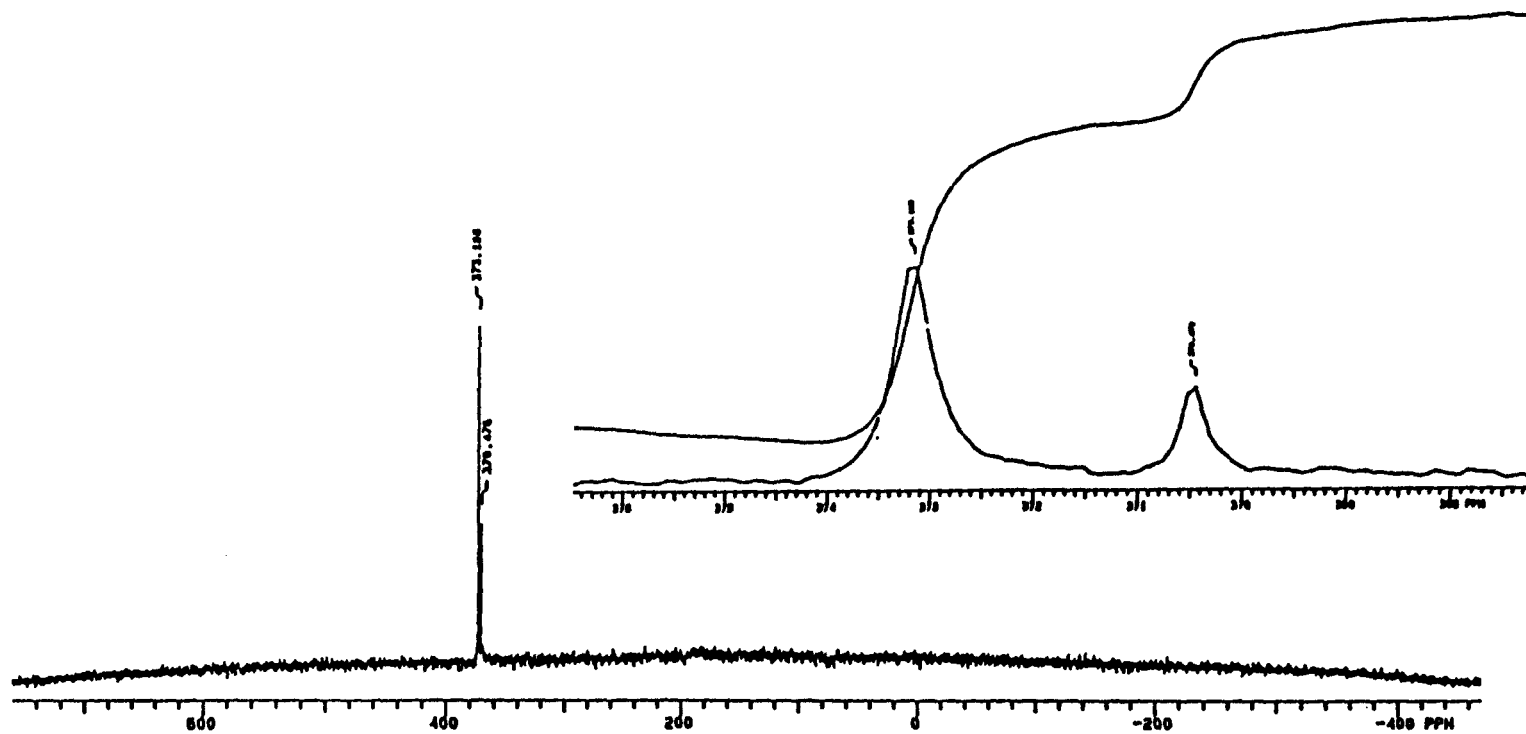
4a. $(CO)_5CrC(NEt_2)(H)$ in $CDCl_3$ - ^{17}O at $20\pm1°C$.
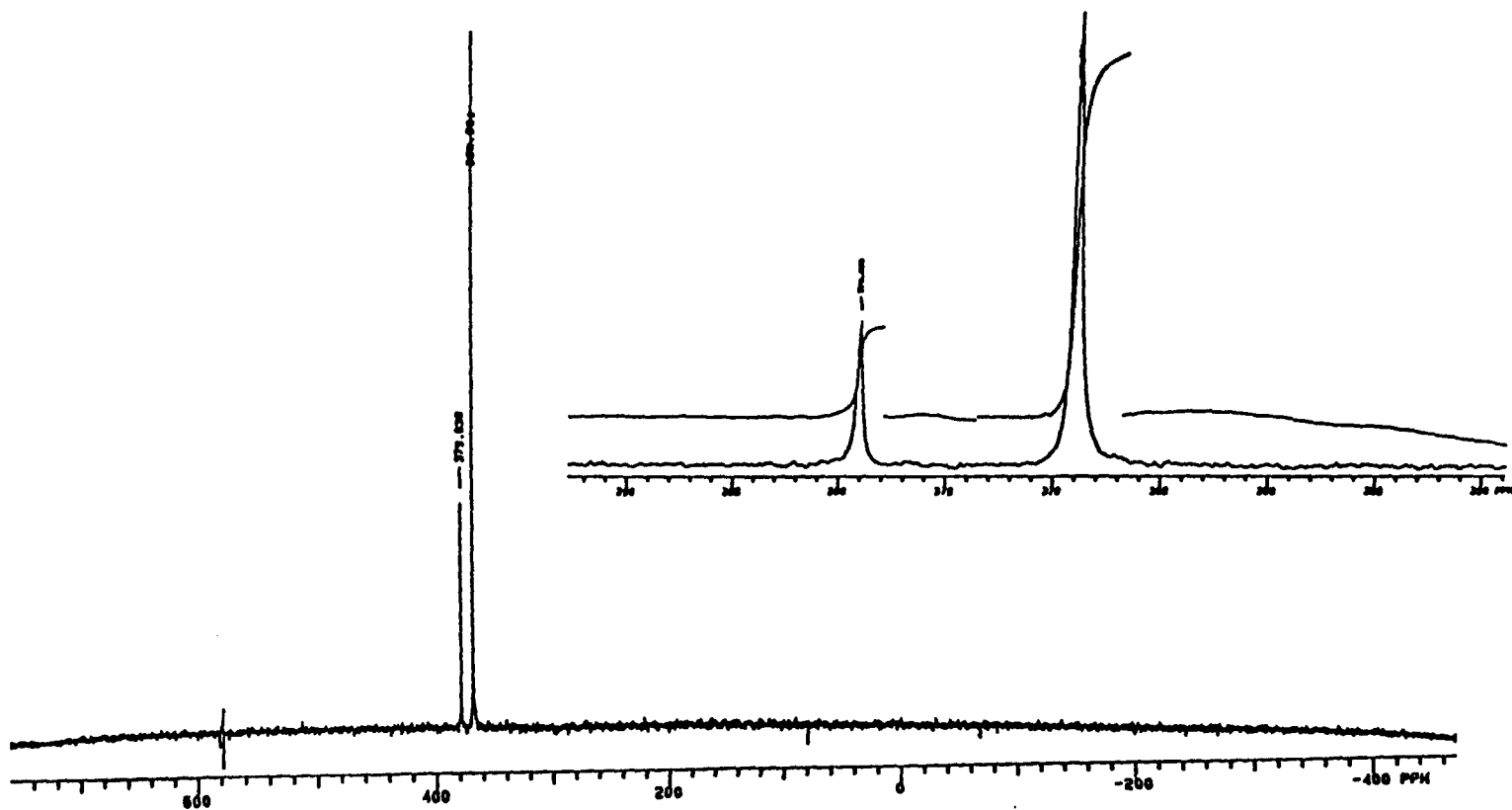
5a. (CO)$_5$CrC(NMe$_2$)(H) in CDCl$_3$ - ^{17}O at 20±1°C.
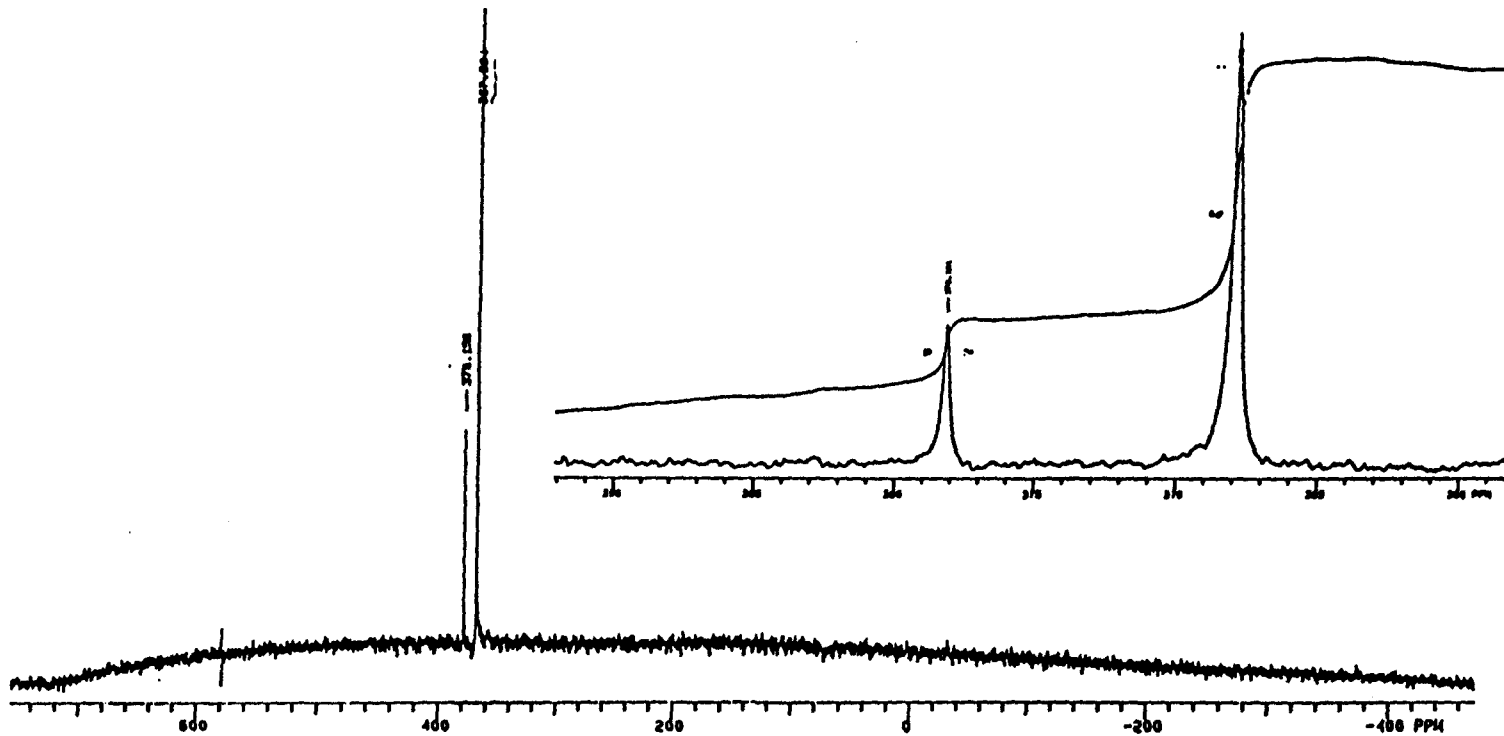
6a. (CO)$_5$CrC(NMe$_2$)(Me) in CDCl$_3$ - ^{17}O at 20±1°C.
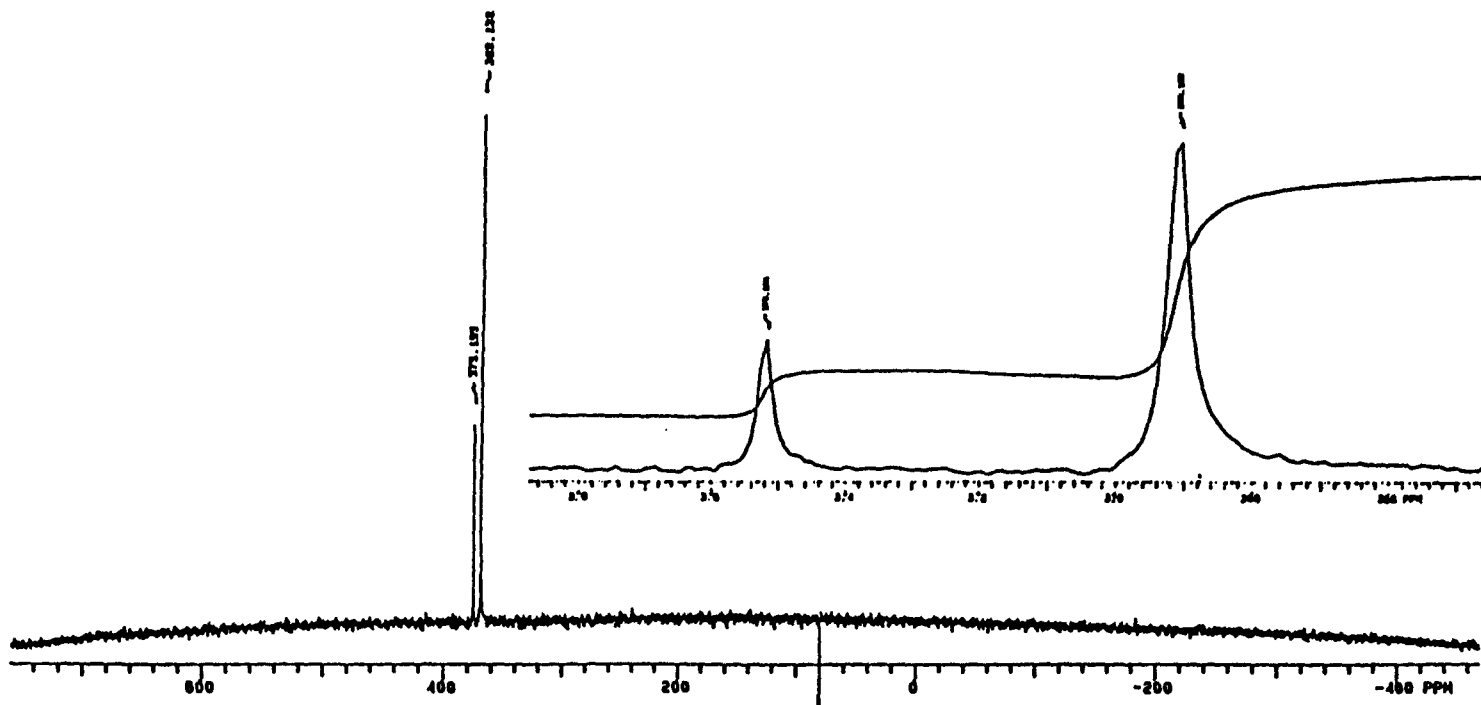
6a'. $(CO)_5CrC(NMe_2)(Me)$ in $C_6D_6 - {}^{17}O$ at $20\pm1°C$.
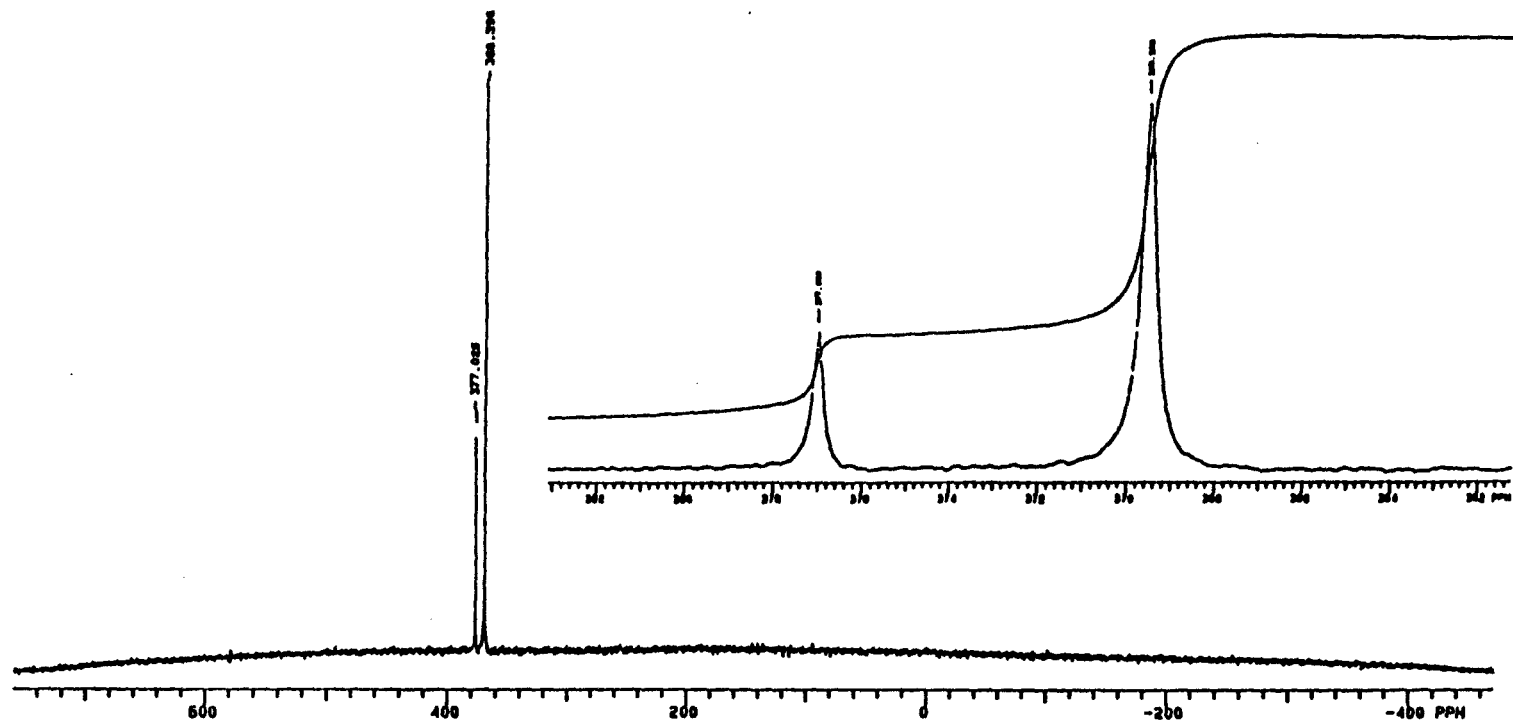
7a. $(CO)_5CrC(NH_2)(Ph)$ in $CDCl_3$ - ^{17}O at $20\pm1°C$.
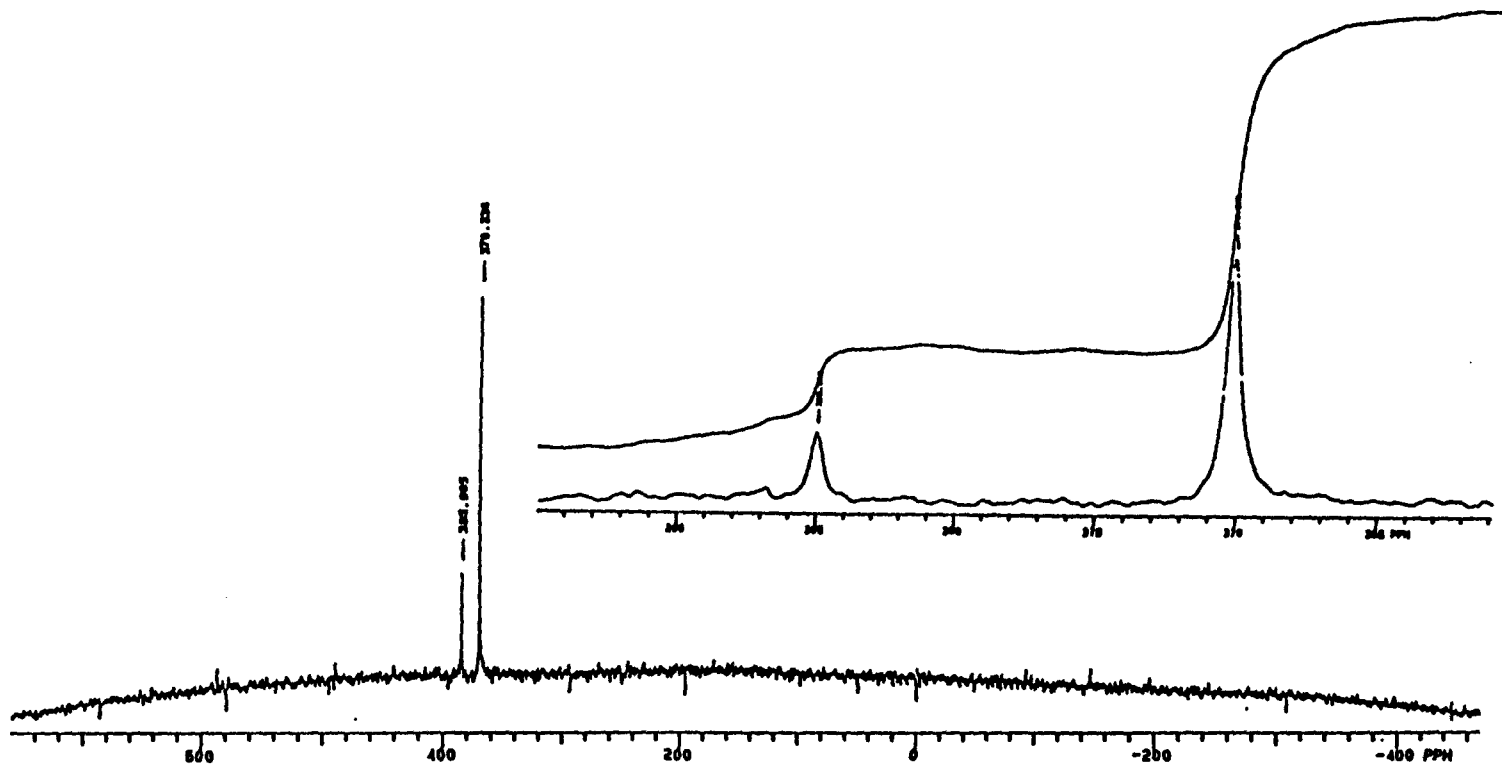
1b. $(CO)_5CrC(Ph)(OEt)$ in $CDCl_3$ - ^{13}C at $20\pm1°C$.
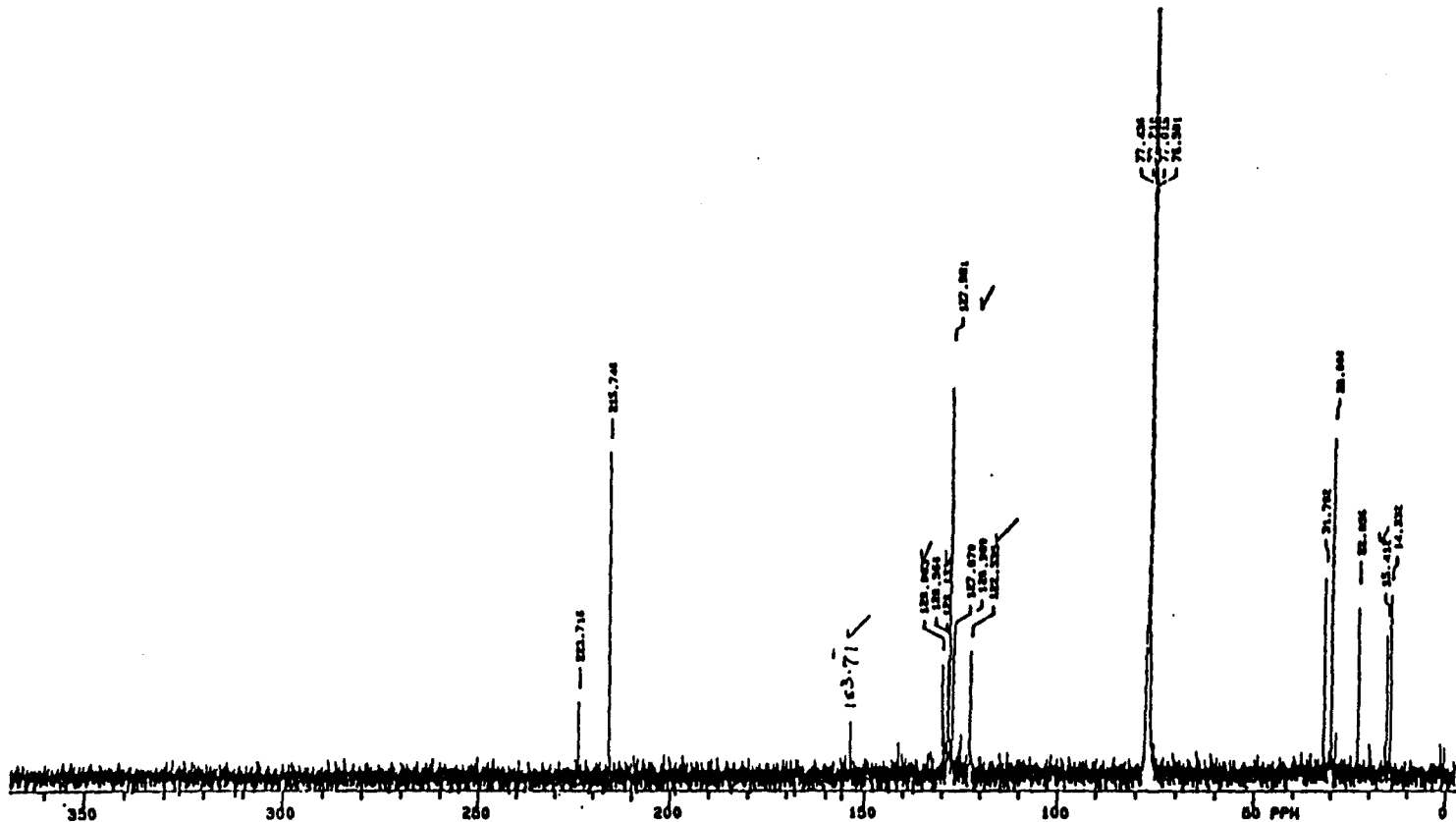
2b. $(CO)_5CrC(NMe_2)(OEt)$ in $CDCl_3$ - ^{13}C at $20\pm1^\circ C$.
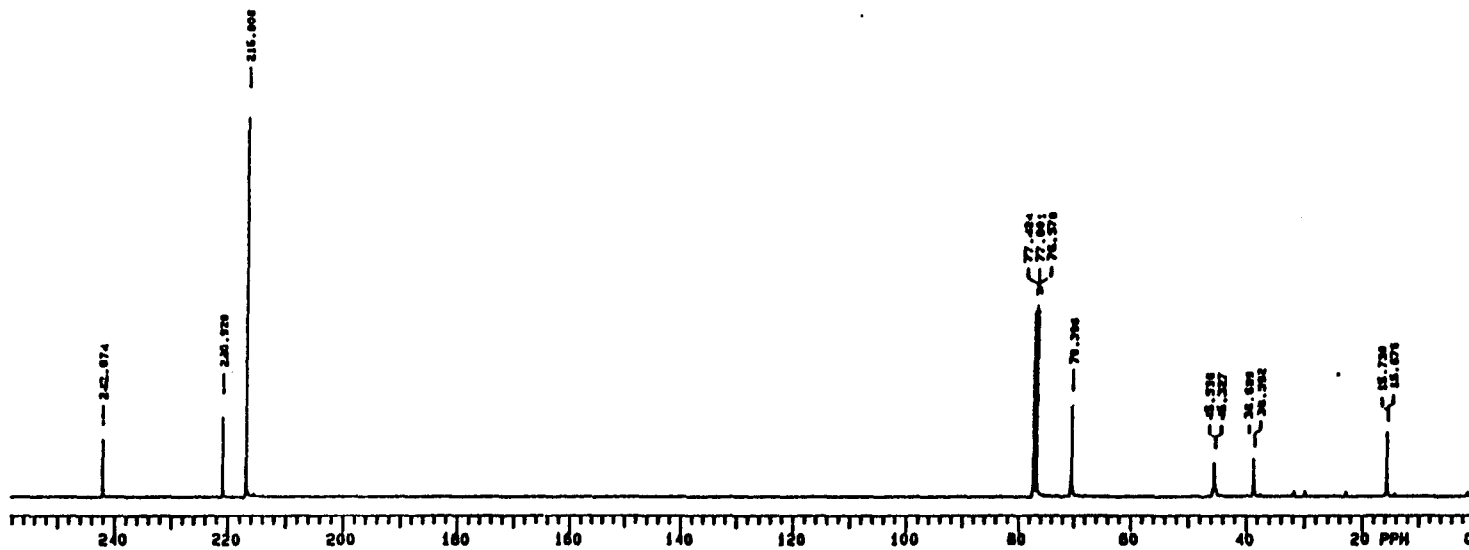
3b. $(CO)_5CrC(NMe_2)(OMe)$ in $CDCl_3$ - ^{13}C at $20\pm1°C$.
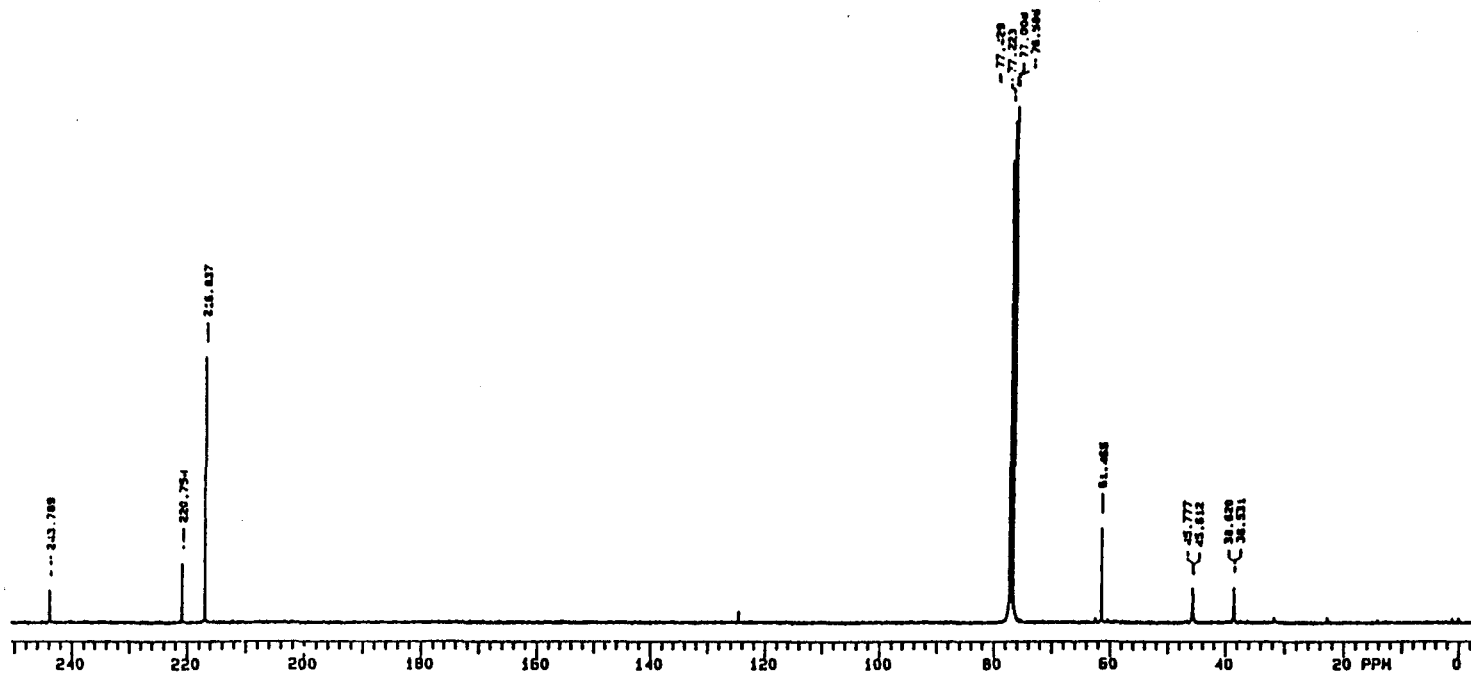
4b. (CO)$_5$CrC(NEt$_2$)(H) in CDCl$_3$ - ^{13}C at 20±1°C.
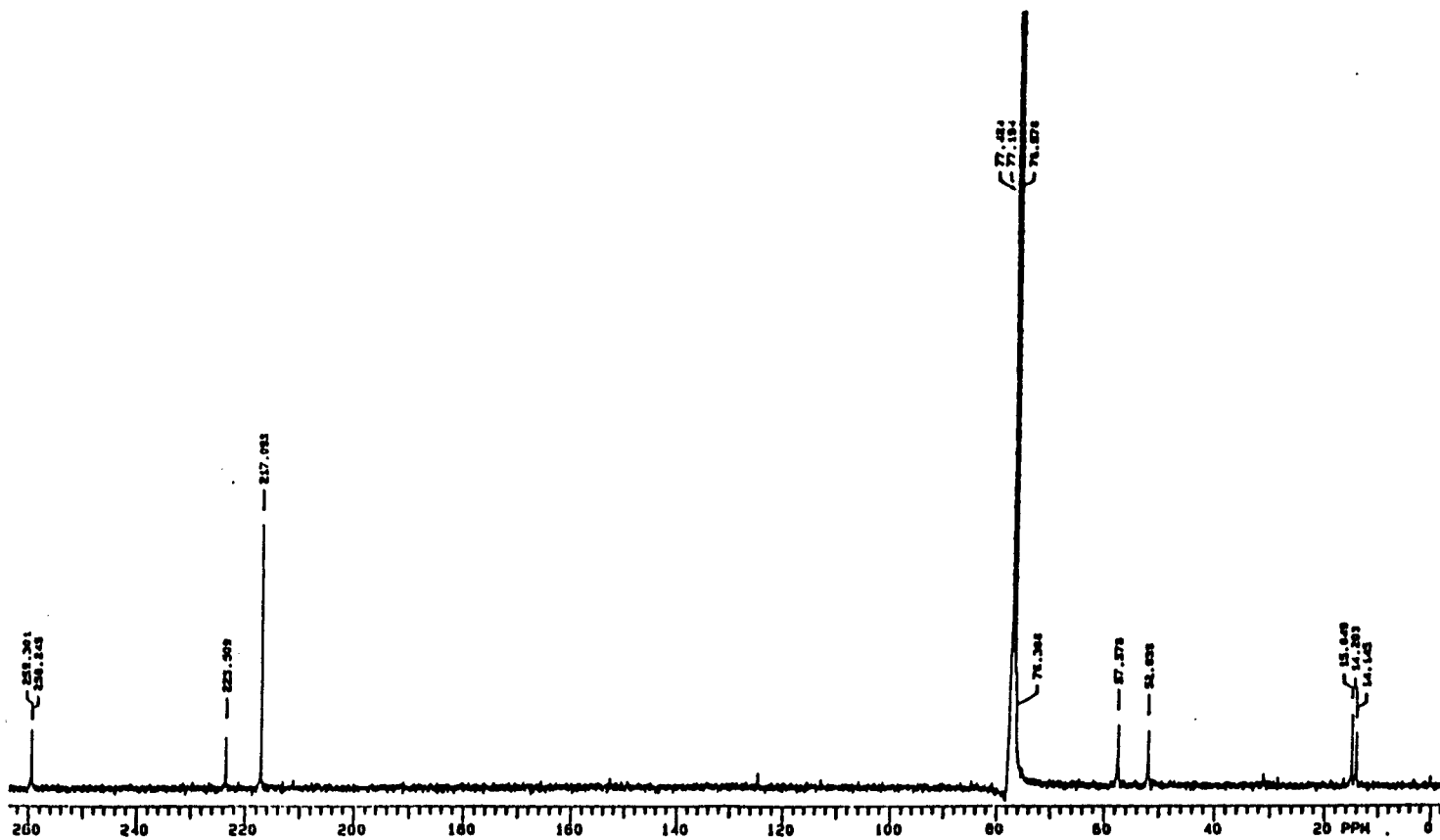
5b. $(CO)_5CrC(NMe_2)(H)$ in C_6D_6 - ^{13}C at $20\pm1°C$.
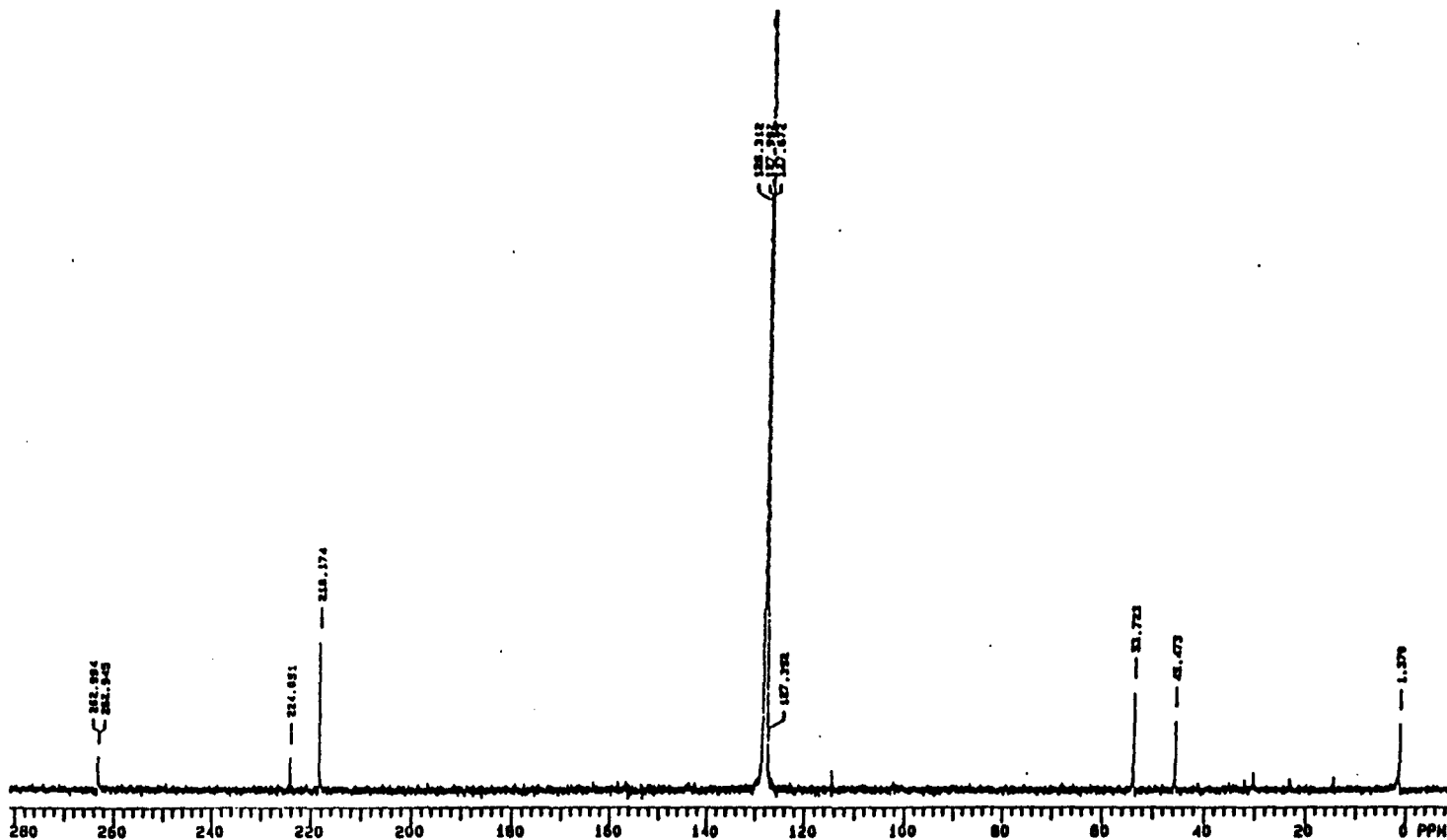
6b. $(CO)_5CrC(NMe_2)(Me)$ in $CDCl_3$ - ^{13}C at $20\pm1^{\circ}C$.

09
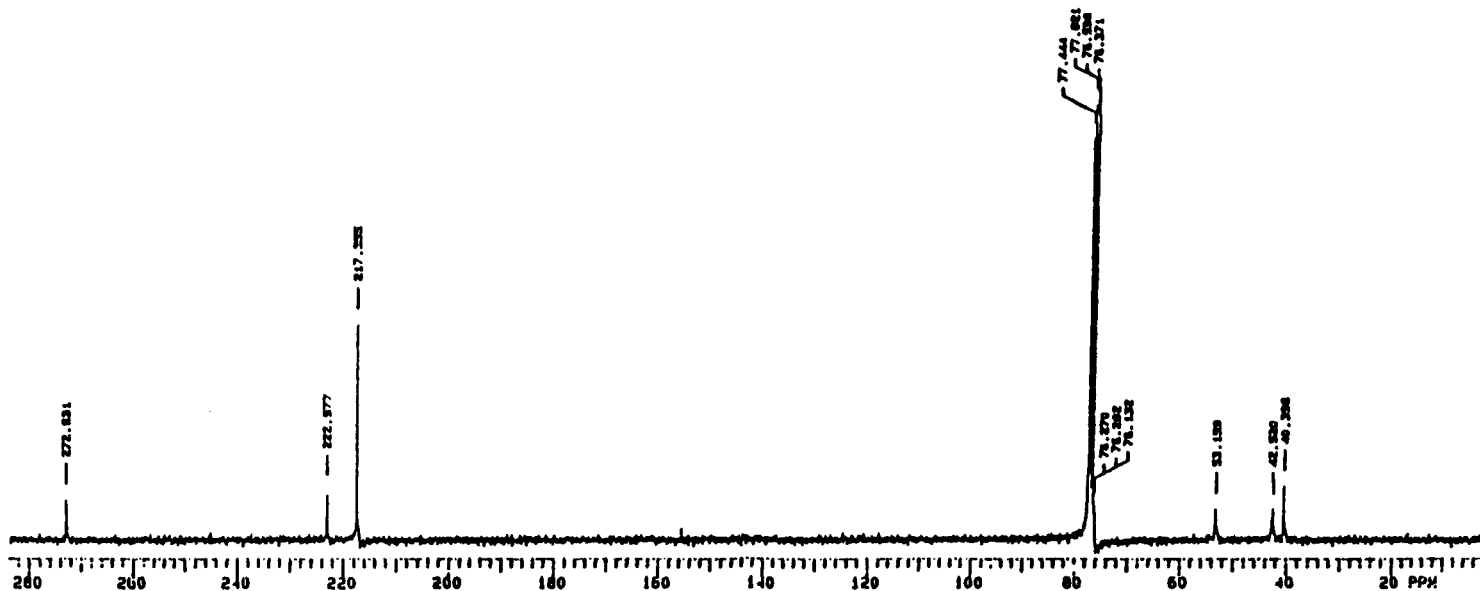
7b. (CO)$_5$CrC(NH$_2$)(Ph) in CDCl$_3$ - ^{13}C at 20±1°C.
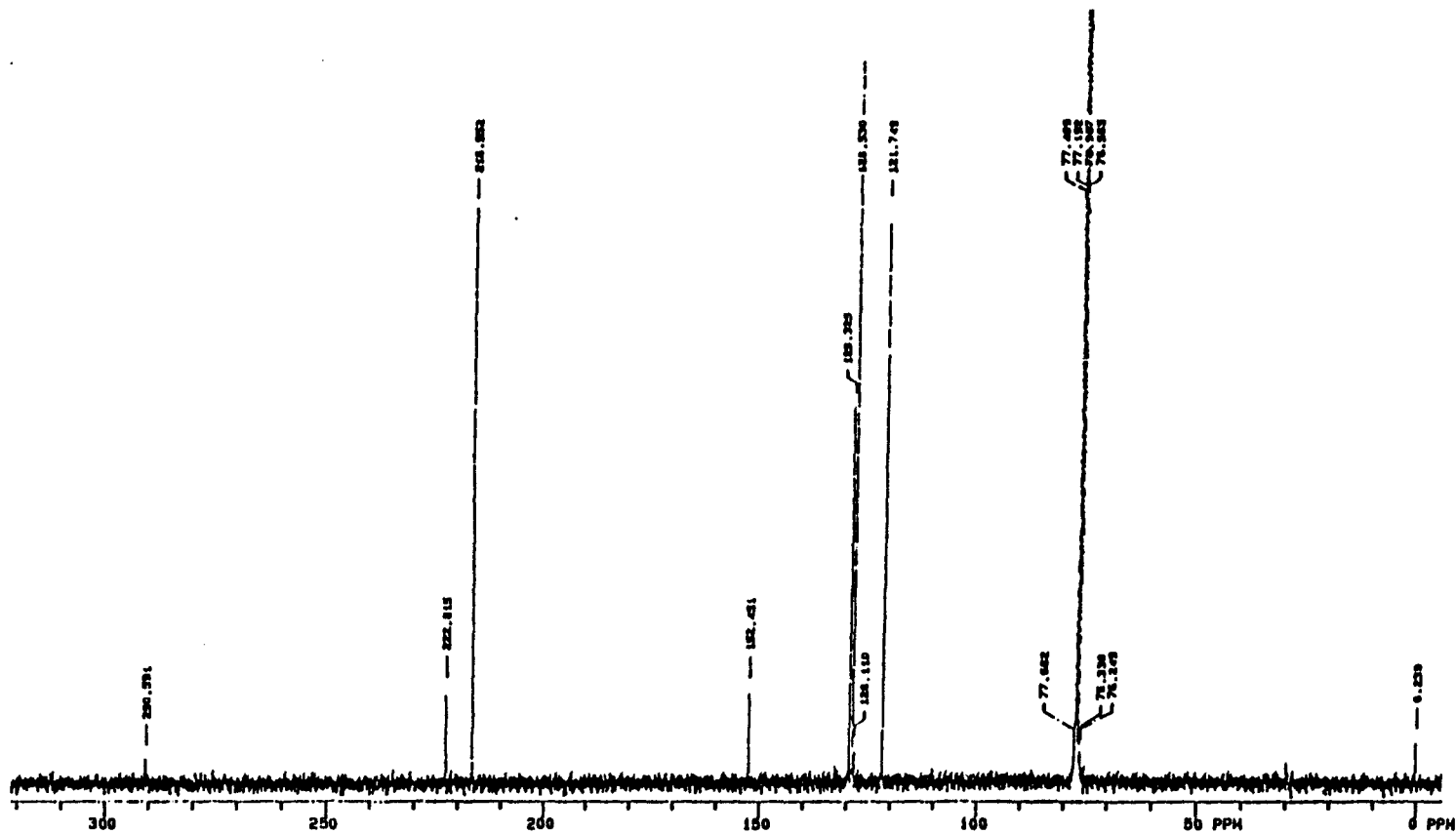
1c. $(CO)_5CrC(Ph)(OEt)$ in $CDCl_3$ - ^1H at $20\pm1°C$.
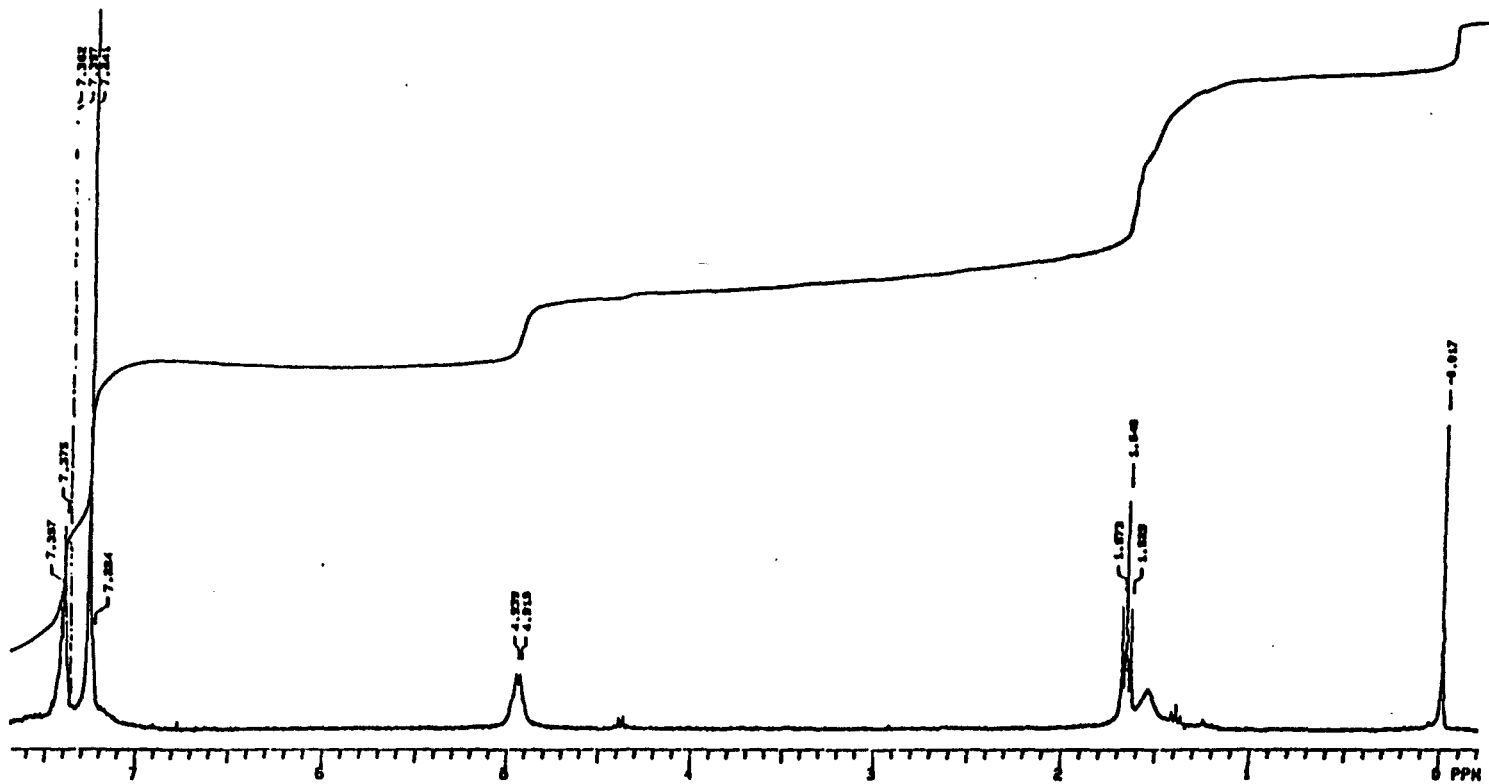
2c. $(CO)_5CrC(NMe_2)(OEt)$ in $CDCl_3$ - ^1H at $20\pm1°C$.
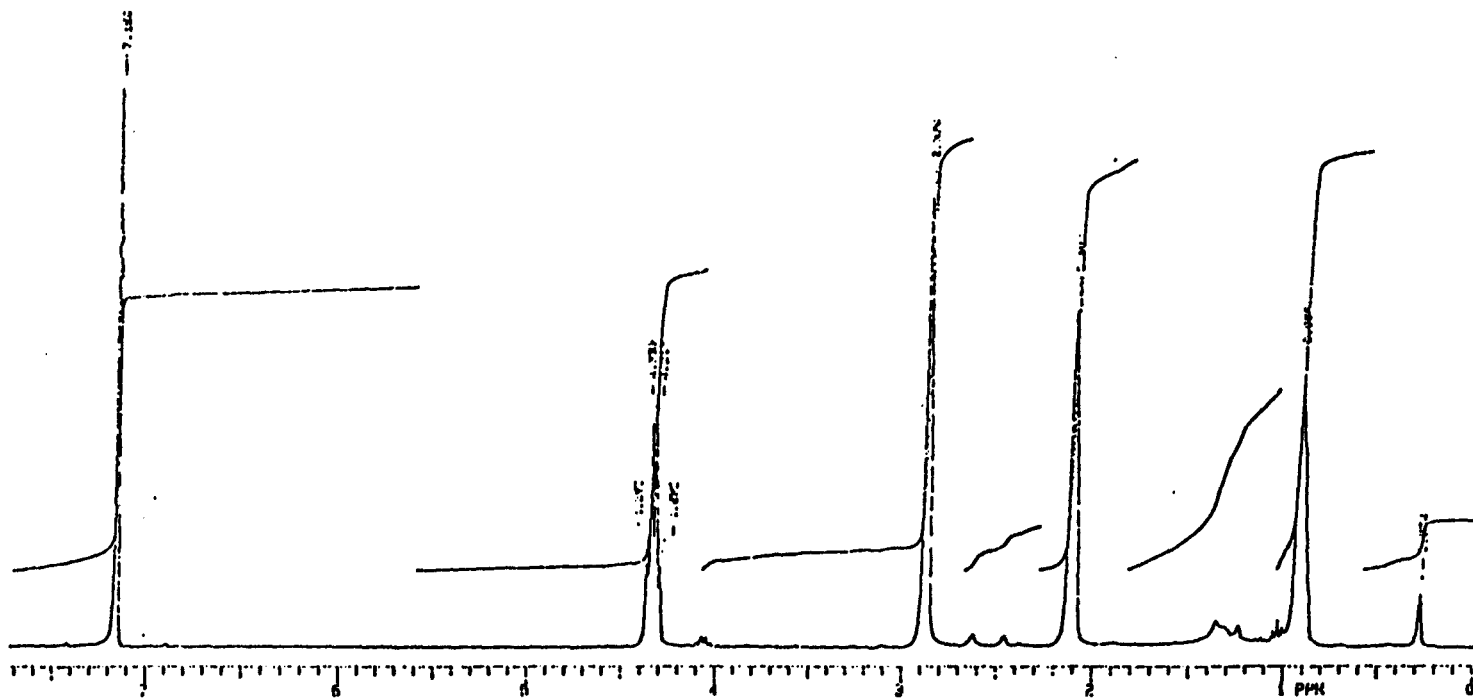
3c. $(CO)_5CrC(NMe_2)(OMe)$ in $CDCl_3$ - ^1H at 20±1°C.
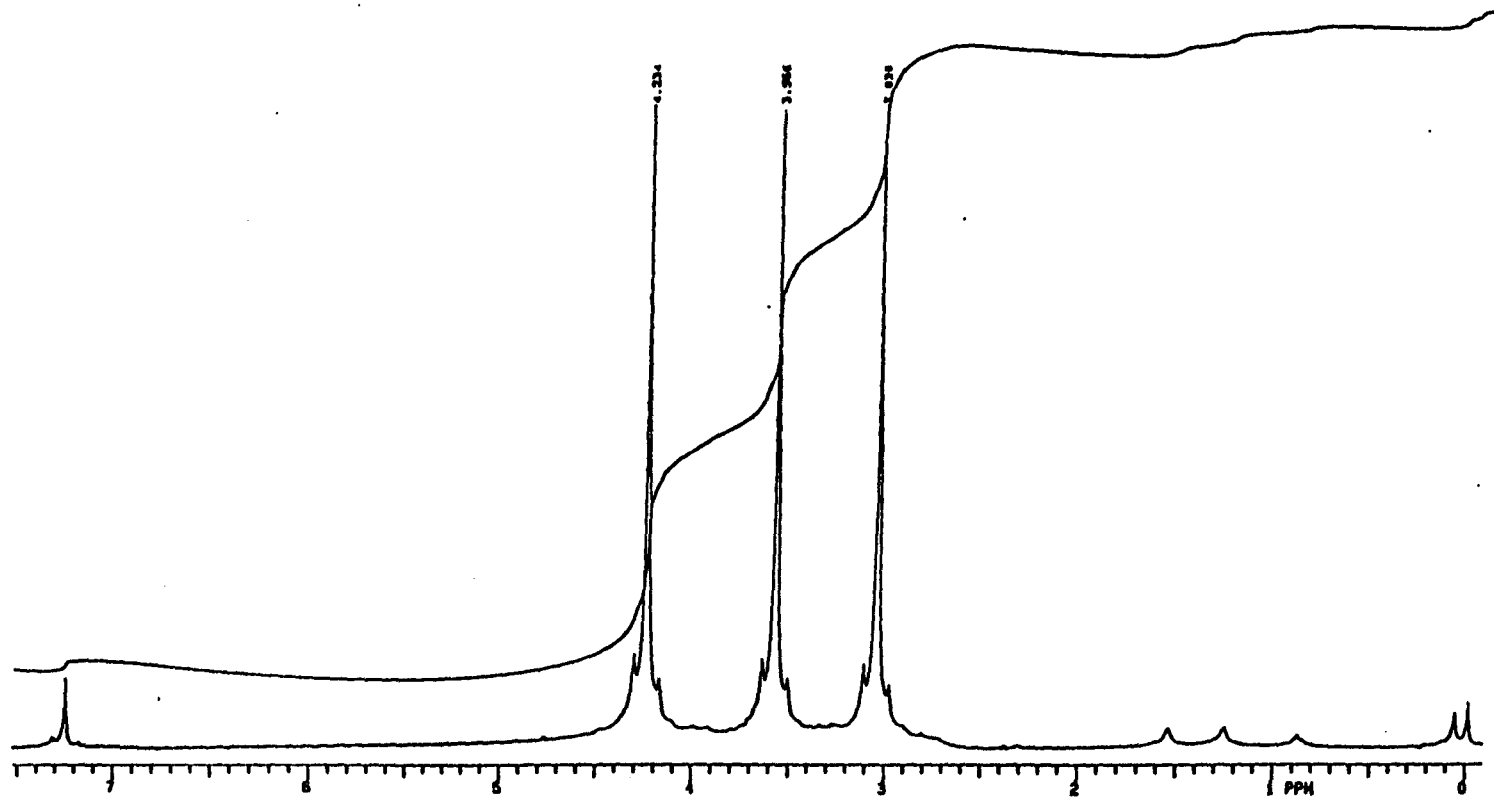
4c. $(CO)_5CrC(NEt_2)(H)$ in $CDCl_3$ - ^1H at 20±1°C.
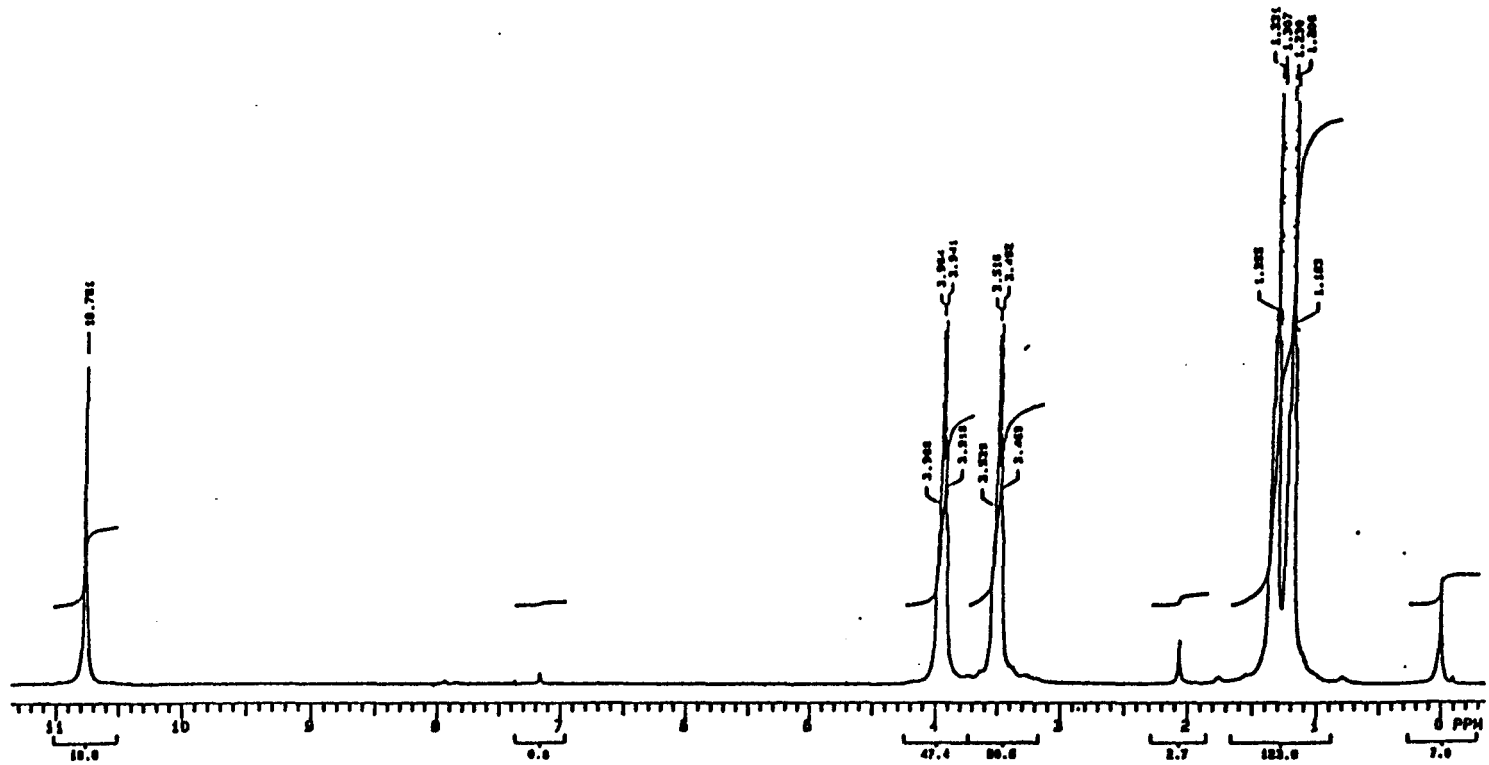
5c. $(CO)_5CrC(NMe_2)(H)$ in C_6D_6 - ^1H at 20±1°C.

99
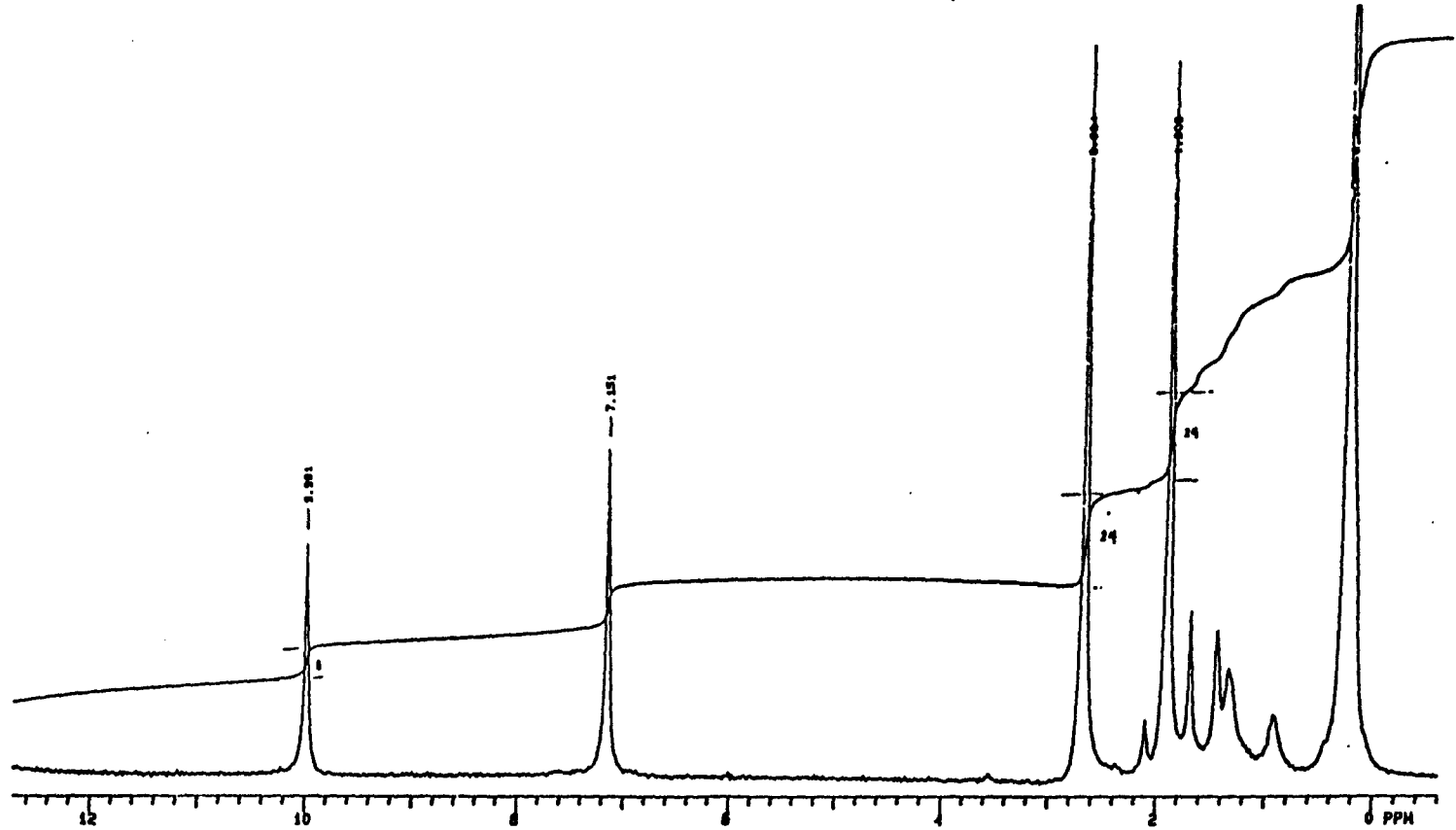
6c. (CO)$_5$CrC(NMe$_2$)(Me) in CDCl$_3$ - ^{1}H at 20±1°C.
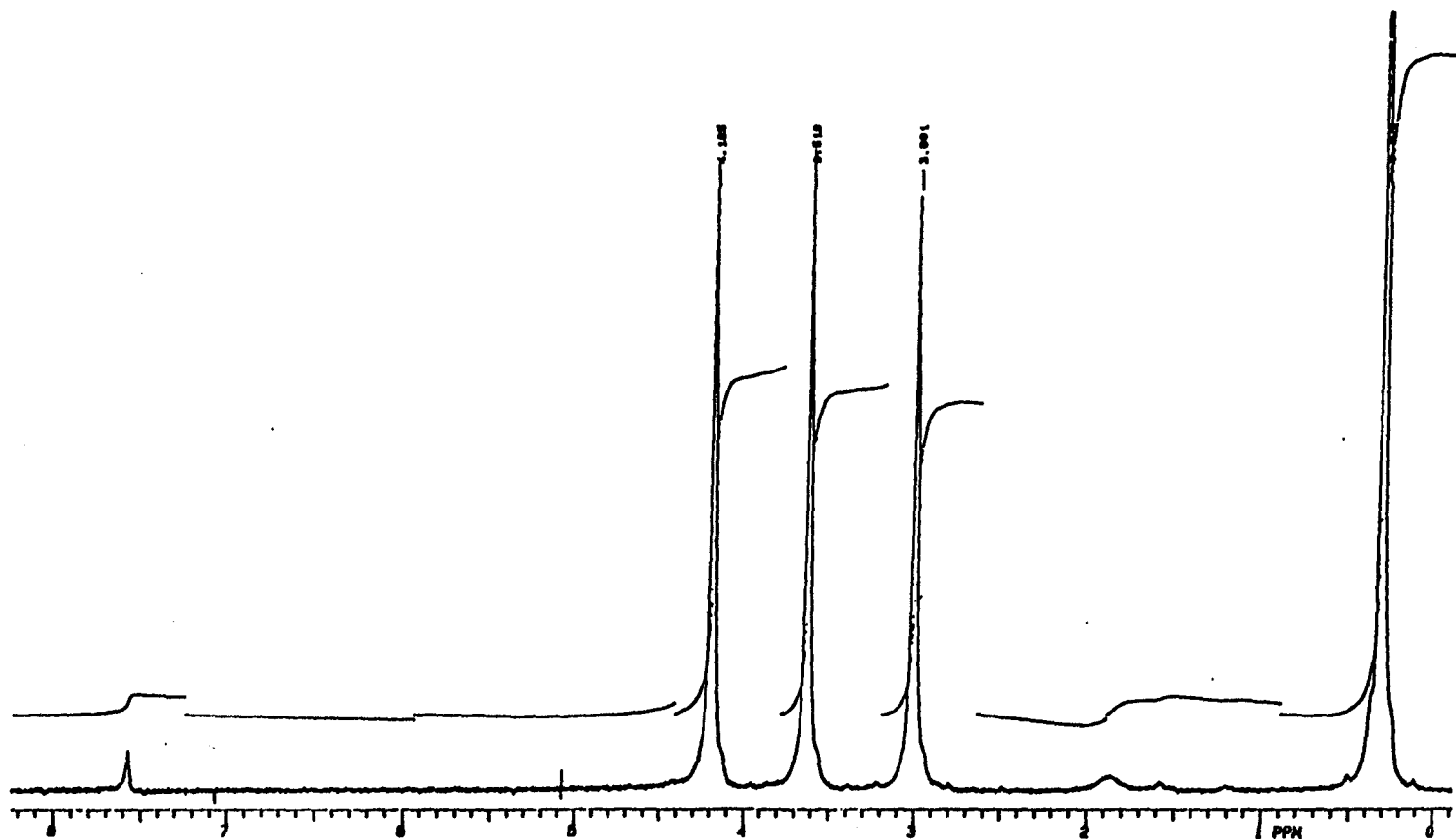
7c. $(CO)_5CrC(NH_2)(Ph)$ in $CDCl_3$ - ^1H at $20\pm1°C$.
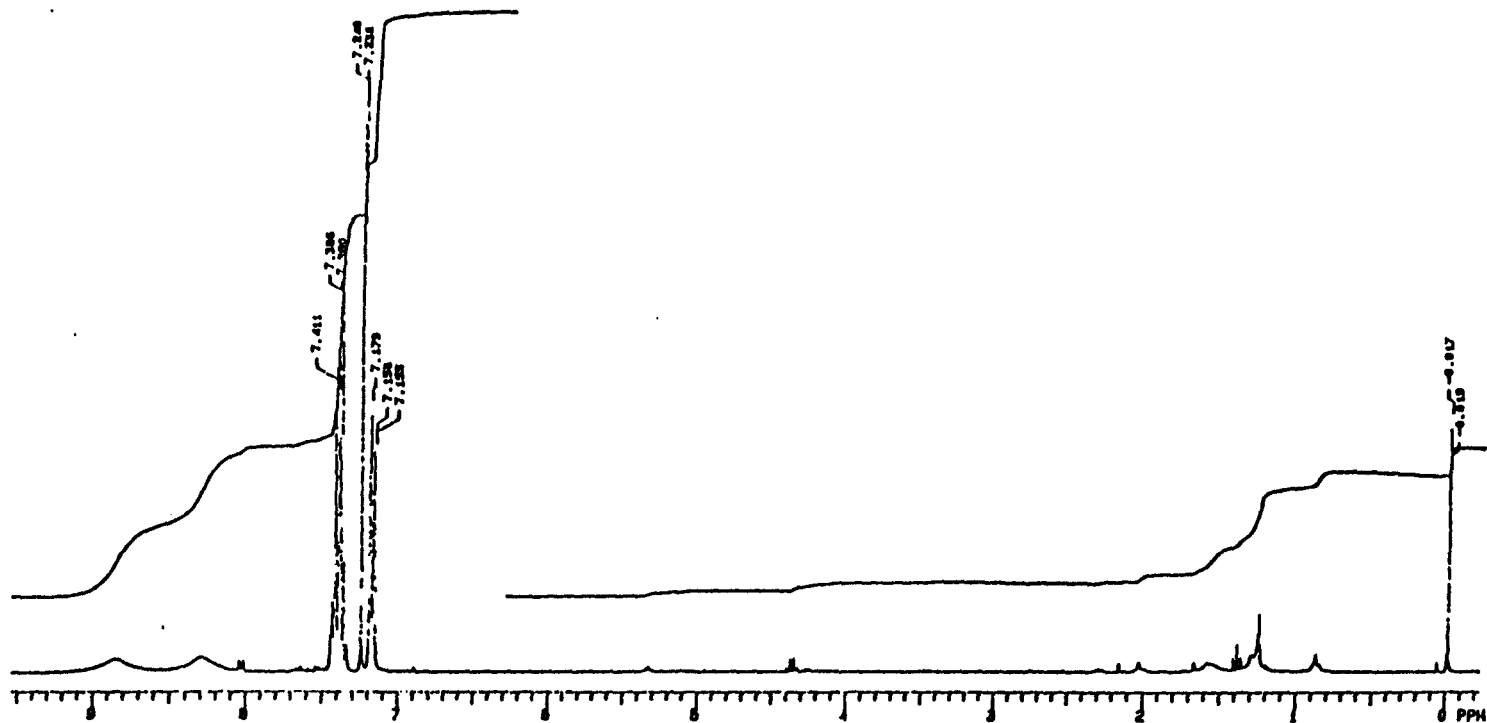
LE08#6   x1   Bgd=1   15-JUL-92 15:20+0:00:22   70-250SE   EI+
BpM=0   I=2.9v   Hm=0   TIC=99340000   Acnt:LOYOLA   Sys:LREI
C9H9NO6Cr   PT= 0°   Cal:LEM
                                                                              #6   1.0
                                                                              18706000
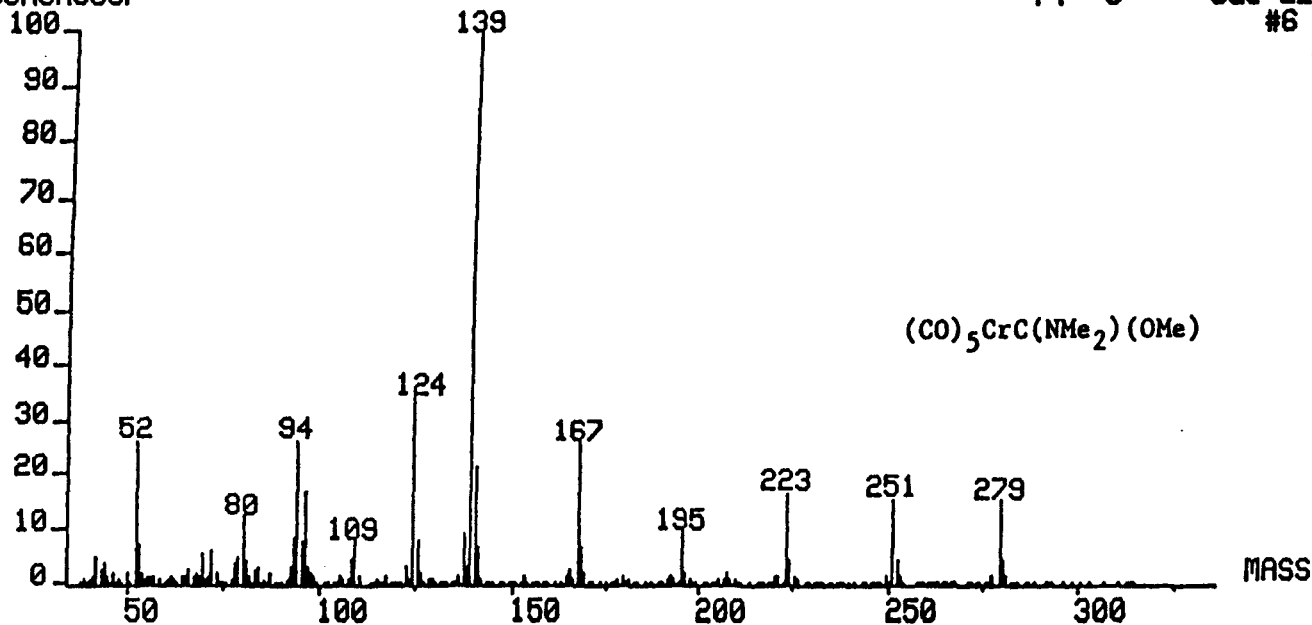   6361000

$(CO)_5CrC(NMe_2)(OMe)$

Peaks labeled: 52, 80, 94, 109, 124, 139, 167, 195, 223, 251, 279

Intensity axis: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100

MASS axis: 50, 100, 150, 200, 250, 300

```
LE08#6              x1      Bgd=1      15-JUL-92 15:20+0:00:22   70-250SE   EI+            1.1
BpM=0        I=2.9v    Hm=0       TIC=99340000              Acnt:LOYOLA      Sys:LREI
C9H9N06Cr                                                       PT= 0       Cal:LEM
```

Peak No	Mass	% Base	Peak No	Mass	% Base
1	42.0	4.5	33	168.0	6.1
2	43.1	2.1	34	195.0	9.0
3	44.1	3.5	35	223.0	16.1
4	52.0	25.9	36	224.0	4.1
5	53.0	6.7	37	251.0	15.1
6	66.0	2.6	38	252.0	3.9
7	69.5	5.0	39	279.0	14.9
8	72.1	5.7	40	280.0	4.1
9	78.0	3.4			
10	79.0	4.7			
11	80.0	12.1			
12	81.0	3.8			
13	83.0	2.1			
14	83.5	3.1			
15	92.0	2.6			
16	93.0	8.0			
17	94.0	26.0			
18	95.0	7.5			
19	96.0	16.7			
20	97.0	3.0			
21	108.0	3.9			
22	109.0	7.4			
23	122.0	2.8			
24	124.0	34.0			
25	125.0	7.3			
26	137.0	8.8			
27	138.0	2.9 F			
28	139.0	100.0 F			
29	140.0	21.2 F			
30	141.0	6.4			
31	165.0	2.2			
32	167.0	25.8			

LE84#B   x1   Bgd=1   23-JUN-92 17:00+0:00:29   70-250SE   EI+   1.1
BpM=0   I=6.2v   Hm=0   TIC=161117000   Acnt:LOYOLA   Sys:LREI
                                                    PT= 0   Cal:LEL
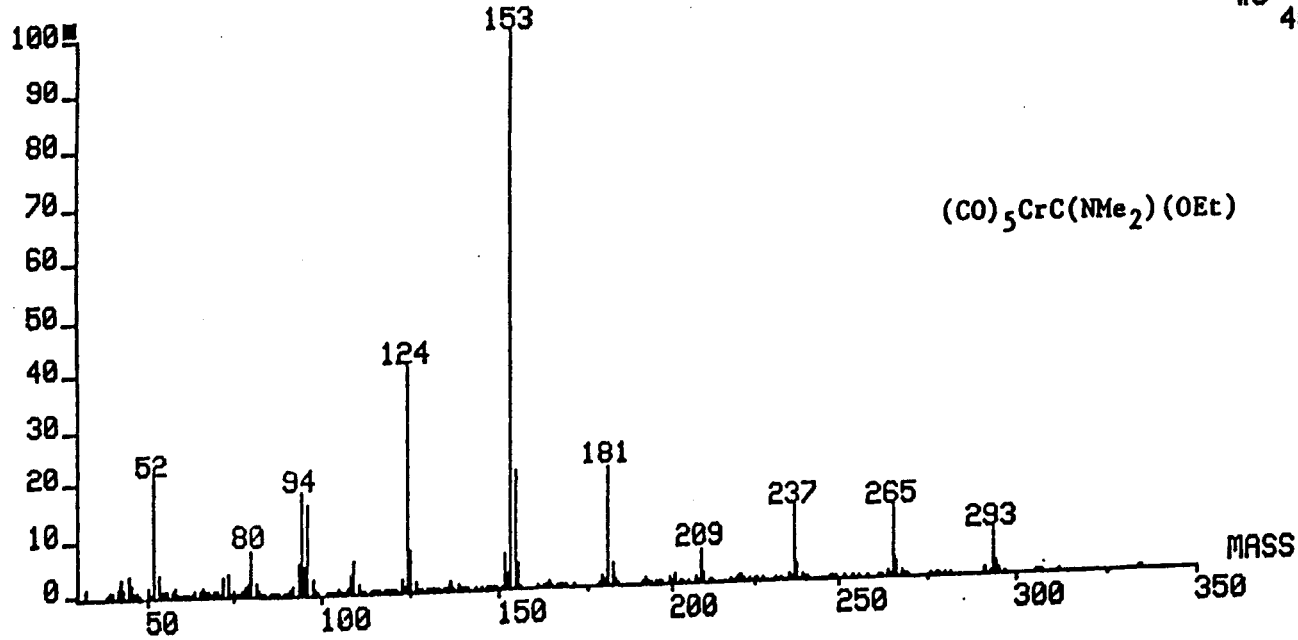
| Peak No	Mass	% Base	Peak No	Mass	% Base
1	41.0	1.0	33	110.0	1.0
2	42.0	2.7	34	122.0	1.9
3	43.0	1.2	35	124.0	40.7
4	44.0	3.5	36	125.0	6.8
5	45.0	1.5	37	126.0	1.4
6	46.5	0.5	38	136.0	0.9
7	49.9	0.9	39	151.0	5.7
8	51.9	21.2	40	152.0	2.2 F
9	52.9	3.4	41	153.0	100.0 F
10	53.9	0.8	42	154.0	20.8 F
11	56.0	0.6	43	155.0	4.1
12	57.1	0.5	44	163.9	0.5
13	58.1	1.1	45	179.0	1.0
14	65.9	0.9	46	180.0	0.6
15	67.0	0.6	47	.181.0	20.8
16	68.0	0.8	48	182.0	3.3
17	72.0	2.6	49	183.0	0.8
18	73.0	3.3	50	199.1	0.8
19	75.0	0.7	51	201.0	0.9
20	78.0	1.1	52	207.0	0.6
21	79.0	1.9	53	209.0	5.4
22	79.9	7.6	54	.210.0	1.0
23	81.0	1.7	55	219.9	0.7
24	82.0	0.7	56	235.0	0.6
25	92.0	1.0	57	237.0	12.6
26	93.0	5.0	58	238.0	2.3
27	94.0	17.6	59	239.0	0.5
28	95.0	4.3	60	263.0	0.5
29	96.0	15.6	61	265.0	11.7
30	97.0	2.1	62	266.0	2.3
31	108.0	2.9	63	267.0	0.6
32	109.0	5.3	64	293.0	7.4.
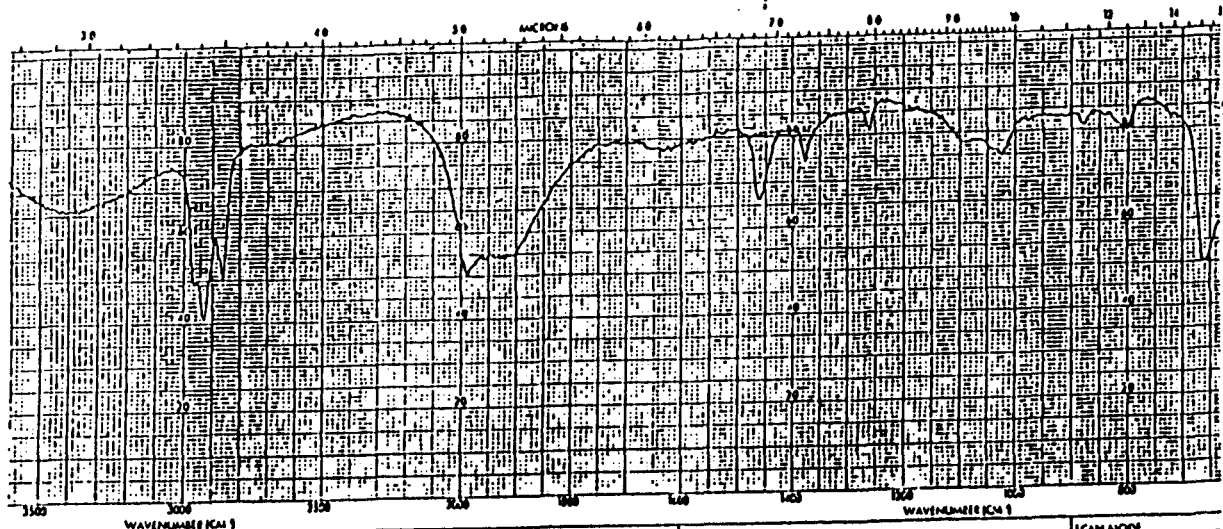
Standard (use mineral oil)

SOLVENT _____
CONCENTRATION _____
CELL PATH _____
REFERENCE _____

REMARKS

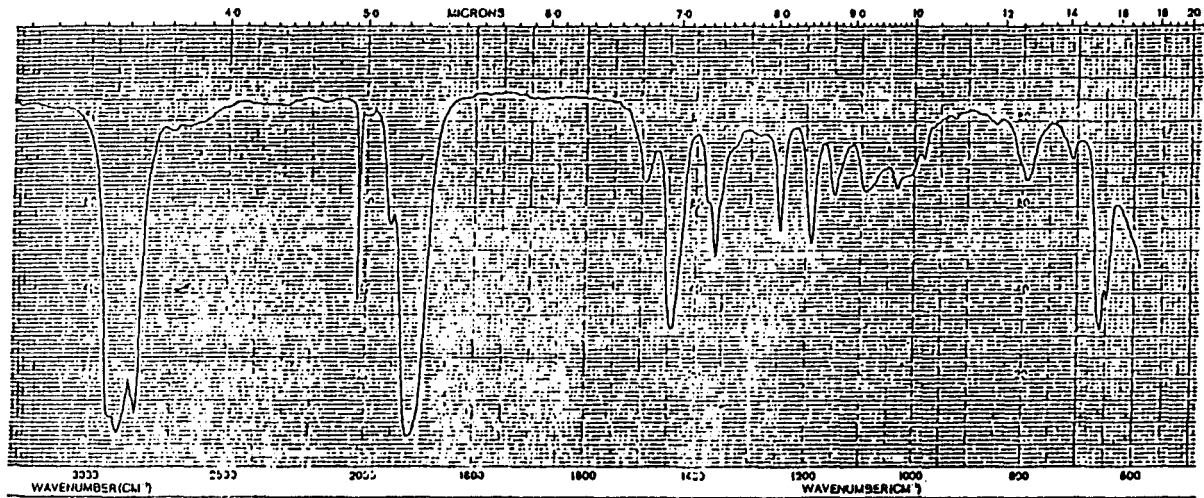$(CO)_6Cr$

SCAN MODE _____
SLIT _____ TIME CONSTANT _____
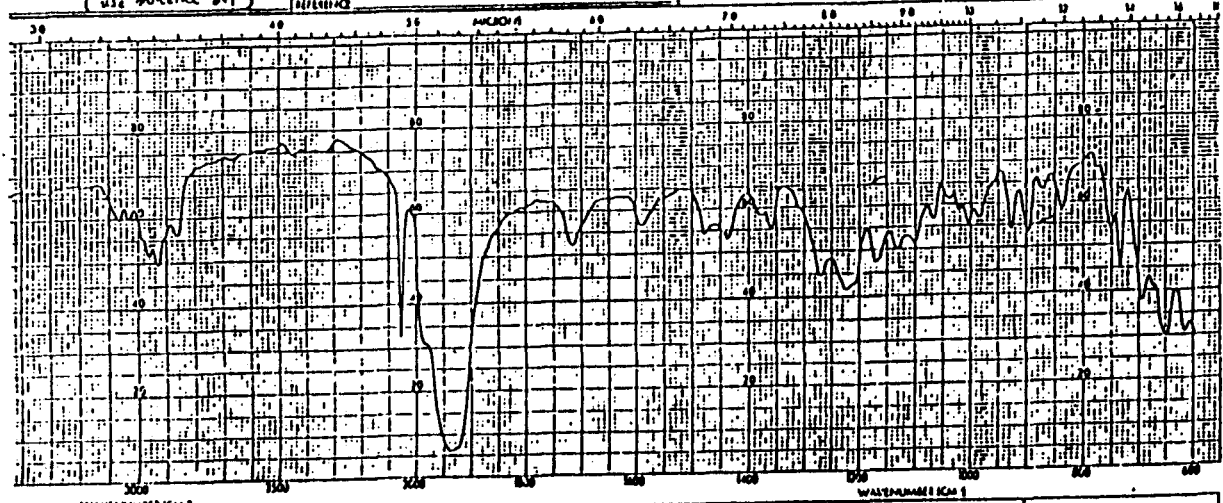
Compound 1.

SOLVENT _____ neat
CONCENTRATION _____ neat
CELL PATH _____
REFERENCE _____

REMARKS

$(CO)_5CrC(Ph)(OEt)$

SCAN MODE _____
SLIT _____ TIME CONSTANT _____

MICRONS

WAVENUMBER(CM⁻¹) ... WAVENUMBER(CM⁻¹)

SOLVENT	mineral oil	REMARKS		SLIT PROGRAM		T A 50	ABSCISSA EXP
CONCENTRATION				SCAN TIME 12 min			TIME DRIVE cm/min
CELL PATH				MULTIPLIER		ORDINATE EXP	
REFERENCE				TIME CONSTANT			OPERATOR DATE REF

Compound 3. $(CO)_5CrC(OMe)(NMe_2)$

MICRONS

WAVENUMBER(CM⁻¹) ... WAVENUMBER(CM⁻¹)

SOLVENT	mineral oil	REMARKS		SLIT PROGRAM		T A 50	ABSCISSA EXP
CONCENTRATION				SCAN TIME 12 min			TIME DRIVE cm/min
CELL PATH				MULTIPLIER		ORDINATE EXP	
REFERENCE				TIME CONSTANT			OPERATOR S DATE

Compound 2. $(CO)_5CrC(OEt)(NMe_2)$
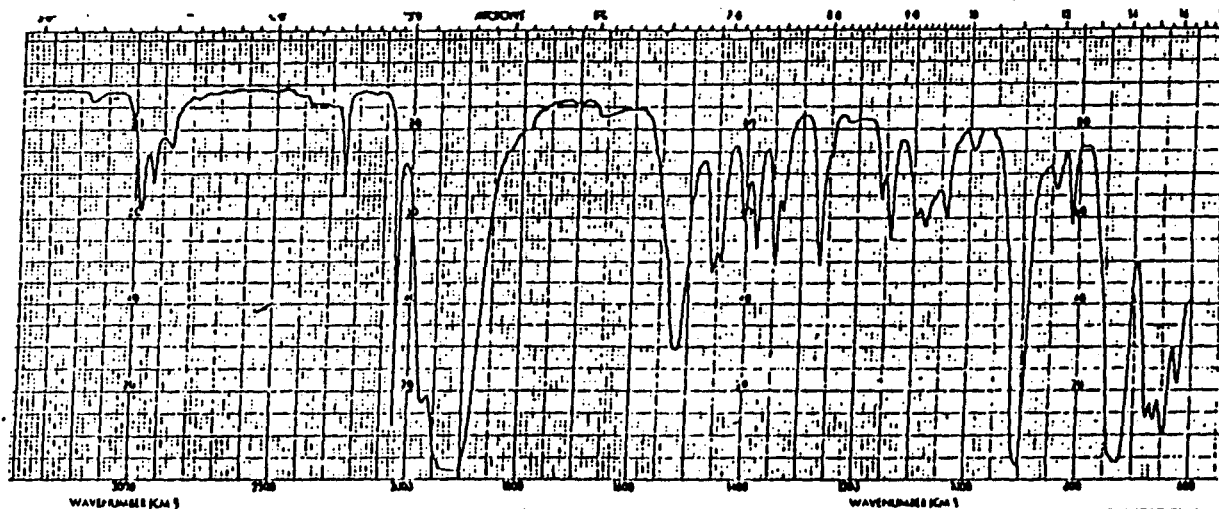
Compound 4.

SOLVENT CDCl₃
CONCENTRATION
CELL PATH
REFERENCE

REMARKS

$(CO)_5CrC(H)(NEt_2)$

SCAN MODE
AIR   TIME CONSTANT
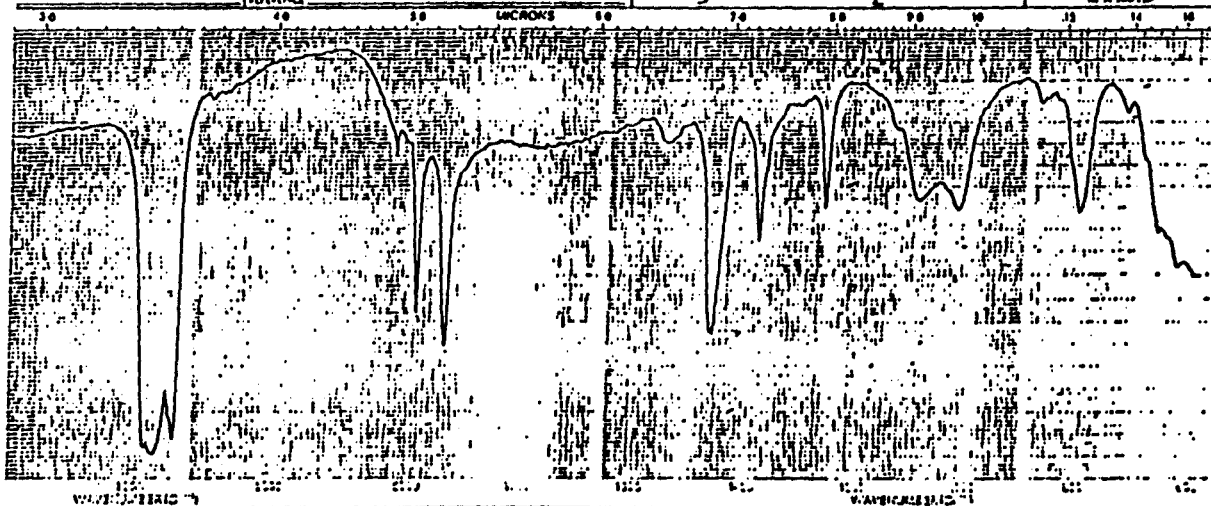
Compound 5.

SOLVENT KBr
CONCENTRATION
CELL PATH
REFERENCE

REMARKS

$(CO)_5CrC(H)(NMe_2)$

SLIT PROGRAM
SCAN TIME   M min
WAVELENGTH
TIME CONSTANT

ORDINATE EXP.

RESOLUTION
TIME CONST

OPERATOR   DATE KMI

Compound 7.

SOLVENT CCl_4
CONCENTRATION
CELL PATH
REFERENCE

REMARKS

$(CO)_5CrC(Ph)(NH_2)$

SCAN MODE
SLIT   TIME CONSTANT
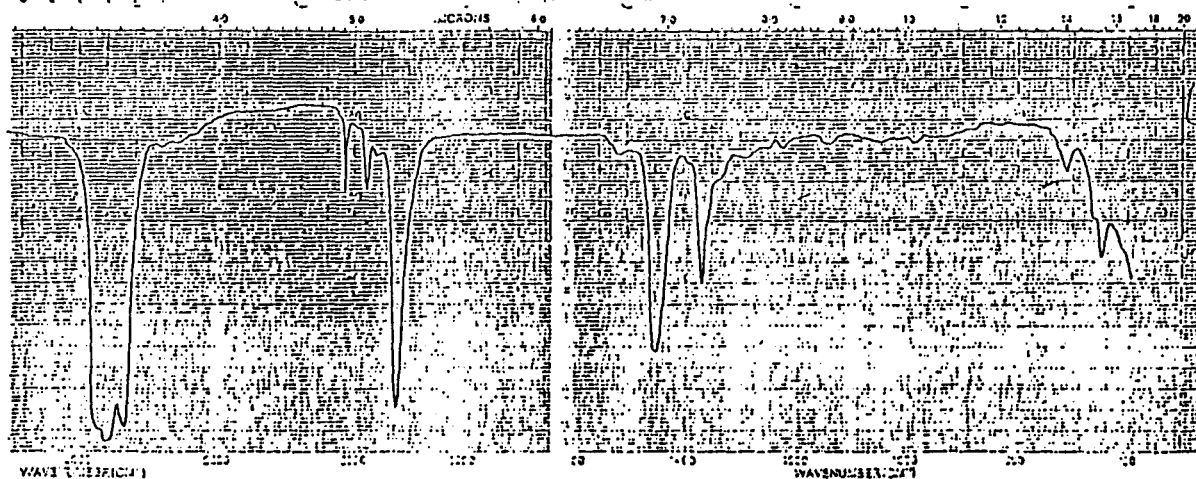
Compound 6.

SOLVENT   nujol oil
CONCENTRATION
CELL PATH
REFERENCE

REMARKS

$(CO)_5CrC(Me)(NMe_2)$

SLIT PASSAGE
SCAN TIME   12 min
SAMPLER
TIME CONSTANT

ORDINATE EXP

ABSCISSA EXP
TIME DRIVE
OPERATOR   JL   DATE

0.692

TAP H₂O

0.681

DC H₂O

0.003

ppm

D₂O

78
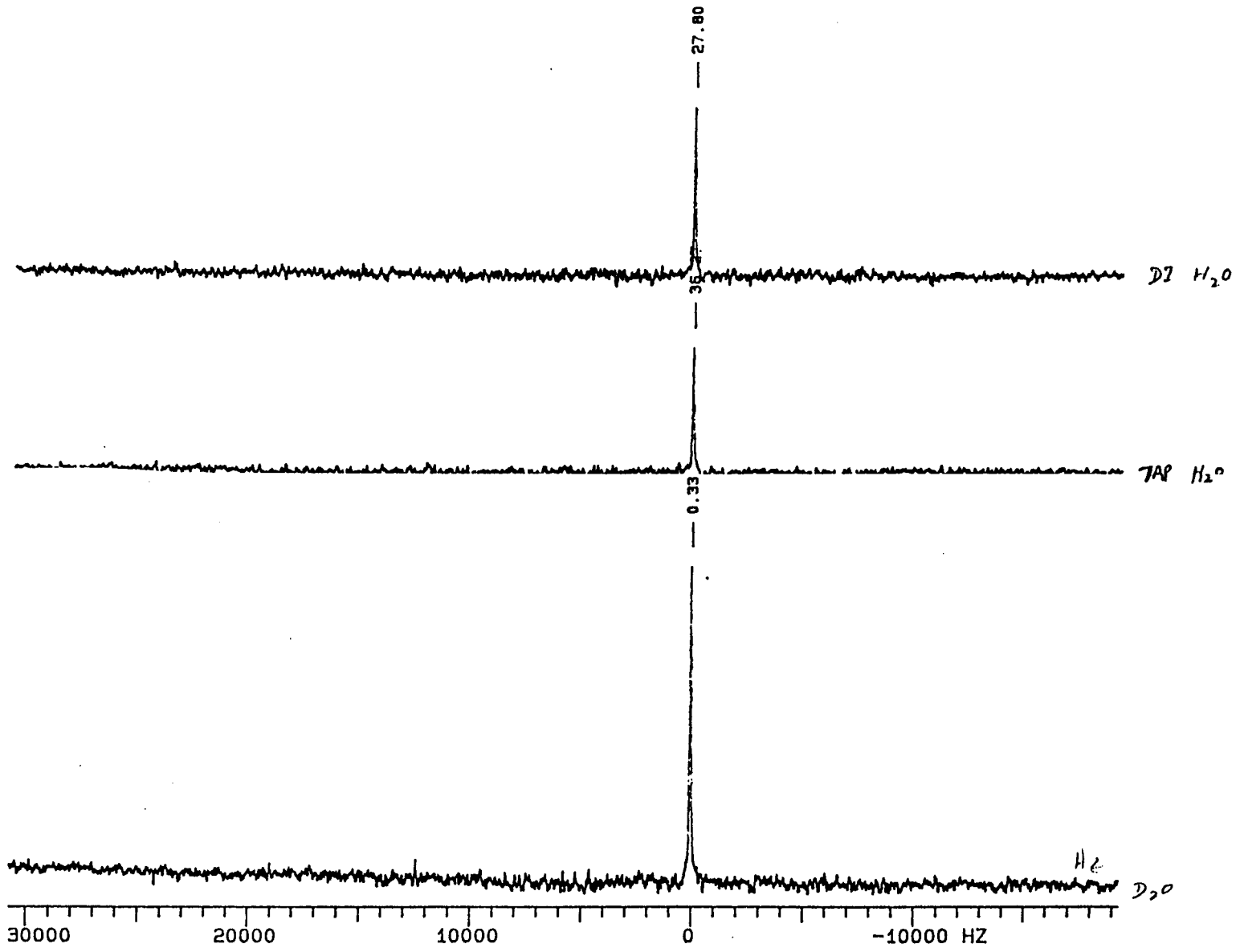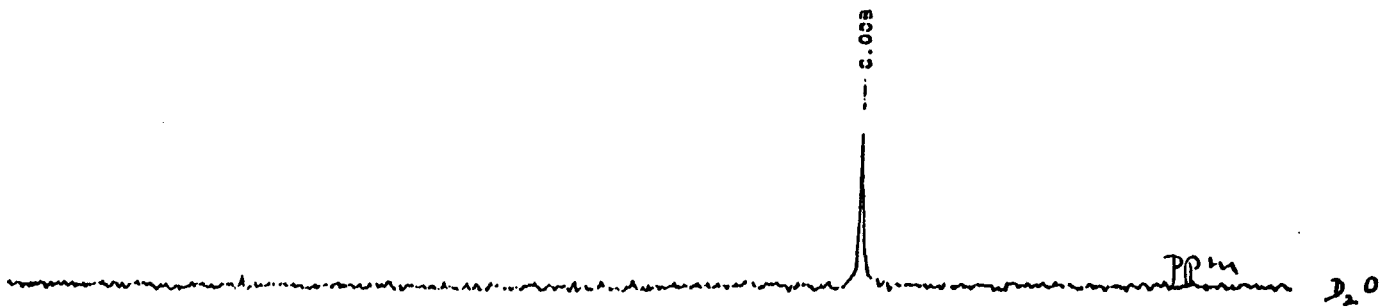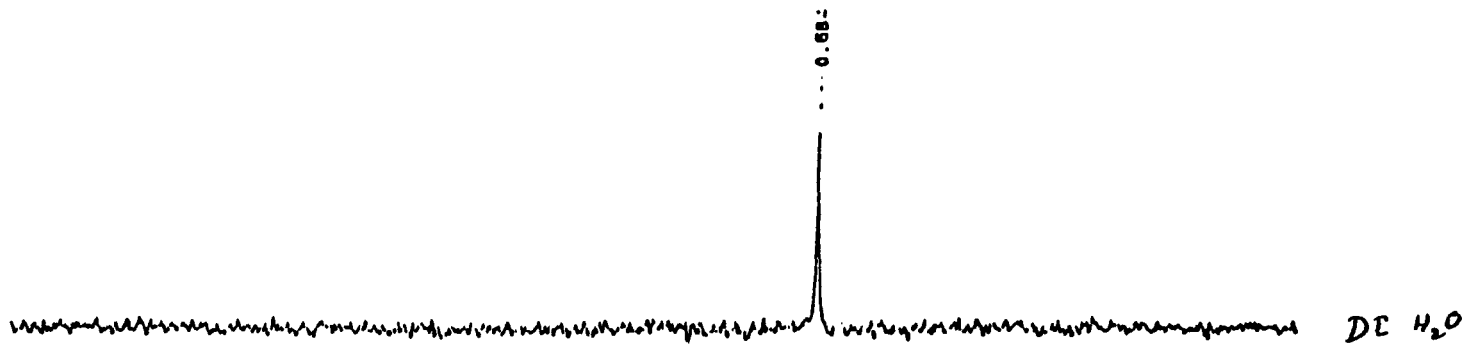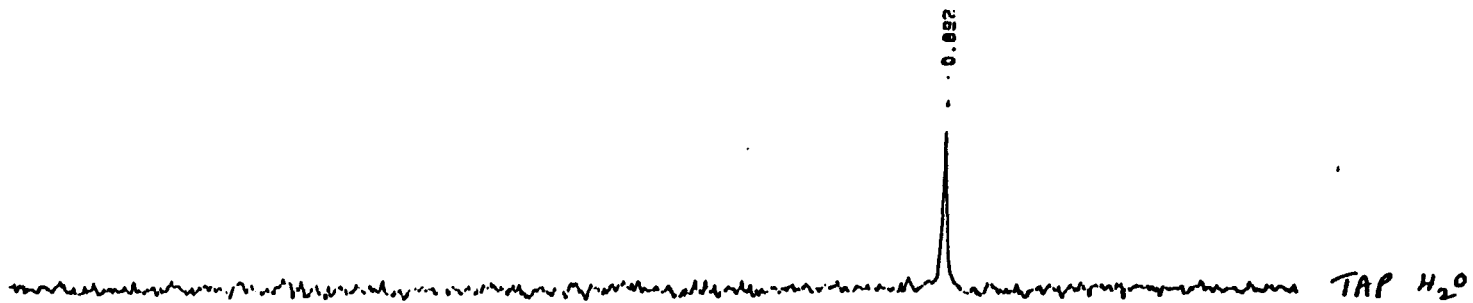
REFERENCE

1. Hine, J. <u>Divalent Carbon</u> Ronald Press, New York, **1964**.

2. Regitz, M. and Maas, G. <u>Diazo Compound</u> Academic: New York, **1986**. 170-184.

3. Liu, M. T. H. <u>Chem. Soc. Rev.</u> **1882**, *11*, 127-140; Frey, H. M. <u>Adv. Photochem.</u> **1966**, *4*, 225-256.

4. Jones, M., Jr. Moss, R. A., <u>Reactive Intermediates</u> Wiley-Inter-science: New York, **1978-1985**, *Vols.* 1-3.

5. Robinson, G. C. *Tetrahedron Lett.* **1965**, 1749.

6. Robinson, G. C. U.S. Patent **1964**, 1,363,460 (to Ethyl Corporation).

7. Goh, S. H; Closs, L. E. and Closs, G. L. *J. Org. Chem.* **1969**, *34*, 25.

8. Lind, H and Deutschman, A. J. Jr. *J. Org. Chem.* **1967**, *32*, 326.

9. Joines, R. C.; Turner, A. B. and Jones, W. M. *J. Am.Chem. Soc.* **1969**, *91*, 7754.

10. Ring D. F. and Rabinovitch, B. S. *Can. J. Chem.* **1968**, *46*, 2435.

11. Herzberg, G. and Shoosmith, J.; *Nature* (London), **1959**, *183*, 1801.

12. Trozzolo, A. M.; Wasserman, E. <u>Carbenes</u> Moss, R. A., Jones, M., Jr., Eds., Wiley: New York, **1973**, *Vol. II*, 185.

13. Wasserman, E.; Kuck, V. J.; Hutton, R. S. and Yager, W. A. *J Am. Chem. Soc.* **1970**, *92*, 7491

14. Wasserman, E.; Yager, W. A. and Kuck, V. J. *Chem. Phy. Lett.* **1970**, 7, (4), 409.

15. Lin, C. T. and Gaspar, P. P. *Tetrahedron Lett.* **1980**, *21*, 3553.

16. Platz, M. S. *J. Am. Chem. Soc.* **1988**, *21*, 236.

17. Fischer, E. O. and Maasböl, A. *Angew. Chem. Int. Ed.* **1964**, *3*, 580.

18. Darrensbourg, M. Y. and Darrensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32.

19. Klabunde, U. and Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141.

20. Schwindt, M. A.; Lejon, T. and Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

21. Semmelhack, M. F. and Lee, G. E. *Organometallic* **1987**, 7, 1839.

22. Connor, J. A. and Fischer, E. O. *J. Chem. Soc. (A)* **1969**, 578.

23. Gansow, O. A., Kimura, B. Y., Dobson, G. R. and Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922.

24. Gasow, O. A., Schexnayder, D. A. and Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406.

25. Bodner, G. M. and Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335.

26. Hickey, J. P.; Wilkinson, J. R. and Todd, L. J. *Organometallic* **1979**, *179*, 159.

27. Kawada, Y.; Sugawara, T. and Iwamura, H. *Okazaki IMS Annual Review* **1979** 113.

28. Wulff, W. D.; Kaesler, R.W. *Organometallic* **1985**, 4, 1461.

29. Dötz, K. H.; Erben, H. G.; Harms, K. *J. Chem. Soc.. Chem. Commun.* **1989**, 692.

30. Moss, R. A. Carbene Jones, M., Jr., Moss, R. A., Ed.; Wiley: New York, **1973** Vol. I, 153.

31. Moss, R. A.; Fedorynski, M. and Shieh, W. *J. Am. Chem. Soc.* **1979**, *101*, 4736.

32. a) Crumrine, D. S. unpublished results. b) Kawada, Y. and Iwamura, H. *Okazaki IMS Annual Review* **1980**, 110.

33. Hansch, C. and Leo. A. <u>Substituent Contants for Correlation Analysis in Chemistry and Biology</u> John Wiley & Sons, Inc. New York, **1979**.

34. Darrensbourg, M. Y. and Darrensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32.

35. Fischer, E. O. and Kollmeier, H. J. *Chem. Ber.* **1971**, *104*, 1339.

36. Schwindt, M. A.; Lejon, T. and Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

37. Hartshorn, A. J. and Turner, K. J. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

38. Hafner, A.; Hegedus, L. S.; DeWeck, G.; Hawkins, B. and Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

39. MS assignments are written for successive losses starting from the parent ion.

40. Exact mass could not be determined for this compound as the parent ion lies too close to the perfluorokerosene calibration peak.

APPROVAL SHEET

The thesis submitted by Shuyuan Liao has been read and approved by the following committee:

>   Dr. David S. Crumrine, Director
>   Associate Professor, Chemistry
>   Loyola University of Chicago
>
>   Dr. Mary K. Boyd
>   Associate Professor, Chemistry
>   Loyola University of Chicago
>
>   Dr. Albert W. Herlinger
>   Associate Professor, Chemistry
>   Loyola University of Chicago

The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated and the thesis is now given final approval by the committee with reference to the content and form.

The thesis is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

4/16/93
_____   _____
      Date   Director's Signature