UNPRECEDENTED STABILITIES

of

19-ELECTRON COMPLEXES

by

KEITH JOHN KEANA

A THESIS

Presented to the Department of Chemistry
and the Honors College of the University of Oregon
in partial fulfillment of the requirements
for the degree of
Bachelor of Arts

June 1991

An Abstract of the Thesis of

Keith John Keana for the degree of Bachelor of Arts in the Department of Chemistry to be taken June 1991.

Title: UNPRECEDENTED STABILITIES OF 19-ELECTRON COMPLEXES

Approved: [redacted]
Dr. David R. Tyler

Current research in organometallic chemistry has expanded to include both stable and short-lived odd electron species containing 17- and 19-valence electrons. These complexes are intrinsically different from the 16- and 18-electron variety and are counterexamples to the generally accepted 16-/ 18-electron rule. Unfortunately, the 16-/ 18-electron rule provides no insight into the stability or reactivity of the odd-electron species. The term $18+\delta$ is used to describe 19-electron complexes that contain a reduced, radical anion L_2 ligand. This thesis involves the synthesis of new complexes exhibiting $18+\delta$ behavior in an effort to help establish guidelines that describe the chemistry of these species.

ACKNOWLEDGMENTS

I would like to thank Dr. David Tyler, for his guidance, and for making his laboratory available for this research. I would also like to thank Dr. Ken Doxsee and Research Associate Galen Martin, who served on my thesis comittee. I extend special thanks to Drs. James Long and my father John Keana, for their encouragement and assistance during the course of my research and studies in chemistry. Acknowledgment is made to the National Student Foundation for support. In addition, I express my appreciation to Dr. Steve Tenhaeff and the other members of the Tyler laboratory for their consistent help with any difficulties or quesions that I encountered.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

FIGURE

TABLE

LIST OF SPECTRA

CHAPTER I

INTRODUCTION

The study of chemistry is divided into overlapping subdisciplines, including analytical chemistry, inorganic chemistry, organic chemistry, organometallic chemistry, and physical chemistry. These subdisciplines are usually characterized by the types of chemical compounds studied, and each subdiscipline exhibits well-defined rules and applications associated with the compounds in question.

In particular, the study of organometallic chemistry is a combination of two subdisciplines, organic and inorganic chemistry.[1] Organometallic chemistry has traditionally been the domain of compounds used in homogeneous catalysis. Catalysis is one of three predominant driving forces in chemical research today. Synthetic polymers and chemical synthesis, i.e. medicines, are the other two. Nearly forty percent of current research is focused primarily upon catalysis. Catalysis is the process by which certain elements or compounds facilitate a reaction. Catalysts lower the energy of activation for the reaction by providing an alternative pathway between reactants and products.

Most catalysts are diamagnetic complexes, i.e., there are no unpaired electrons. These compounds obey the powerful 16-/ 18-electron rule. This rule, as set forth by Tolman[2] states that "...diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperature only if the metal's valence shell contains 16 or 18 electrons." Furthermore, the rule states that "organometallic reactions,

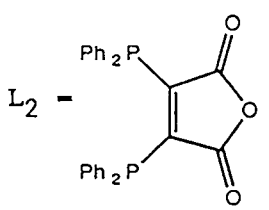
1. It is interesting to note that Vitamin B_{12} is the only naturally occurring organometallic compound.
2. C.A. Tolman, Chem. Soc. Rev. 1, 337-353 (1972).

including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons."

However, research over the past few years has expanded to include both stable and short-lived odd-electron species containing 17- and 19-valence electrons. These complexes are intrinsically different from the 16- and 18-electron variety and are counterexamples to the generally accepted rule. Unfortunately, the 16-/ 18-electron rule provides no insights into the stability or reactivity of the odd-electron species. Since it is always of interest to chemists to study new classes of molecules, effort has been put forth to establish guidelines that describe the chemistry of these species.

In general, the 19-electron complexes are rather new to organometallic chemistry. There have been very few studies of the reaction chemistry of these highly unusual complexes. However, definitive evidence that 19-electron complexes are formed comes directly from experiments in which 19-electron complexes are stable products of the reaction.

Eq 1 $$Co_2(CO)_8 \rightleftharpoons \underset{17e\text{-}}{2\ Co(CO)_4} \xrightarrow{L_2} \underset{19e\text{-}}{Co(CO)_3L_2} + CO$$



2,3-bis(diphenylphosphino)maleic anhydride

In particular, the work of D. Tyler and subsequent work by Kochi, Basolo,and Trogler, and others provides strong evidence for the existence of these species.[3,4] Unfortunately, many of these complexes are short-lived and difficult, if not impossible, to isolate. Therefore, 19-electron

3. W.C. Trogler (Ed), Organometallic Radical Processes, Elsevier, Amsterdam, in press.
4. D.R. Tyler, F. Mao; Coordination Chemistry Reviews, 97, 119-140, 1990.

complexes are difficult to study. However, one method of overcoming this inherent complication is to model the 19-electron complexes by synthesizing new complexes that exhibit 18+δ behavior[5] and studying their reactivities.

In general, 19-electron complexes are formed as follows. A metal-metal bonded dimer is irradiated with light which causes homolytic cleavage of the metal-metal bond.

Eq 2 $$M_2L_{2n} \overset{h\nu}{\rightleftharpoons} \underset{17e^-}{2\ ML_n}$$

ML_n = $Mn(CO)_5$, $Re(CO)_5$, $CpM(CO)_3$ (M = Cr, Mo, W), $CpFe(CO)_2$, $Co(CO)_4$

The resulting 17-electron complex then reacts with a two-electron donor ligand (L_2) giving the 19-electron complex (eq 1). In theory, the synthesis of new complexes exhibiting different reactivities can be accomplished by using two-electron donor ligands with different reduction potentials.[6] It is my goal, therefore, to synthesize a two-electron donor ligand with a reduction potential between -1.0 and -1.6 volts. The ligand will be allowed to react with several metal-metal bonded dimers in the presence of light to generate new stable 19-electron complexes. The reactivity of the new complexes will be compared with that of known 19- and analogous 18-electron complexes.

---

5. The term 18+δ was coined by Prof. Ted Brown (University of Illinois) to describe those 19-electron adducts that are essentially 18-electron complexes with reduced ligands. The term 18+δ is preferred when the term "19-electron adduct" might lead to confusion about the electronic structure of the adduct.

6. The formal definition of reduction potential is the voltage or potential at which something accepts an electron relative to the standard reference hydrogen electrode which is equal to zero by convention.

CHAPTER II

THEORY and ANTICIPATED RESULTS

In order to understand better my anticipated results, it is first necessary to explain the theory involved concerning the stability of the 19-electron complexes. This will be best understood using the molecular orbital diagrams in Fig.1.

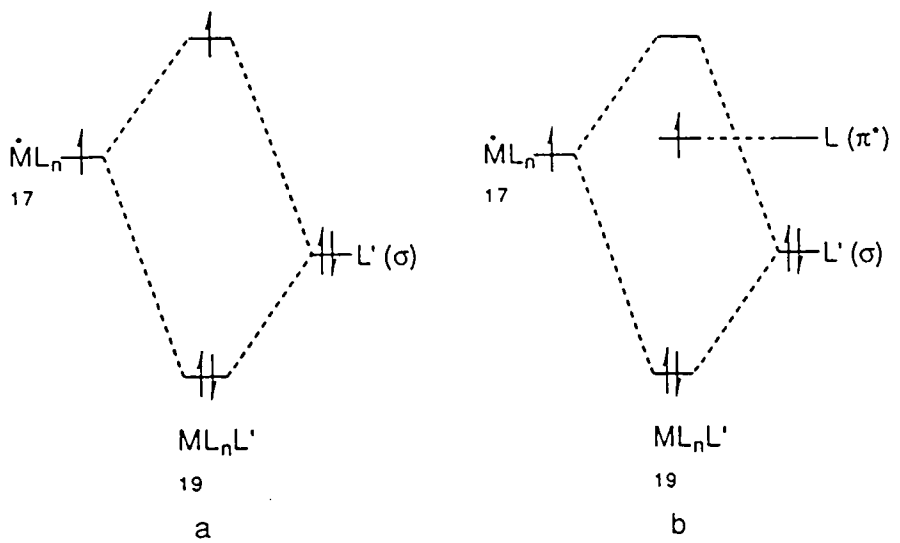


Fig. 1. (a) A simplified molecular orbital scheme for the interaction of a ligand with a 17-electron metal radical. (b) The molecular orbital scheme for the case in which the ligand also has a low energy π^* orbital.

In diagram a the extra electron is located in a high energy metal-ligand antibonding orbital,[7] destabilizing the complex. However, in diagram b the ligand L' has an antibonding orbital (usually a π^* orbital) that is much lower in energy than the metal-ligand antibonding orbital and the extra electron will reside there, leading to stabilization of the complex. This

7. When two molecules react forming a complex, two orbitals are created-- a bonding orbital (always of lower energy), and an antibonding orbital (always of higher energy). Energetic considerations dictate that bonding orbitals are filled with electrons first, then any extra electrons are placed in the high energy destabilizing antibonding orbitals (denoted π^*).

important phenomenon permits the manipulation of the reactivity of these complexes by synthesizing ligands which possess π^* orbitals with different energies.

How can this be done? When molecules exhibit conjugation, i.e. two double bonds separated by a single bond, they become more stable due to the delocalization of electrons. Secondly, electronegative elements, i.e. elements that withdraw electrons, also delocalize electrons, thereby providing a more stable environment. One may predict that substituting an electronegative element in a molecule with a less electronegative element will destabilize the molecule and increase its reactivity. In terms of the diagrams in Fig. 1, the ligand-based π^* orbital will be higher in energy than before the substitution was done, making the complex more reactive.

Infrared spectroscopy is a convenient tool for monitoring electron density changes on a metal center within a series of similar metal carbonyl complexes. An increase in the electron density around the metal atom weakens and destablizes its carbonyl bonds. Therefore, a change to a ligand which results in increased electron density on the metal atom translates into a characteristic shift in the carbonyl region of the infrared spectrum to lower energy (i.e. lower wavenumber). This effect is nicely illustrated by the following two sets of complexes, (ref. 12).

Table I

Entry	complex	ν(C≡O), cm-1	solvent
1	$CpMo(CO)_3PPh_3^{+a}$	2062, 2001, 1975	CH_2Cl_2
2	$CpMo(CO)_3PEt_3^{+a}$	2056 s, 1993m, 1966 vs	CH_2Cl_2
3	$CpMo(CO)_2(PPh_3)_2^{+a}$	1978 s, 1901 vs	CH_2Cl_2
4	$CpMo(CO)_2(PEt_3)_2^{+a}$	1961 s, 1883 vs	CH_2Cl_2

[a] Cp= η^5-C_5H_5

Entries two and four involve metal atoms coordinated to relatively strongly electron donating $(C_2H_5)_3P$ groups, while entries one and three are coordinated to the more electron withdrawing $(C_6H_5)_3P$ groups.

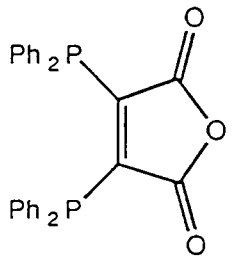
CHAPTER III

EXPERIMENTAL METHODS

General. Unless otherwise noted, all manipulations were done under an inert atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. All solvents were freshly distilled from benzophenone prior to use. NMR spectra were taken in $[^2H]$-C_3H_6O or $[^2H]$-$CHCl_3$ on a General Electric QE-300. Shifts are relative to residual proton peaks in the solvent. IR spectra were taken from KBr pellets, or in THF or CH_2Cl_2 solutions on a Nicolet 5DXB Fourier Transform Infrared (FT-IR) spectrometer, in order to observe frequency shifts in the C≡O stretching region of the spectrum.

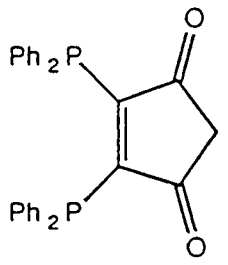
FIGURE 2

Structures
of



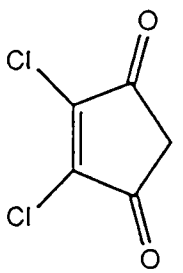
A

2,3-bis(diphenylphosphino)maleic anhydride[7]



B

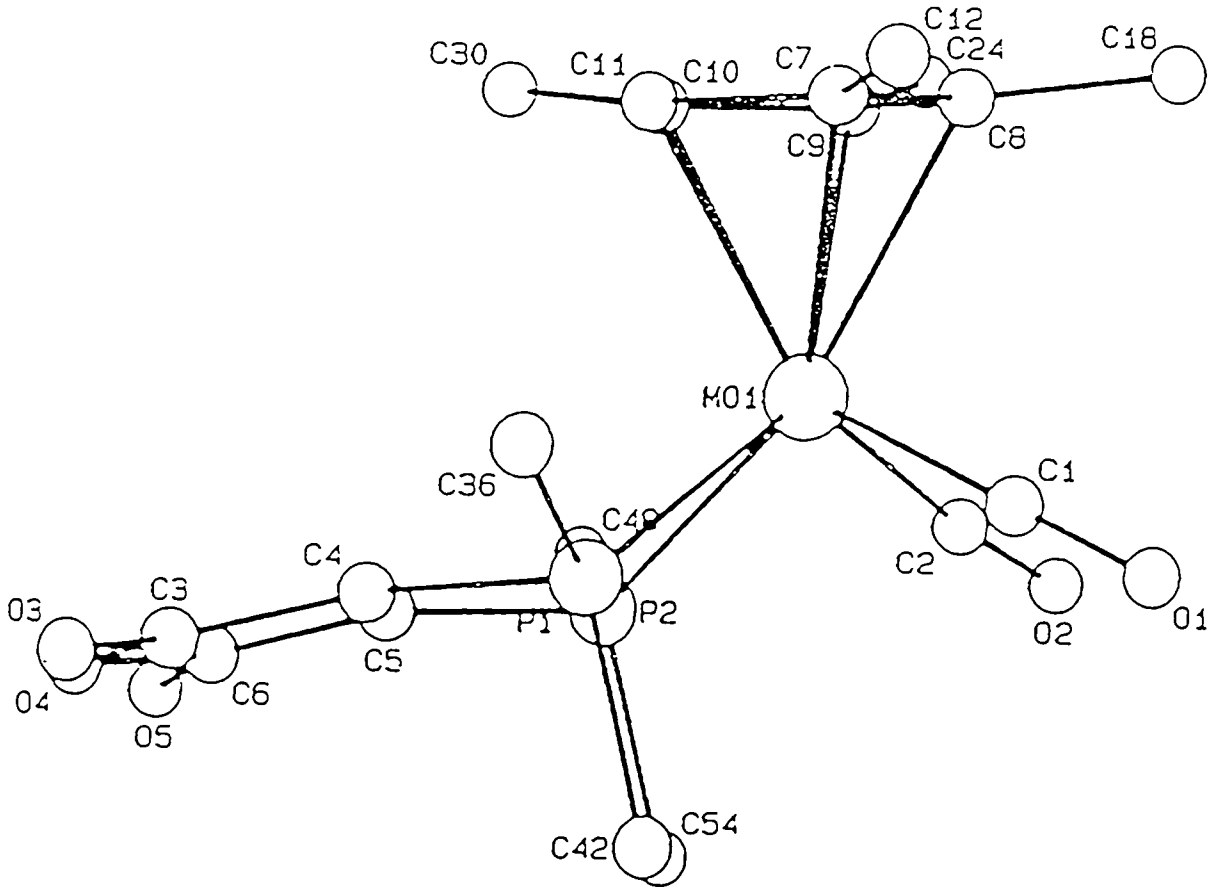
2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione



C

2,3-dichloro-2-cyclopenten-1,4-dione

FIGURE 3



Crystal structure of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ complex (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride). The phenyl groups on the P atoms and C_5 ring have been omitted for clarity. The four-legged piano stool geometry is apparent in this view.

FIGURE 4

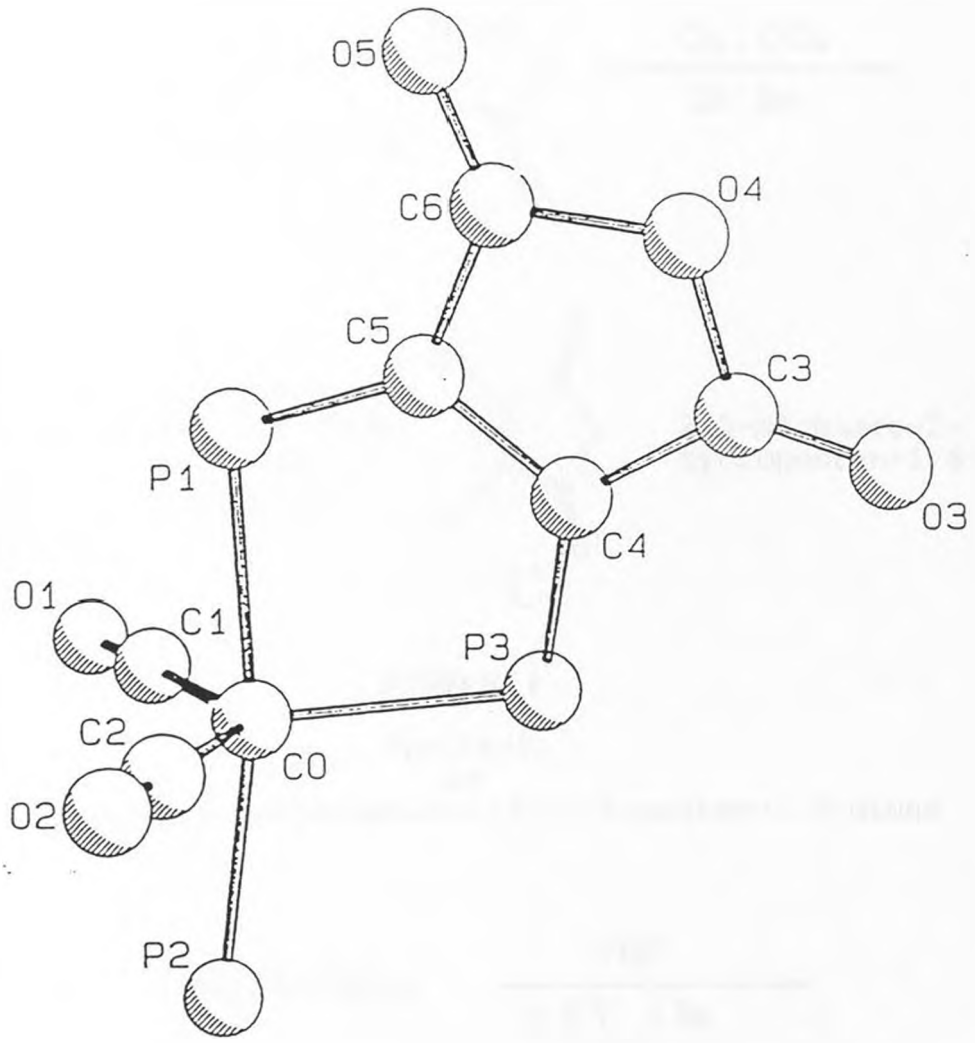


FIGURE 11. Crystal structure of the $Co(CO)_2L_2PPh_3$ complex [L_2 = 2,3 -bis(diphenylphosphino)maleic anhydride]. The phenyl groups on the P atoms have been removed for clarity.

FIGURE 5

Synthesis
of
2,3-dichloro-2-cyclopenten-1,4-dione

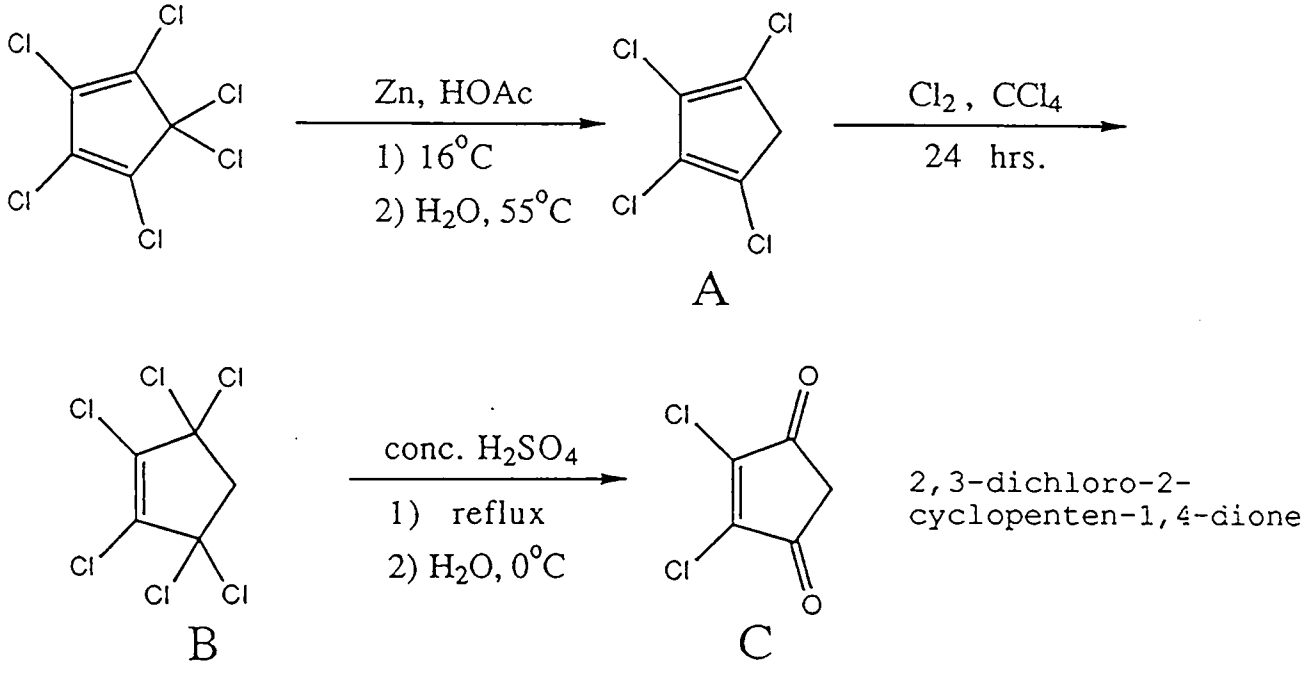


FIGURE 6

Synthesis
of
2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione

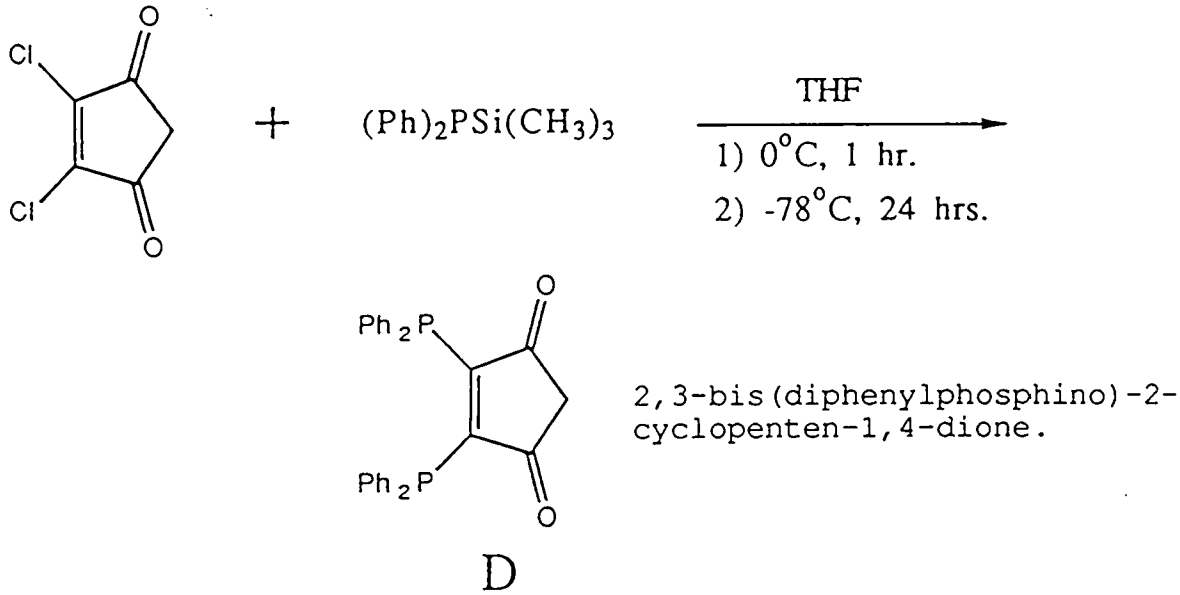
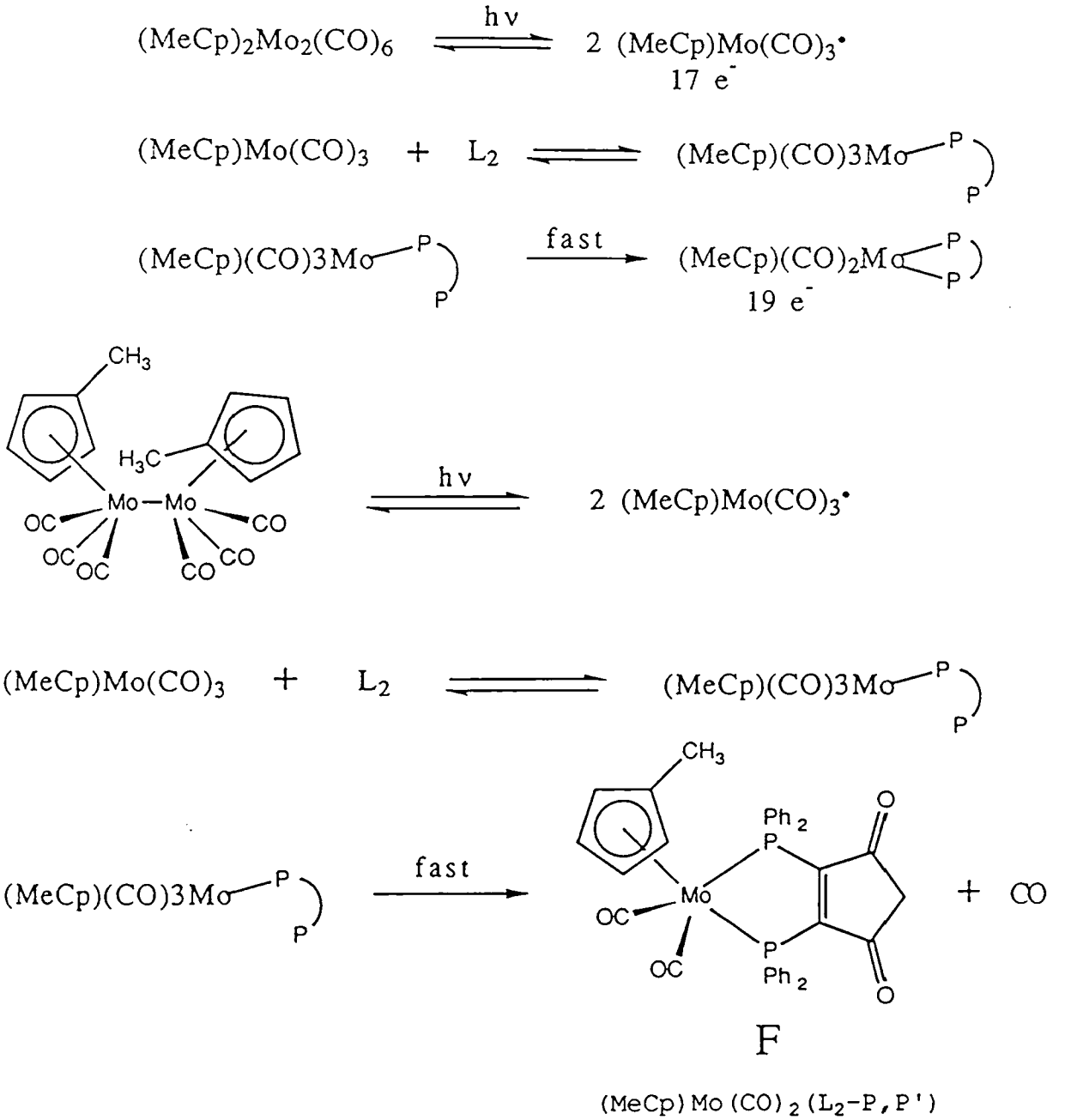


FIGURE 7

Formation of $(MeCp)Mo(CO)_2(L_2\text{-}P,P')$

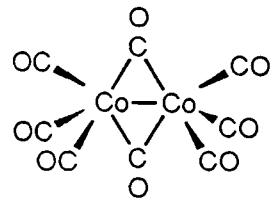


F

$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$

FIGURE 8

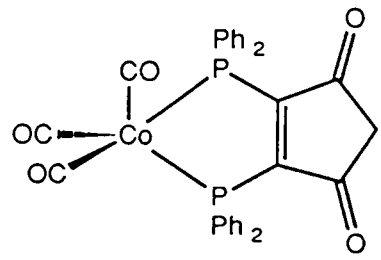
Formation of $Co(CO)_3(L_2\text{-}P,P')$



$\rightleftharpoons$ $2\ Co(CO)_4$

$17\ e^-$

$Co(CO)_4 + L_2 \rightleftharpoons$



$+ \quad CO$

G

$Co(CO)_3(L_2\text{-}P,P')$

FIGURE 9

Disproportionation reaction.

$Co_2(CO)_8 \rightleftharpoons 2\ Co(CO)_4$

$Co(CO)_4 + L_2 \longrightarrow Co(CO)_3L_2 + CO$

$Co(CO)_3L_2 + Co_2(CO)_8 \longrightarrow Co(CO)_3L_2^+ + Co_2(CO)_8^-$

$Co_2(CO)_8^- \longrightarrow Co(CO)_4^- + Co(CO)_4$

A. 1,2,3,4-tetrachloro-1,3-cyclopentadiene. To a solution of (40 mL, 0.25 mol) hexachlorocyclopentadiene in 150 mL acetic acid was slowly added (40.0 g, 0.63 mol) zinc powder at 16 to 18°C. The mixture was then poured into 400 mL H_2O at 55 to 60°C and immediately filtered through a medium glass frit. White crystals formed upon cooling, and were recrystalized from methanol and/or sublimed, (29.5 g, 58%).

NMR: $\delta(CDCl_3)$, 3.388 ppm (s, 2H).

B. 1,1,2,3,4,4-hexachloro-2-cyclopentene. In a solution of (14.75 g, 0.072 mol) of A in 120 mL carbon tetrachloride was bubbled ultra pure Cl_2 gas for 24 hours. The solvent was removed under reduced pressure. Fractional distilation, (47°C, 0.1 Torr), resulted in a clear transparent liquid, (16.375 g, 82%).

NMR: $\delta(CDCl_3)$, 4.037 ppm (s, 2H).

C. 2,3-dichloro-2-cyclopenten-1,4-dione (5). (15 g, 0.0546 mol) of B was refluxed in 150 mL concentrated sulfuric acid for 90 min. The mixture was cooled to room temperature and poured into a beaker containing ice and filtered through a medium glass frit. White crystals were recrystalized from methanol and from THF/hexane, (6.03 g, 64.2%).

NMR: $\delta(CDCl_3)$, 3.248 ppm (s, 2H).

D. 2,3-(bis)-diphenylphosphino-2-cyclopenten-1,4-dione (6). To (5.0 g, 0.0303 mol) of C dissolved in 50 mL dry THF at 0°C was added (15.64 g, 0.0605 mol) E slowly over 1 hour. The mixture was placed in dry ice for 24 hours and filtered under nitrogen. The resulting solid was vacuum dried

and purified via column cromotography as follows. To a 16 by 2 inch column slury packed with silica gel in hexane, was placed 8.0 g of the solid. The separation was carried out using 10%, 25%, and 50% EtOAc/hexane solutions. The liquid fractions were examined by spotting on TLC plates, combined, and the solvent evaporated affording yellow crystals, (2.66 g, 33%, mp. 166°C). NMR: δ(Acetone-^{2}H), 3.040 ppm (s, 2H); 7.25 ppm (m, 20H).

E. **Diphenyl(trimethylsilyl)phosphine.** To (13.05 mL, 0.075 mol) diphenylphosphine in 50 mL THF, 0°C, was slowly added (46 mL, 0.075 mol) 1.64 M n-butyllithium in hexane. The mixture was let warm to room temperature and to it was added (9.5 mL, 0.0748 mol) chlorotrimethylsilane, freshly distilled over CaH_2. The mixture was refluxed for one half hour and filtered under nitrogen through one gram celite path. The solvent was removed under reduced pressure for 24 hours. Fractional distilation, (105°C, 0.2 Torr), yielded a clear transparent liquid, (15.64 g, 81%).

F. $(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$ (7). $(MeCp)_2Mo_2(CO)_6$, (ref.3), (2.9 mg, 5.6 * 10^{-3} mmol) and D (L_2'), (ref. 7), (23.7 mg, 5.1 * 10^{-2} mmol) were added to one mL of THF. The resulting mixture was transfered to a NaCl IR cell and irradiated ($\lambda > 520$ nm) for two hours. The reaction was observed by Infrared spectroscopy at two minute intervals. Complete spectroscopic data are given in Tables II and III.

G. $Co(CO)_3(L_2'\text{-}P,P')$ (8). A solution of D (L_2'), (0.2 g, .430 mmol), in 10 mL of toluene is added slowly to $Co_2(CO)_8$ (73.6 mg, 0.215 mmol) in 5 mL of toluene at 0°C. The mixture is stired at 0°C for one half hour at which time an evolution of CO and appearance of a green precipitate should be

seen. The solution is filtered and the solid recrystalized from 1,2-dichloro ethane/ether, (0.098 g, 75%). Complete spectroscopic data are given in Tables IV and V.

CHAPTER IV

RESULTS AND DISCUSSION

The first objective of this study is to replace the electronegative oxygen of 2,3-bis(diphenylphosphino)maleic anhydride, Figure 2a, with the less electronegative methylene ($-CH_2-$) group to make 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione, Figure 2b. This synthesis was accomplished using an adaptation of the published method by D. Fenske, (ref. 7). Commercially available hexachlorocyclopentadiene was reacted with zinc powder, chlorinated with Cl_2, and then refluxed in H_2SO_4 to give 2,3-dichloro-2-cyclopenten-1,4-dione, Figure 5c. (C) was reacted with $(Ph)_2PSi(CH_3)_3$ in THF to yield 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione, Figure 6d.

The second objective of this study is to form stable 19-electron complexes. The common approach to the synthesis of 19-electron complexes is the reaction of a two-electron-donor ligand L_2, (L_2 is the chelating phosphine 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione, (ref. this work), or 2,3-bis(diphenylphosphino)maleic anhydride, (ref. 15)), with a 17-electron metal radical (eq 1, page 2). The 17-electron radicals needed for the synthesis of the L_2' complexes were formed by photolysis of the Mo-Mo bonds in the $Cp_2Mo_2(CO)_6$ complexes (Cp = η^5-$C_5H_4CH_3$, η^5-C_5H_5) (eq 2, page 3).

Irradiation (λ > 520nm) of a THF solution of $(MeCp)_2Mo_2(CO)_6$ and L_2' at room temperature led to the disappearance of $(MeCp)_2Mo_2(CO)_6$ and the formation of a product with infrared bands at 1962 and 1878 cm^{-1}. The product from this reaction is $(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$, the structure of which is shown in Figure 7f, page 12.

Table II. Infrared Data for $(MeCp)Mo(CO)_2L_2$ Complexes

complex	ν(C≡O), cm-1	ν(C=O), cm-1	ref.
L_2[a,c]		1838 m, 1816 w, 1763 s	15
L_2'[b,c]		1743 s, 1710 vs, 1682 w	this work
$(MeCp)_2Mo_2(CO)_6$[c]	2010 w, 1953 vs, 1910 s		15
$(MeCp)Mo(CO)_3(L_2\text{-}P)$[a,c]	2049 s, 1981 s, 1958 s	1737 m, 1673 s	15
$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$[a,c]	1967 s, 1900 s	1741 s, 1669 s	15
$(MeCp)Mo(CO)_3(L_2'\text{-}P)$[b,c]	2036 s, 1962 s, 1955 s		this work
$(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$[b,c]	1962 s, 1878 s	1590 s, 1570 m	this work

[a] L_2 = 2,3-bis(diphenylphosphino)maleic anhydride.
[b] L_2' = 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione. [c] In THF.

Table III. Infrared Data for $CpMo(CO)_2L_2^{+/-}$ Complexes

complex	ν(C≡O), cm-1	solvent	ref.
$CpMo(CO)_2(PPh_3)_2^+$	1978 s, 1901 vs	CH_2Cl_2	12
$CpMo(CO)_2(dppe)^+$	1980 s, 1915 s	CH_2Cl_2	12
$Cp'Mo(CO)_2L_2^+$[a,b]	2025 s, 1995 s, 1955 s	THF	
$Cp'Mo(CO)_3^-$[b]	1899 s, 1789 s, 1749 s	THF	16

[a] L_2 = 2,3-bis(diphenylphosphino)maleic anhydride.
[b] Cp′ = η^5-$C_5H_4CH_3$

Comparison of the infrared spectrum of $(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$ with the spectra of similar complexes involving L_2 = 2,3-bis(diphenylphosphino)-maleic anhydride listed in Tables II and III shows a shift towards lower energy in the metal carbonyl stretch absorption. The downward shift in energy suggests that the ligand 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione places more electron density on the coordinated metal atom.

Also, note in Table II that the carbonyl bands of the chelate ligands in $(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$ are shifted to lower energy compared to those of the free ligand. The shift towards lower energy suggests that the unpaired electron is localized upon the chelate ligand.

If the unpaired electron is primarily localized on the L_2' ligand, then structural distortion of the L_2' ligand is expected because the π^* orbital is occupied. Such distortions have been noted in the structures of

other 18+δ complexes containing the L_2 ligand, (ref. 7,11). The following resonance forms for the reduced L_2' ligand adequately explain these distortions:

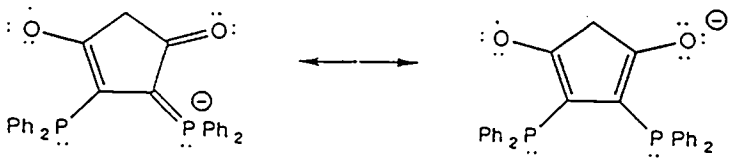


Figure 10.

Evidence for similar distortions in the $(MeCp)Mo(CO)_2(L_2'\text{-}P,P')$ complex, L_2' = 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione, may be seen in the relatively large frequency shift of the ligand carbonyl stretch bands. The shift of 150 cm^{-1} towards lower energy, resulting in absorption at 1590 and 1570 cm^{-1}, strongly suggests the presence of the resonance structures in Figure 10. The large frequency shift in ligand carbonyl stretch bands is also oberved in the following $Co(CO)_3(L_2'\text{-}P,P')$ complex.

The reaction of the $Co_2(CO)_8$ dimer with L_2' to form $Co(CO)_3(L_2'\text{-}P,P')$ follows the same general scheme except that it is not necessary to irradiate the $Co_2(CO)_8$ dimer. A toluene solution of $Co_2(CO)_8$ and 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione led to the formation of a product with infrared bands at 2081, 2033, and 2011 cm^{-1} as well as at 1964 and 1921 cm^{-1}. The product leading to absorption at 2081, 2033, and 2011 cm^{-1} is likely to be 19-electron $Co(CO)_3(L_2'\text{-}P,P')$. Comparison of the infrared spectrum with the spectra of similar 19-electron and 18-electron $Co(CO)_3L_2^+$ complexes listed in Tables IV and V shows that the spectra are very similar. This similarity suggests that the 19-electron adduct is an 18+δ complex; i.e., the complex contains Co in the +2 oxidation state and a reduced, radical anion L_2' ligand.

Table IV. Infrared Data for $Co(CO)_3L_2$ Complexes

complex	ν(C≡O), cm-1	ν(C=O), cm-1	ref.
L_2[a,d]		1838 m, 1816 w 1763 s	11
L_2'[b,e]		1742 s, 1705 vs	this work
$Co(CO)_3L_2$[a,c]	2077 s, 2027 s, 2006 vs	1747 s, 1679 s	11
$Co(CO)_3L_2$[a,d]	2080 s, 2031 s, 2009 vs	1742 s, 1670 s	11
$Co(CO)_3L_2'$[b,e]	2081 vs, 2033 s, 2011 s	1618 s, 1589 vs	this work

Table V. Infrared Data for $Co(CO)_3L_2^{+/-}$ Complexes

complex	ν(C≡O), cm-1	ν(C=O), cm-1	ref.
$[Co(CO)_3L_2^+]I^-$ [a,c]	2040 w, 2017 m, 1966 s	1845 w, 1780 s	11
$Co(CO)_4^-$[c]	1890 vs, 1857 w	1727 s, 1649 s	11
$Co(CO)_3L_2'^+$ [b,e]	1964 s	1665 s,	this
$Co(CO)_2L_2'^-$ [b,e]	1921 w	1544 s, 1510 m	work

[a]L_2= 2,3-bis(diphenylphosphino)maleic anhydride, [c]In THF, [d]In CH_2Cl_2, [b]L_2' = 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione, [e]In CH_2ClCH_2Cl.

The secondary products, leading to absorption at 1964, 1921 cm^{-1}, and several other wavenumbers hidden under product one, are most likely the 18-electron $Co(CO)_3L_2'^+$ and $Co(CO)_4^-$ species. These species are the products of the disproportionation of $Co_2(CO)_8$ by L_2', Figure 9, page 13.

CHAPTER V

CONCLUDING REMARKS

The reaction of 17-electron organometallic radicals with two-electron donor ligands yields 19-electron adducts. The stability of the 19-electron adducts depends critically on their electronic structure. The relatively stable adducts are perhaps best described as 18-electron complexes with reduced ligands, i.e., 18+δ complexes. The relative stability of the 18+δ complexes is attributed to the fact that the unpaired electron is not in a metal-ligand antibonding orbital but rather in a ligand-based π^* orbital, Figure 1, page 4.

This paper reports the successful generation of the 18+δ $(MeCp)Mo(CO)_2L_2'$ and $Co(CO)_3L_2'$ complexes containing the L_2' ligand 2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione. The $Co(CO)_3L_2'$ complex, however, is considerably less stable and disproportionates, Figure 9, page 13. The instability of $Co(CO)_3L_2'$ is thought to be attributed to the decreased ability of the L_2' ligand to delocalize the unpaired electron.

REFERENCES

1. D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.

2. K.B Wiberg, Laboratory Technique in Organic Chemistry, McGraw-Hill, New York, 1960.

3. R. Birdwhistell, P. Hackett, A.R. Manning; Journal of Organometallic Chemistry, 157, 239-241, 1978.

4. A. Winston, R.N. Kemper; Tetrahedron, 27, 543-548, 1971.

5. Comprehensive Organometallic Chemistry, 5, 30-33, 1982.

6. D. Fenske, J.H. Becher; Chem. Ber., 108, 2115-2123, 1975.

7. D. Fenske, Chem. Ber., 112, 363-375, 1979.

8. D. Fenske, J.H. Becher, M. Heymann; Z. Anorg. Allg. Chem., 475, 27-34, 1981.

9. R.B. King, Organometallic Syntheses, Academic, New York, 1, 114-116, 1965.

10. F. Mao, S.K. Sur, D.R. Tyler; J. Am. Chem. Soc., 111, 7627-7628, 1989.

11. F. Mao, D.R. Tyler, D. Keszler; J. Am. Chem. Soc., 111, 130-134, 1989.

12. F. Mao, D.R. Tyler; Coordination Chemistry Reviews, 97, 119-140, 1990.

13. D. Wittenberg, H. Gilman; Journal of Organic Chemistry, 23, 1063, 1958.

14. W.C. Trogler (Ed), Organometallic Radical Processes, Elsevier, Amsterdam, 1990.

15. F. Mao, C.E. Philbin, T.J.R. Weakley, D.R. Tyler; Organomet., 9, 1510-1516, 1990.

16. J. Organomet. Chem., 99, 263-268, 1975.

GLOSSARY

1. **Coordination complex:** a compound in which an atom or group of atoms is bound to the central atom by a shared pair of electrons supplied by the coordinated group and not by the central atom.

2. **Dimer:** a compound formed by the combination of two identical molecules.

3. **19-electron adduct:** the compound formed when a 17-electron compound is bound to a two-electron donor ligand.

4. **Energy of activation:** the energy barrier that must be overcome in order for the reaction to proceed.

5. **Homogeneous catalysis:** catalysis in which the catalyst and the reagents are in the same phase.

6. **Homolytic cleavage:** the breaking of a chemical bond resulting in two identical molecules.

7. **Ligand:** an atom, group, ion, radical or molecule which bonds to a metal atom or metal ion.

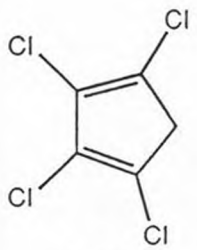
8. **Organometallic compounds:** compounds containing a carbon-metal bond.

9. **Transition metal:** metallic elements with unfilled d orbital electrons.

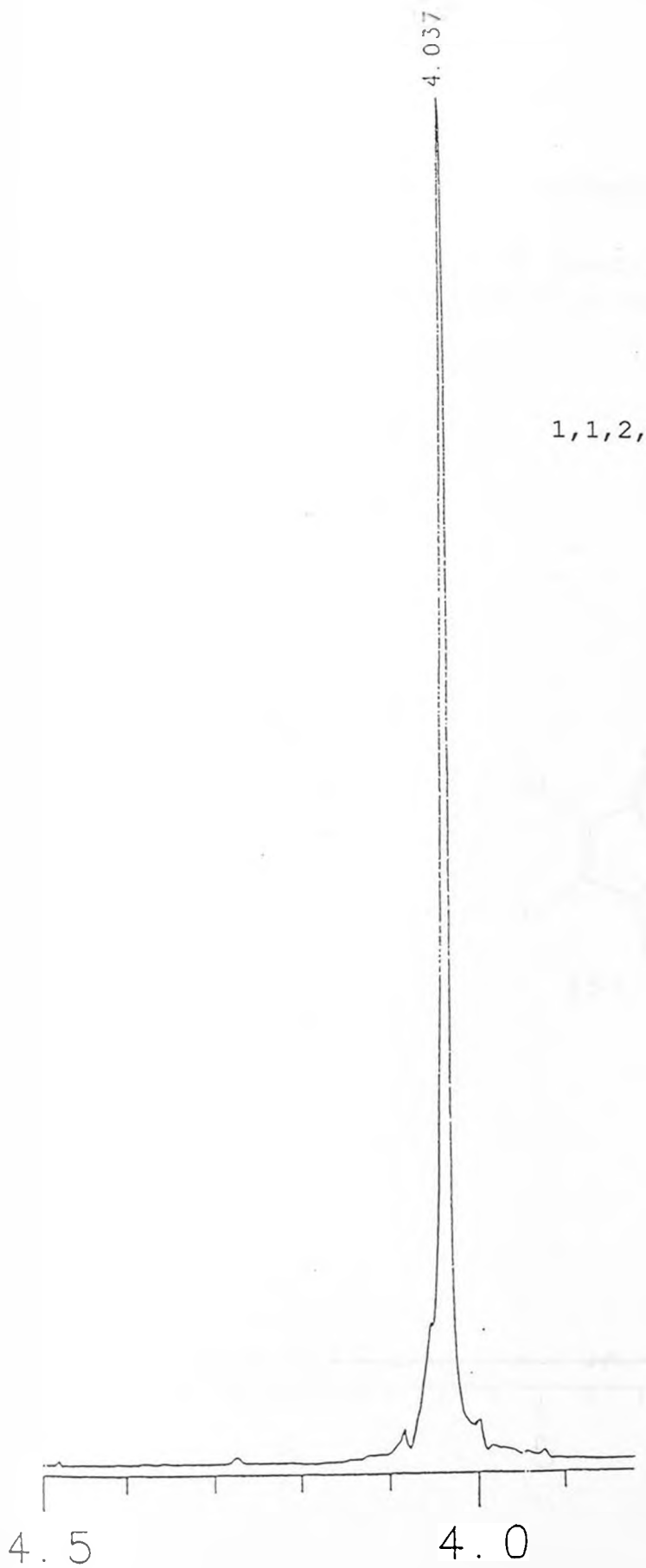
APPENDIX A: PROTON NMR

SPECTRUM 1

^{1}H spectrum of
1,2,3,4-tetrachloro-1,3-cyclopentadiene

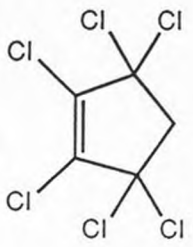


(5)



SPECTRUM 2

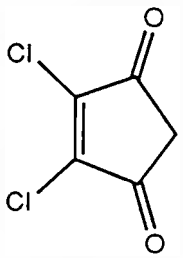
^{1}H spectrum of
1,1,2,3,4,4-hexachloro-2-cyclopentene



(6)

SPECTRUM 3

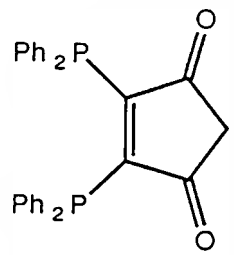
^{1}H spectrum of
2,3-dichloro-2-cyclopenten-1,4-dione



(5)

SPECTRUM 4

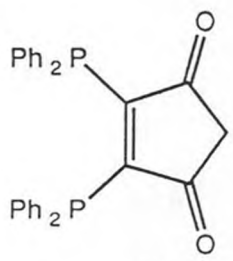
^1H spectrum of
2,3-bis(diphenylphosphino)-2-cyclopenten-1,4-dione



(6)

SPECTRUM 5

^1H spectrum of
2,3-bis(diphenylphosphino)-2-
cyclopenten-1,4-dione

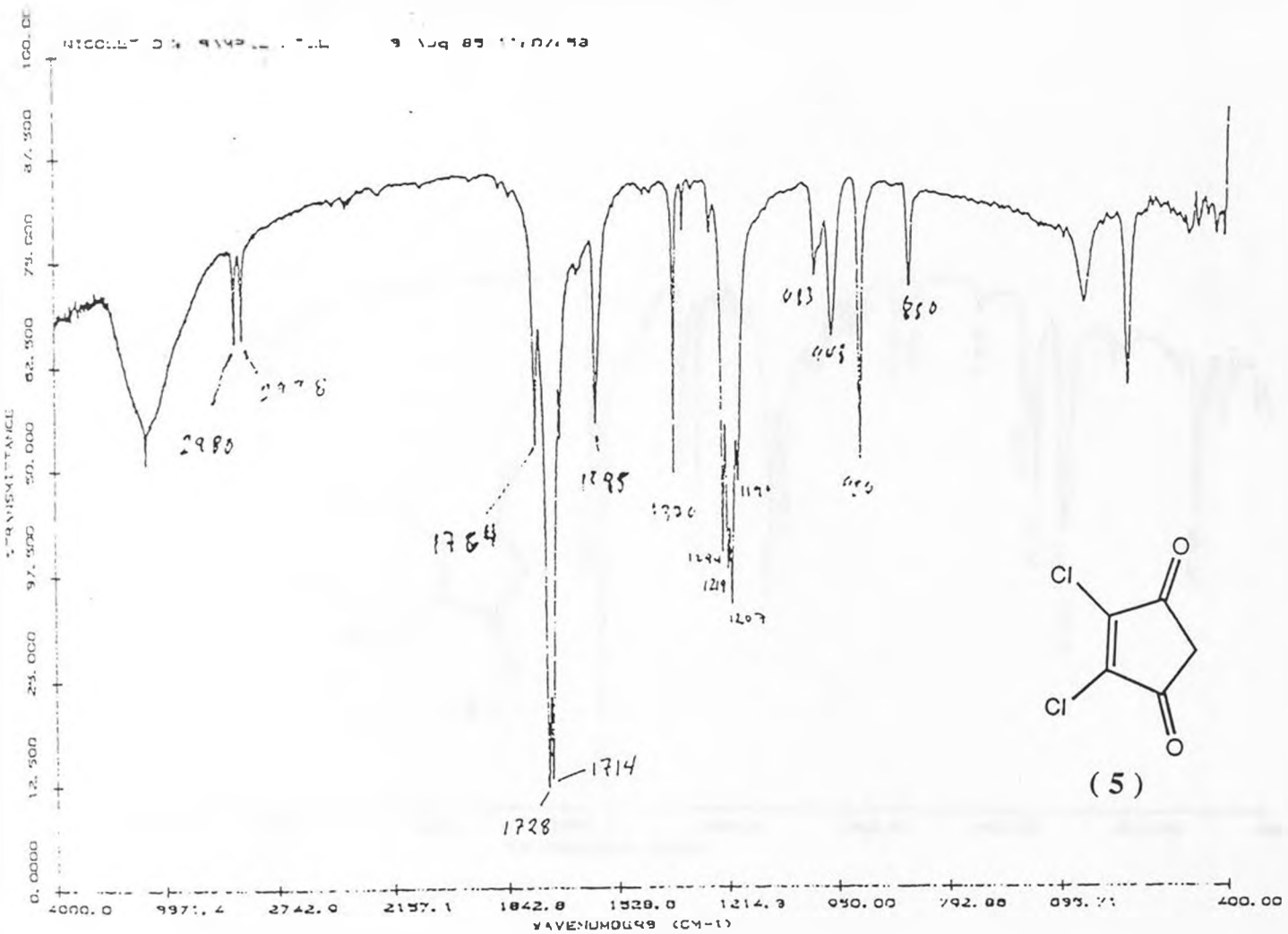


(6)

APPENDIX B: INFRARED ABSORPTION

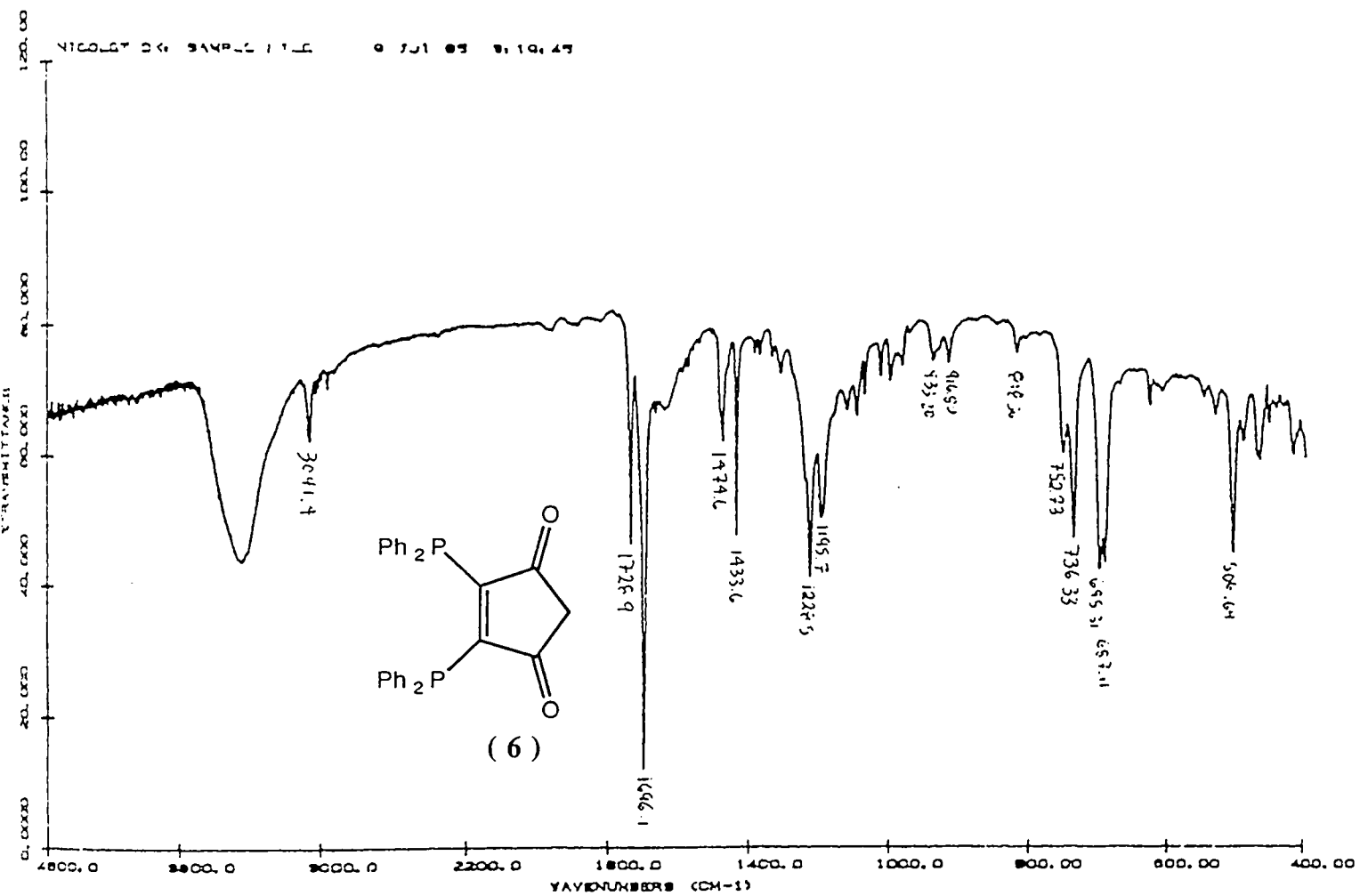
SPECTRUM 6

IR spectrum of
2,3-dichloro-2-cyclopenten-1,4-dione



SPECTRUM 7

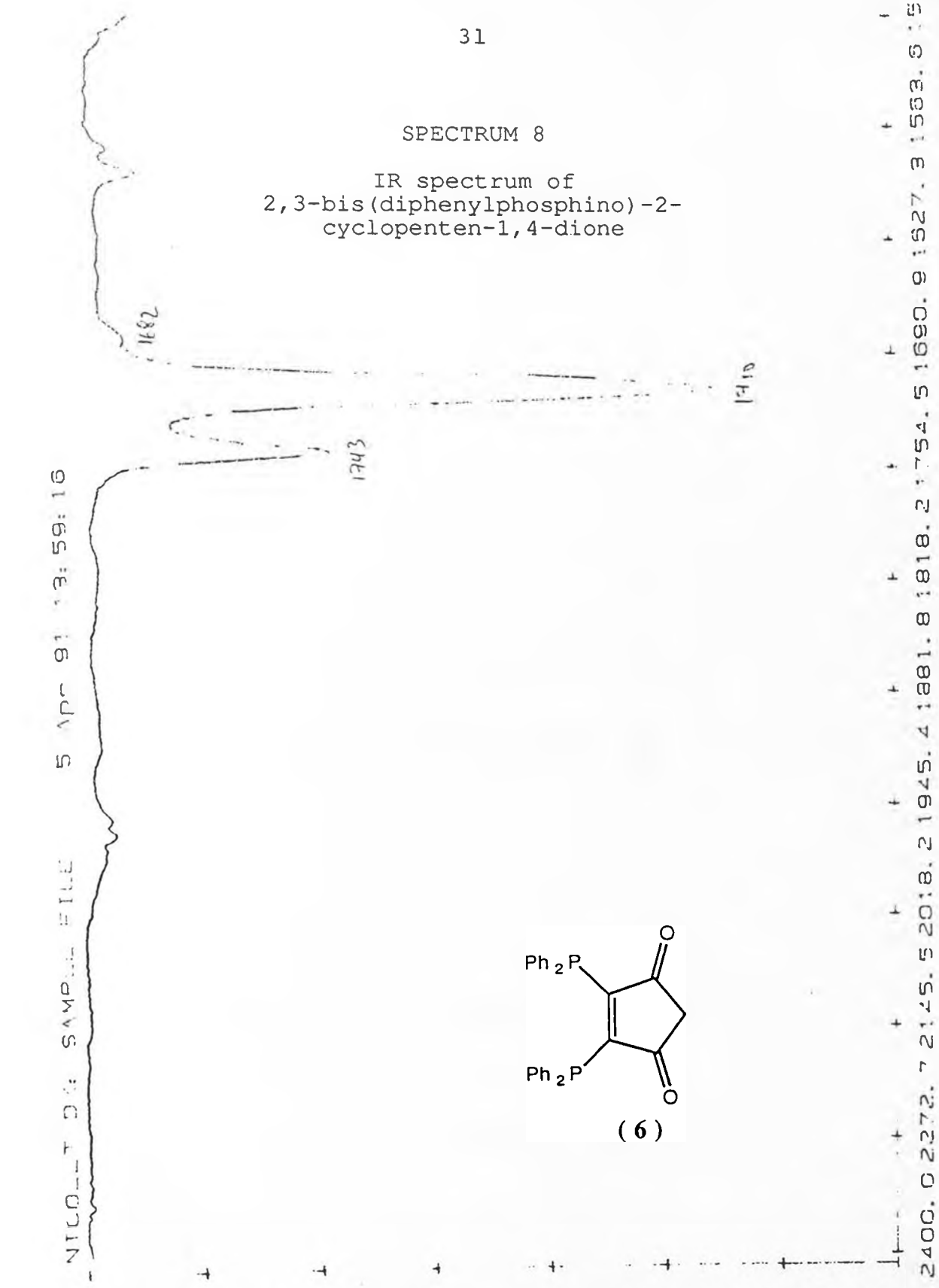
IR spectrum of
2,3-bis(diphenylphosphino)-2-
cyclopenten-1,4-dione



(6)

SPECTRUM 8

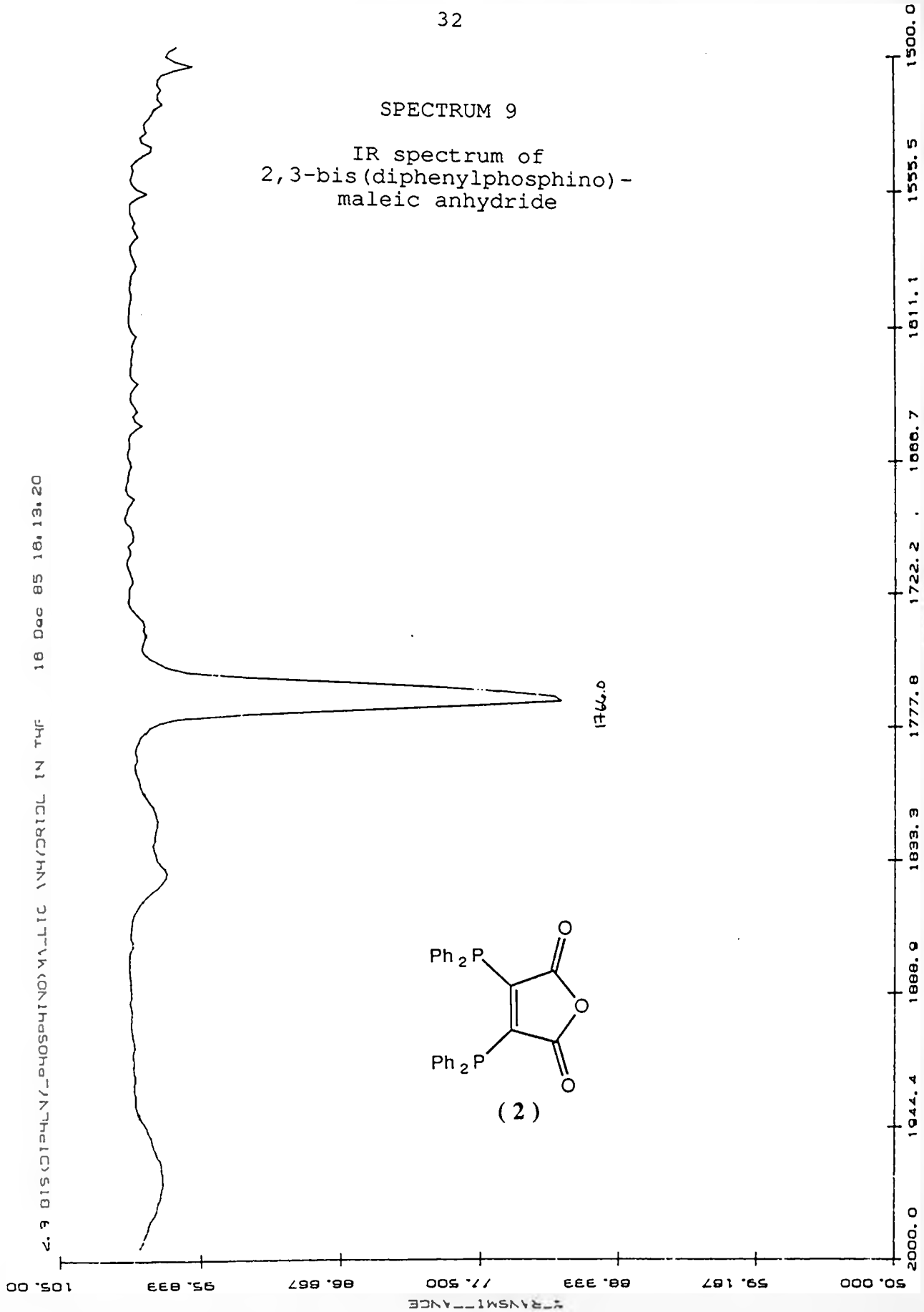
IR spectrum of
2,3-bis(diphenylphosphino)-2-
cyclopenten-1,4-dione



(6)

SPECTRUM 9

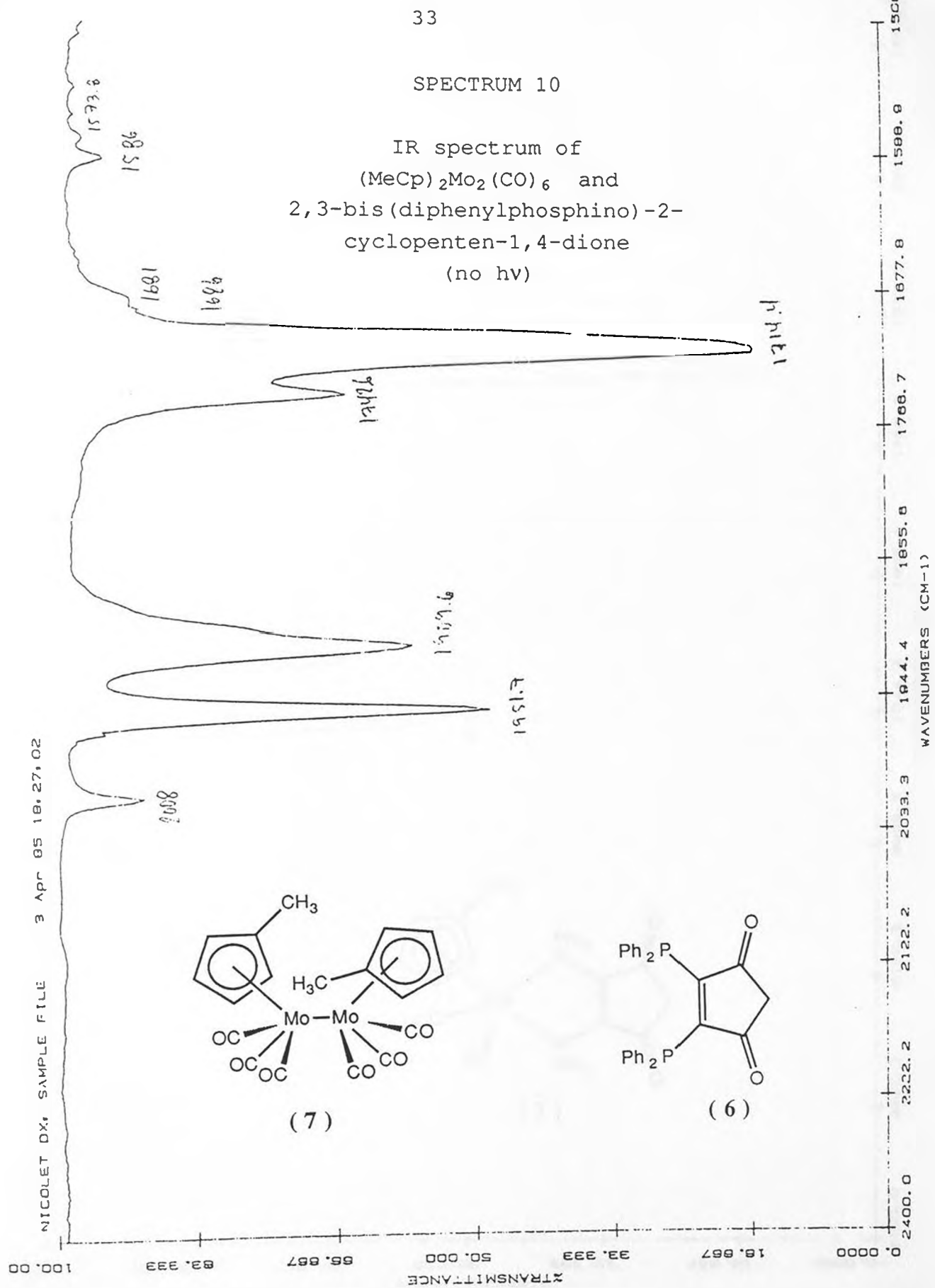
IR spectrum of
2,3-bis(diphenylphosphino)-
maleic anhydride



(2)

SPECTRUM 10

IR spectrum of
$(MeCp)_2Mo_2(CO)_6$ and
2,3-bis(diphenylphosphino)-2-
cyclopenten-1,4-dione
(no hν)

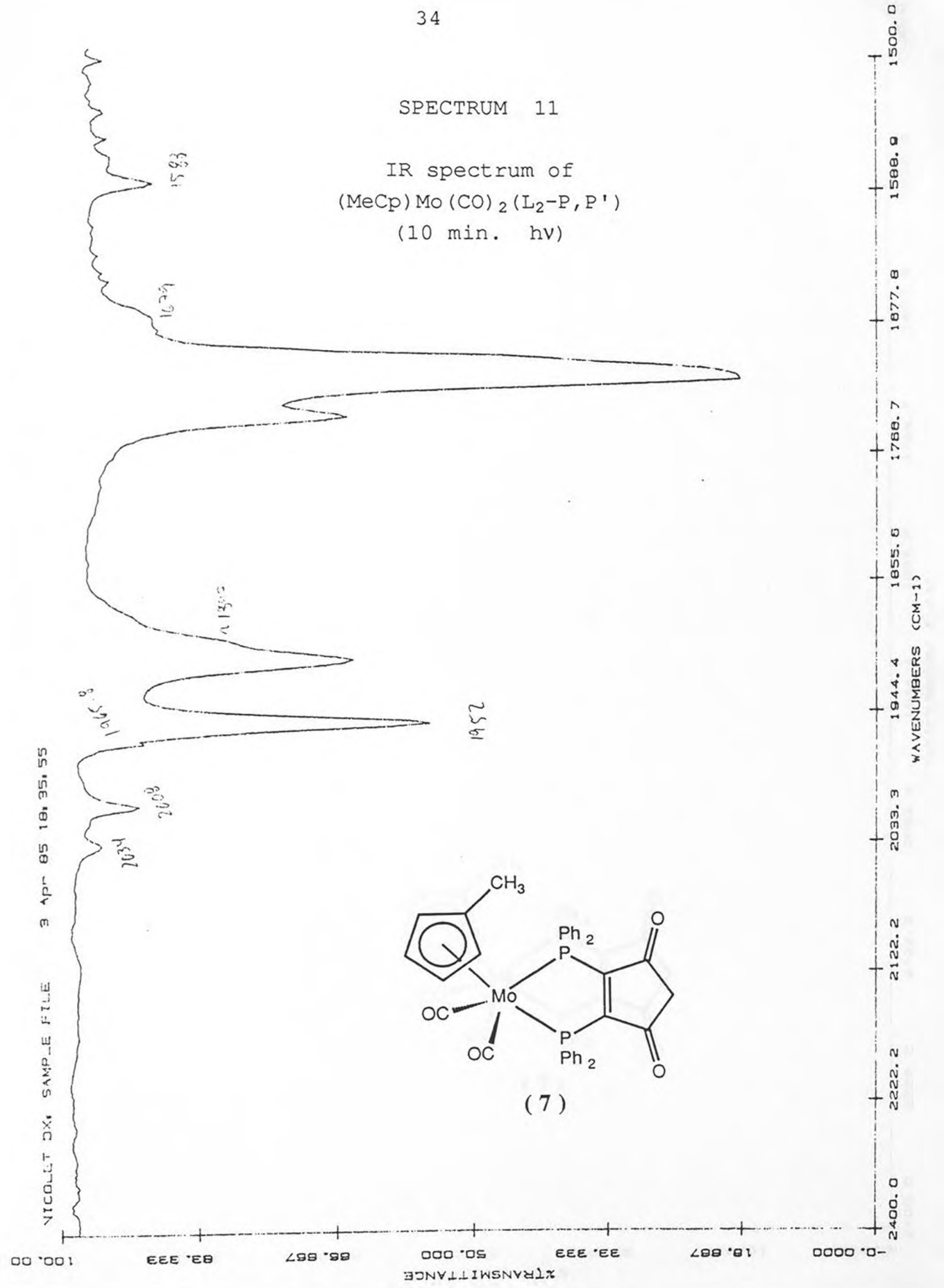


(7)

(6)

SPECTRUM 11

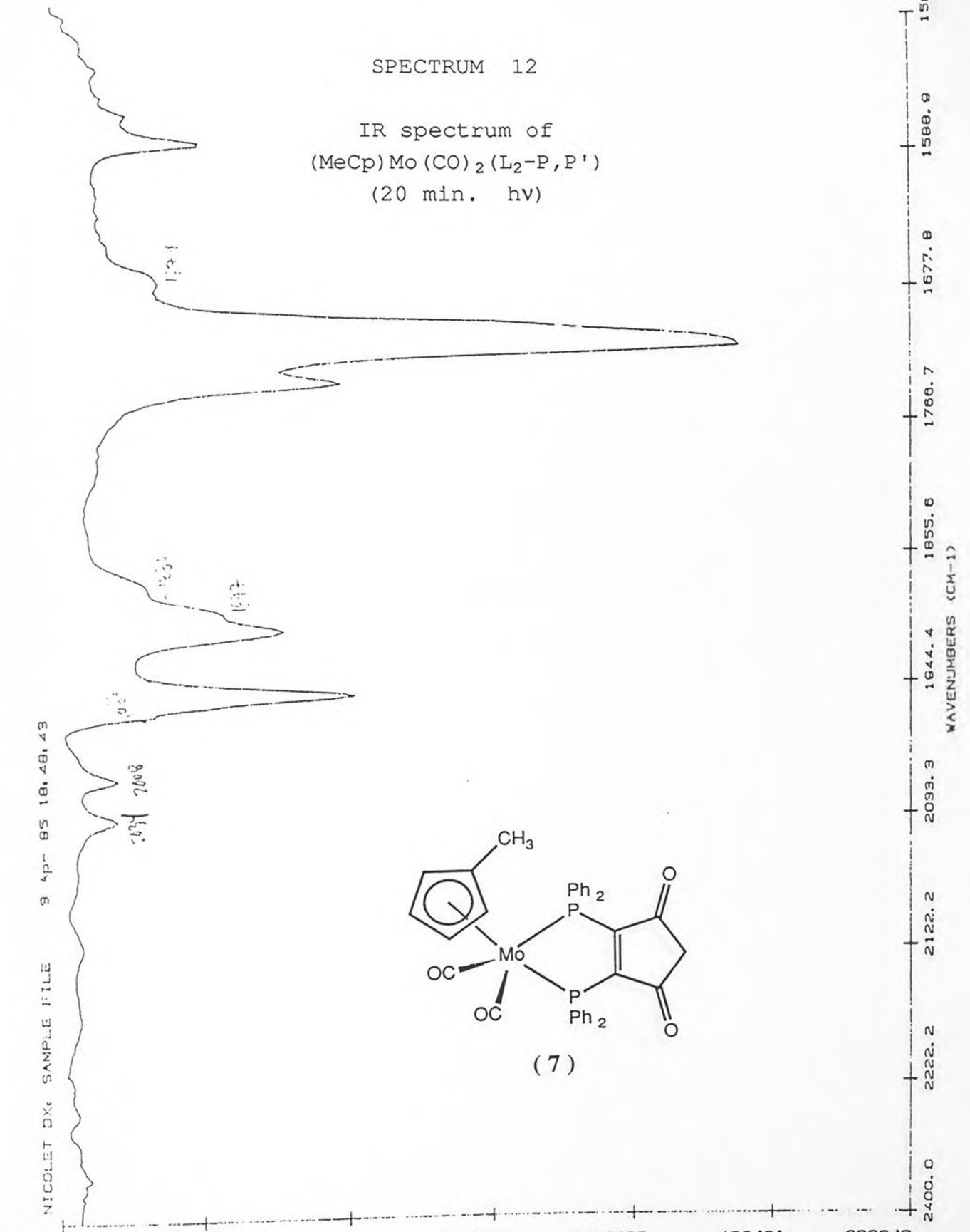
IR spectrum of
$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$
(10 min. hν)



(7)

SPECTRUM 12

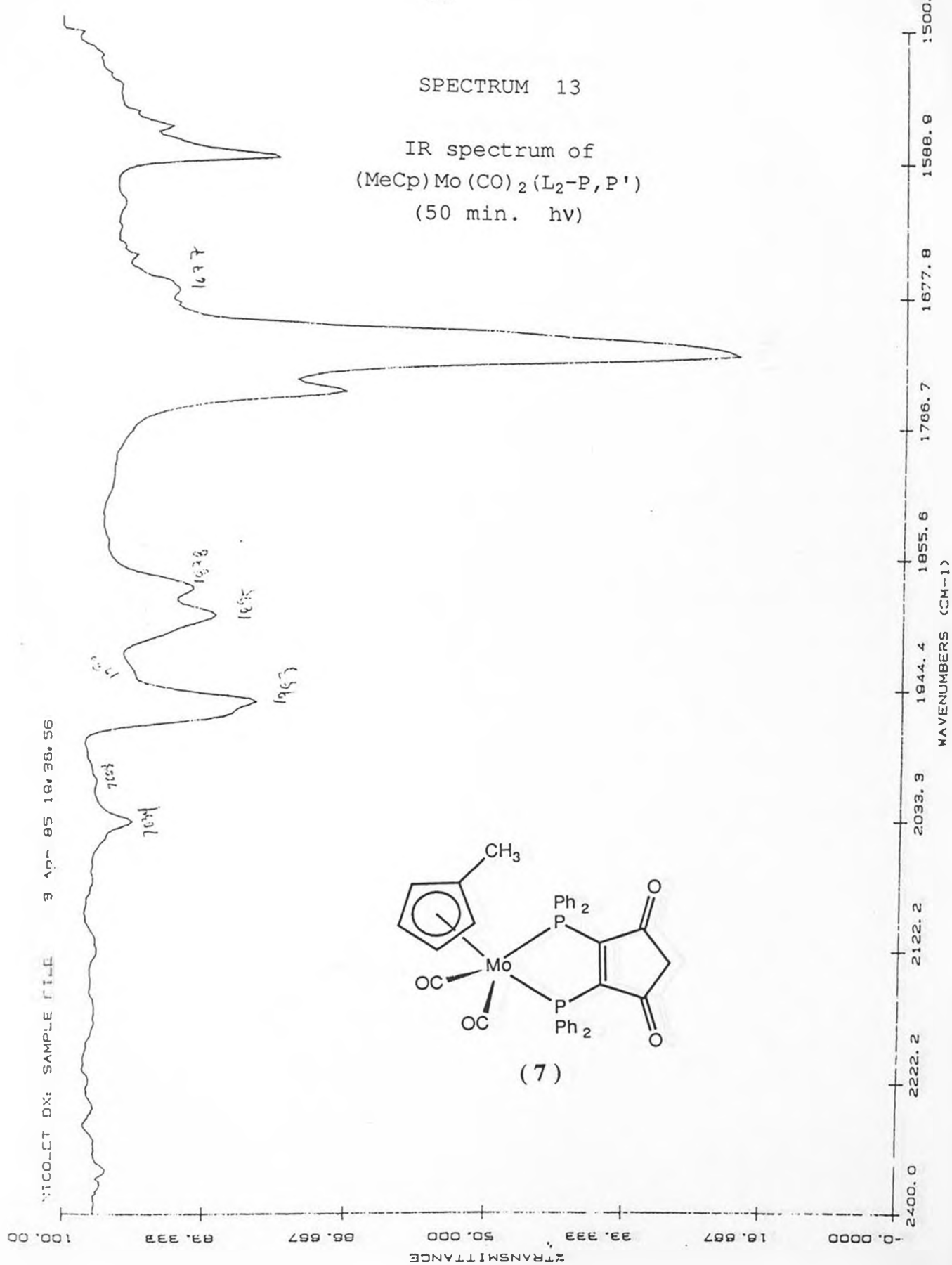
IR spectrum of
$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$
(20 min. hν)



(7)

SPECTRUM 13

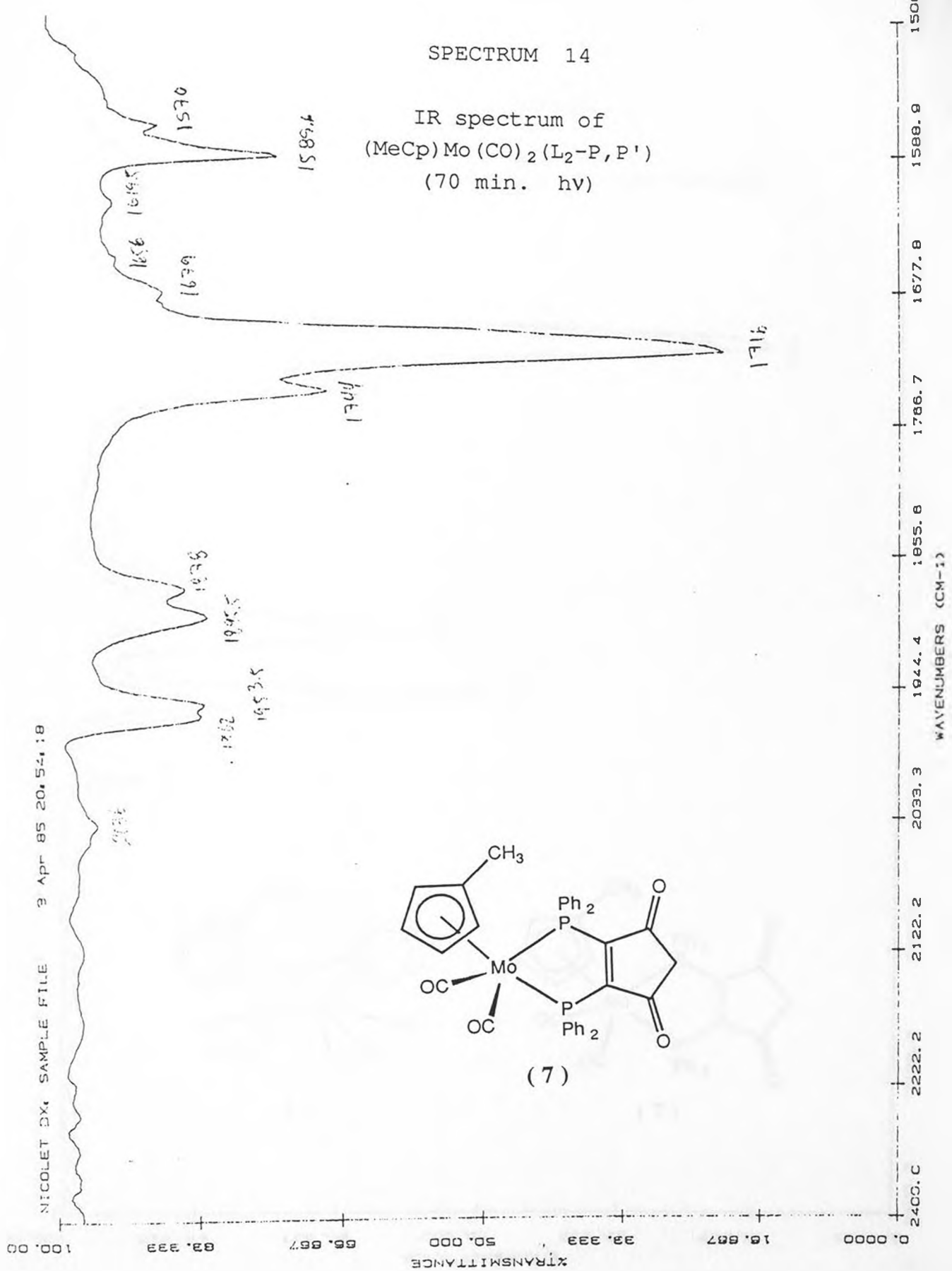
IR spectrum of
$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$
(50 min. hν)



(7)

SPECTRUM 14

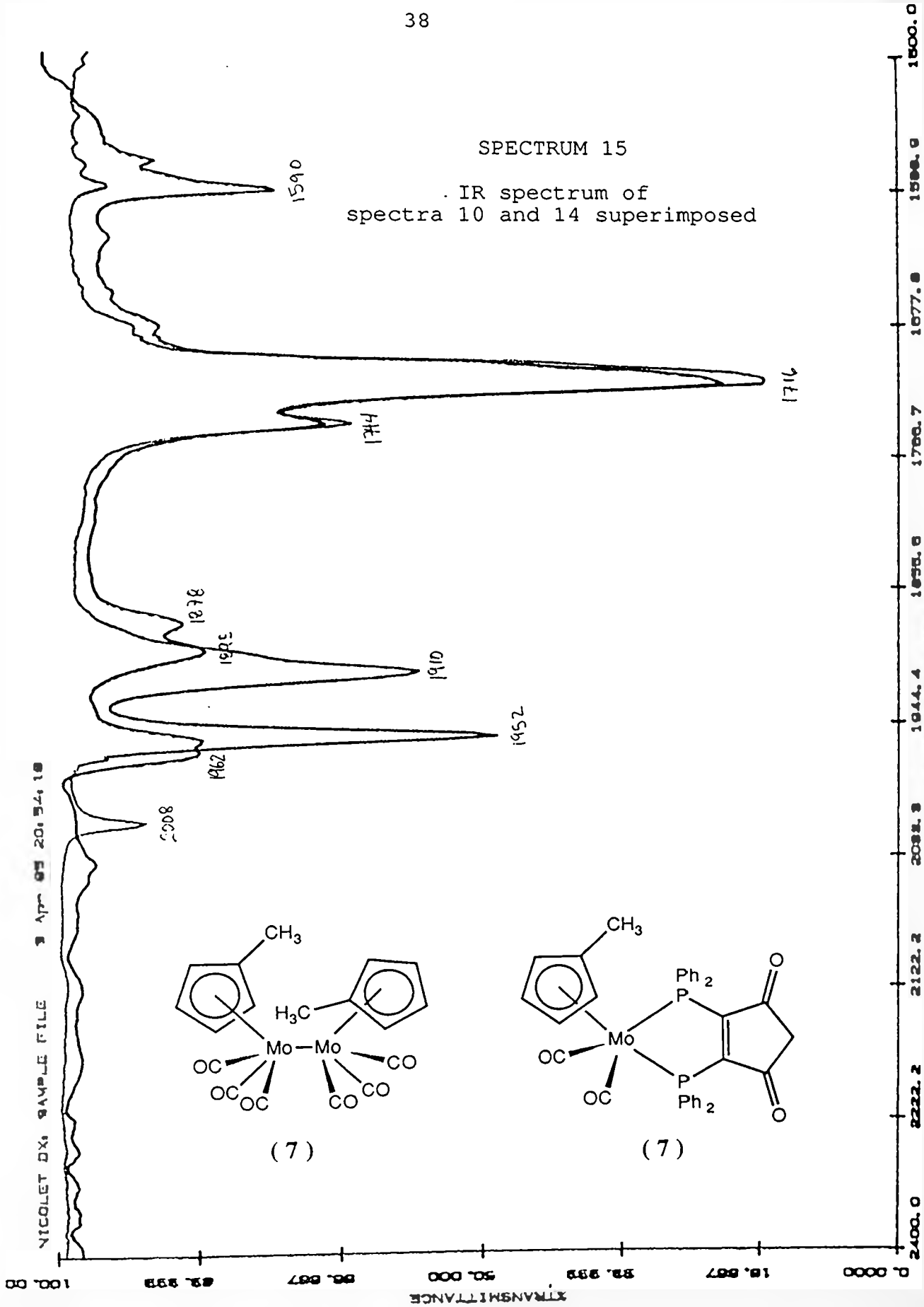
IR spectrum of
$(MeCp)Mo(CO)_2(L_2\text{-}P,P')$
(70 min. hν)



(7)

SPECTRUM 15

IR spectrum of
spectra 10 and 14 superimposed

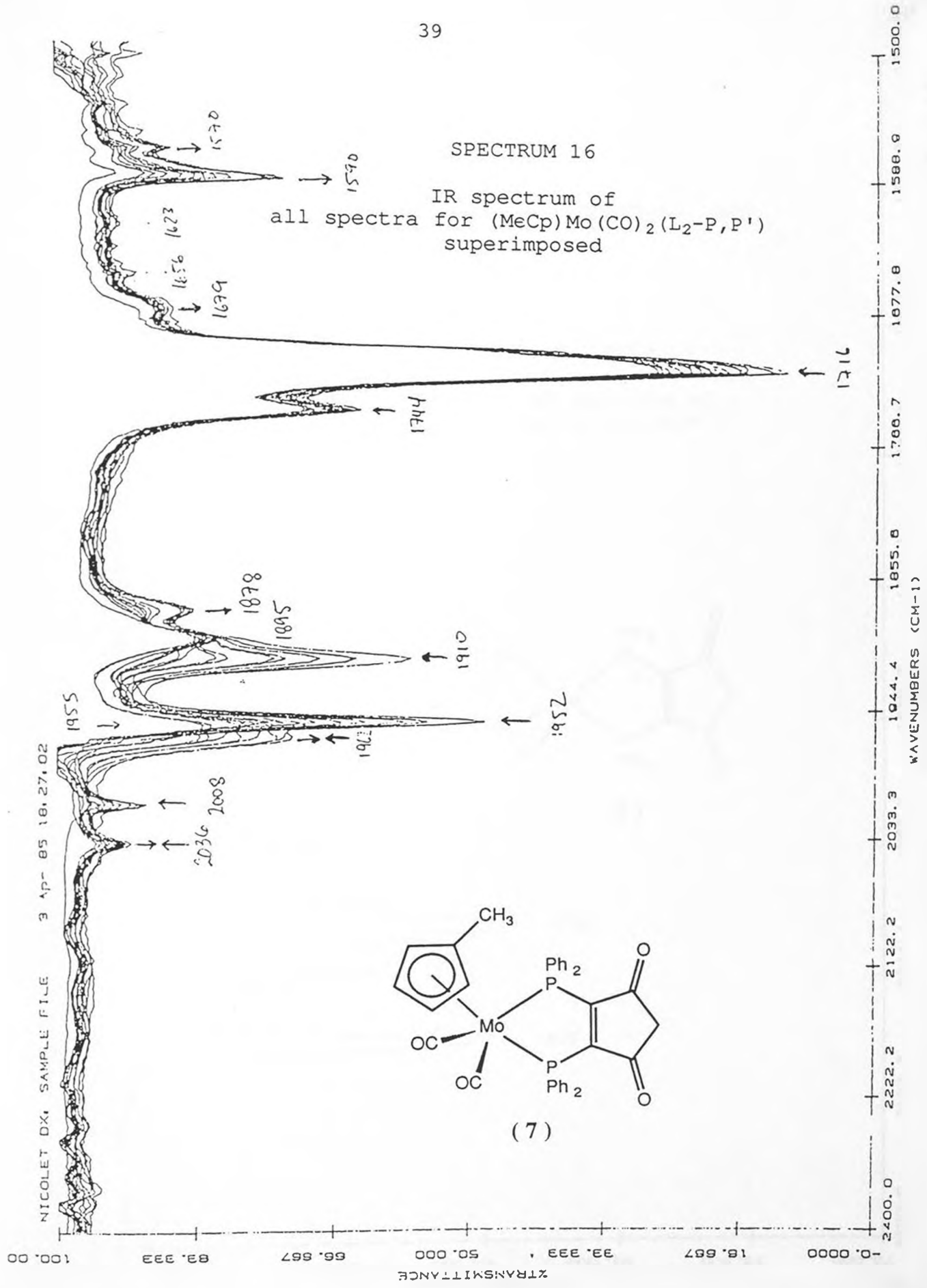


(7)

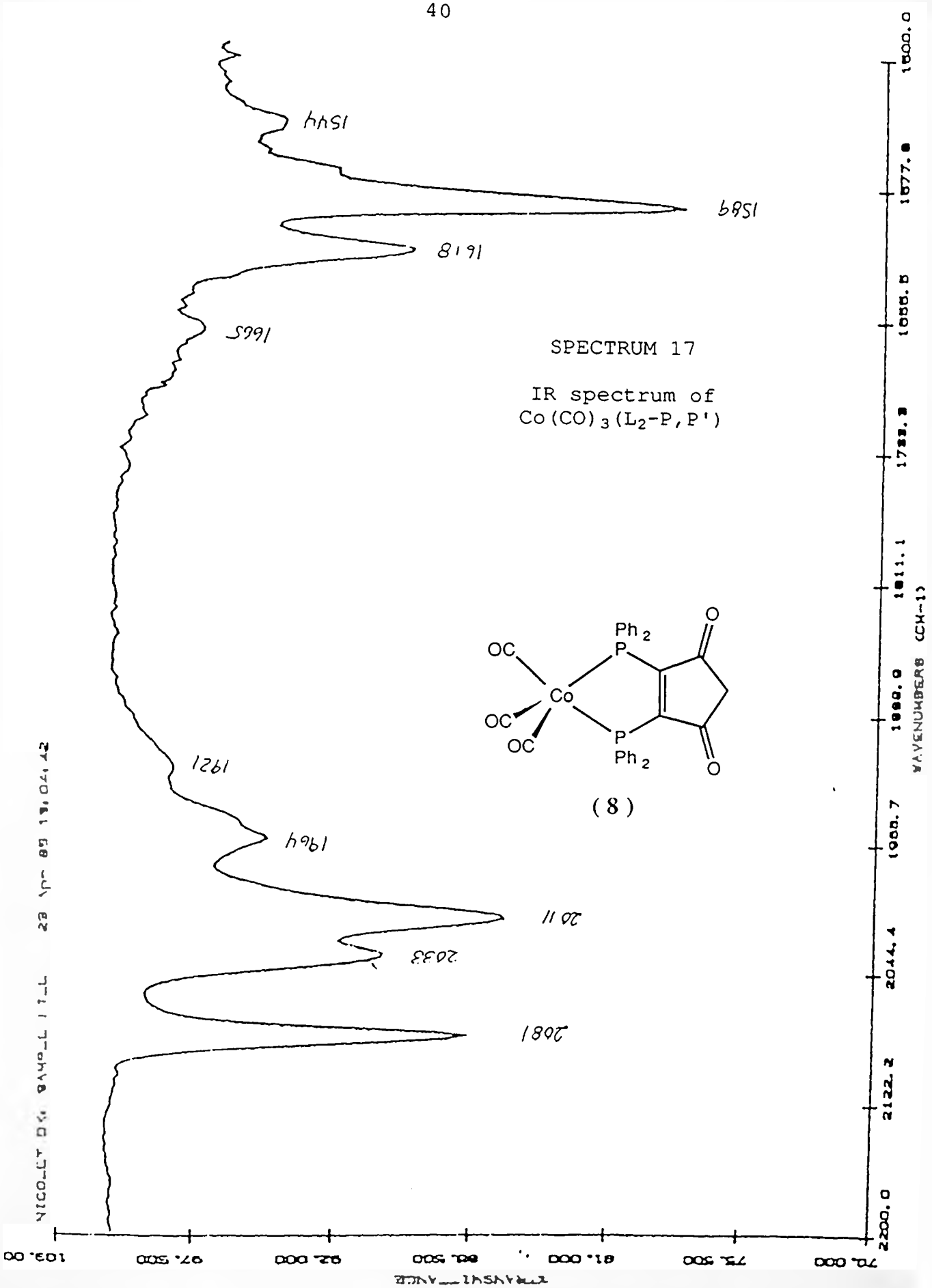
(7)

SPECTRUM 16

IR spectrum of
all spectra for $(MeCp)Mo(CO)_2(L_2\text{-}P,P')$
superimposed



(7)



SPECTRUM 17

IR spectrum of
$Co(CO)_3(L_2\text{-}P,P')$

(8)