

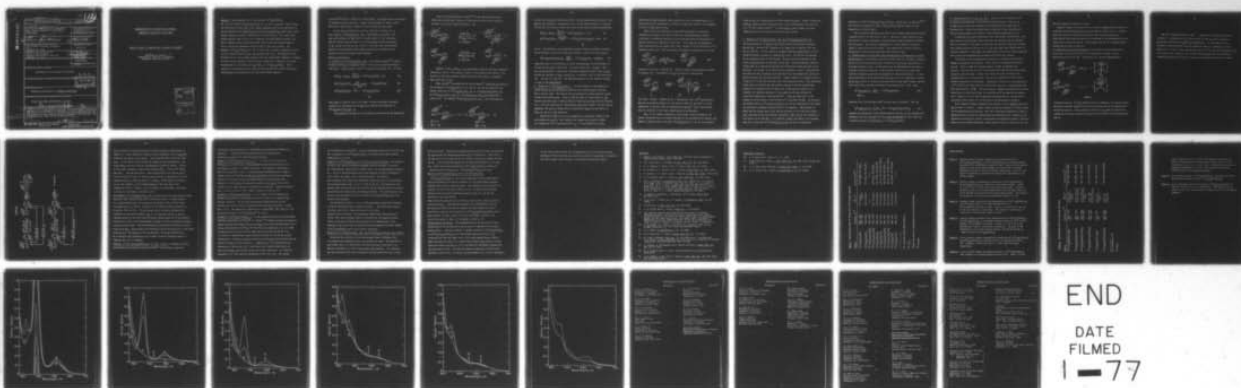
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PHOTOGENERATION OF DINUCLEAR METAL CARBONYLS
CONTAINING A METAL-METAL TRIPLE BOND

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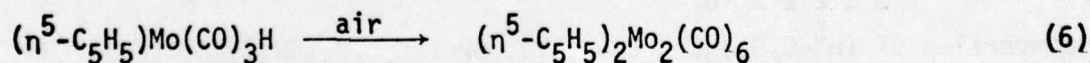
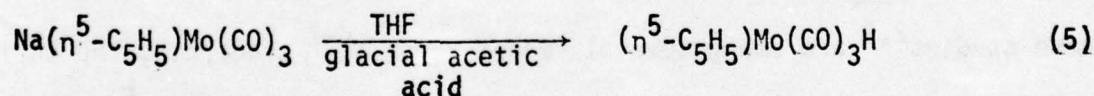
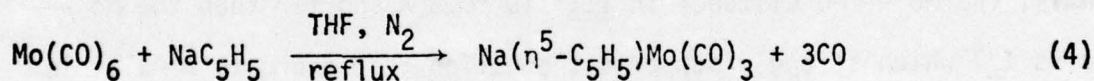
Abstract: The photogeneration of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{M}(\text{CO})_2]$ ($\text{M} = \text{Cr}, \text{Mo}$) is reported. These species are formulated as metal-metal triple bonded complexes which can be generated from the corresponding $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{M}(\text{CO})_3]_2$ metal-metal single bonded complexes by either irradiation at 25° or by heating. All of the triple bonded complexes take up CO at 25° to generate the single bonded complexes, but the Cr complexes require high CO pressure, while the Mo and W species take up CO at or below one atmosphere with half-times of less than a minute. The complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Mo}, \text{W}$) react with a variety of acetylenes at 25° to yield complexes having a M_2C_2 "tetrahedrane-like" core. The mechanism of the formation of the triple bonded complexes from the single bonded complexes is proposed to first involve cleavage of the metal-metal single bond to generate 17-electron intermediates of the formula $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ or $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{M}(\text{CO})_3$. These species are coordinatively labile and lose CO dissociatively yielding 15-electron intermediates which dimerize to give the triple bonded complexes.

structurally⁸ and has a short Cr-Cr (triple) bond. The single bonded hexacarbonyl Cr analogue of VII is not known. Despite some attempts,⁹ no simple ligand additions to VII without cleavage of the Cr-Cr bond have been found.

In this paper we extend the chemistry indicated in reaction (2) to the W complex, $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$, VIII. Additionally, we outline a new, high yield synthesis of VIII which has proven useful in this laboratory. Some new thermal reaction chemistry is also detailed for the Cr complexes V, VI, and VII, but the key new results in this paper deal with the photo-generation of metal-metal triple bonded complexes by irradiation of the analogous metal-metal single bonded complexes.

Results and Discussion

a. Synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$, VIII. The original synthesis¹⁰ of VIII is by heating $\text{W}(\text{CO})_6$ and cyclopentadiene to $\sim 300^\circ$ to give the desired product in $\sim 30\%$ yield. A good synthetic route¹¹ to IV given in reactions (4) - (6) only

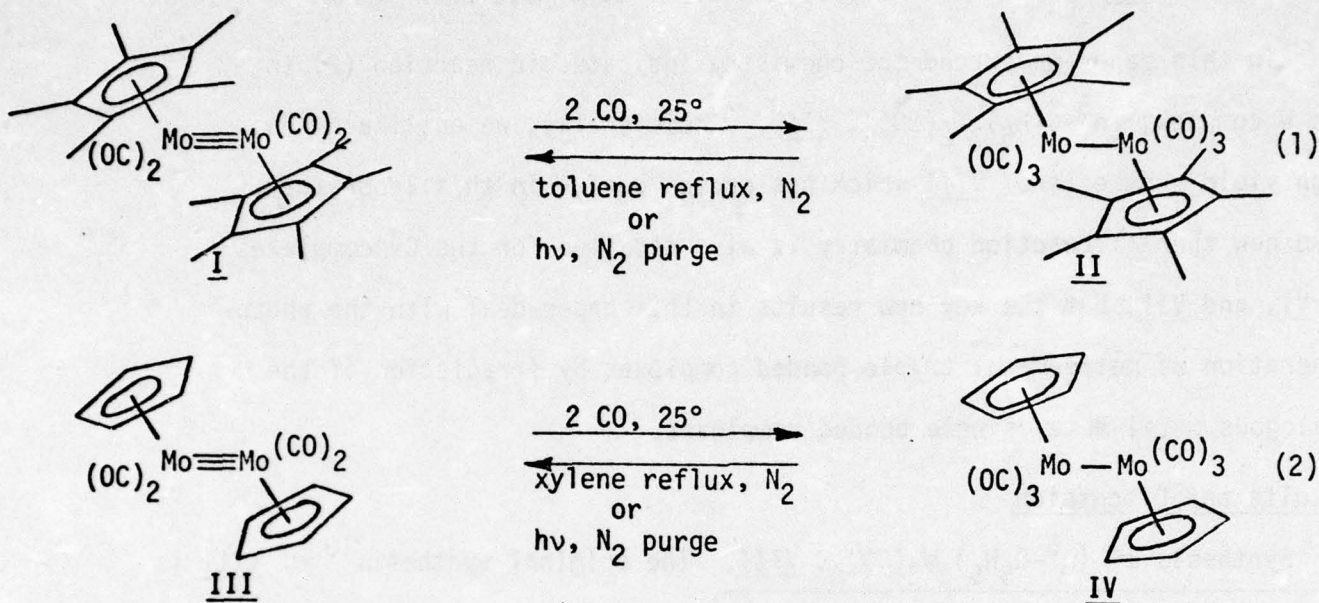


IV

gives VIII in yields of $< 10\%$ in our hands. We have discovered a synthetic procedure for the preparation of VIII which involves the thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$, IX.

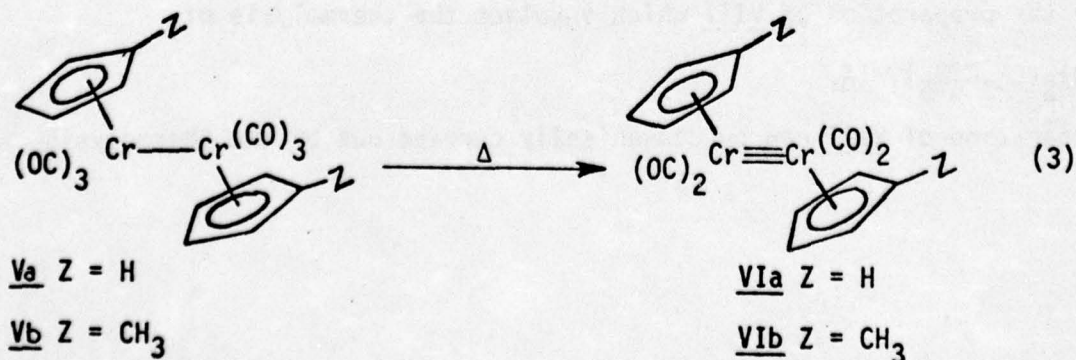
The preparation of VIII can be conveniently carried out by the thermolysis

There are recent preliminary reports^{2,3} of the reversible addition of simple two-electron donor ligands to a metal-metal triple bond as schemed in reactions (1) and (2) involving species I - IV.

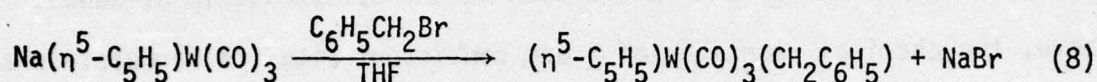
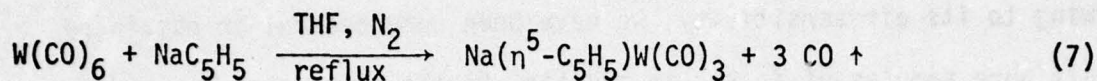


Addition of PPh_3 , $\text{P}(\text{OCH}_3)_3$, I_2 , or acetylenes to III has also been reported.³ Importantly, the Mo — Mo distance in III³ is $\sim 0.8 \text{ \AA}$ shorter than the Mo — Mo distance in IV⁴ which strongly supports the notion that there is a multiple metal-metal bond in III.

These studies^{2,3} are among several recent reports⁴⁻⁷ concerning the chemistry of the species $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). We note the report⁵ of the thermal conversion of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$, Va, or $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))_2\text{Cr}_2(\text{CO})_6$, Vb, to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4$, VIa, and $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_3))_2\text{Cr}_2(\text{CO})_4$, VIb, respectively, reaction (3). The complex $(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Cr}_2(\text{CO})_4$, VII, is well characterized

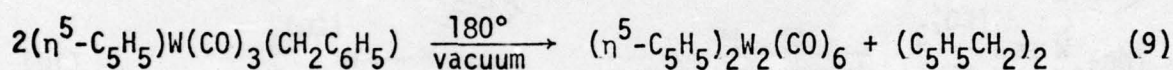


of IX in an evacuated, sealed tube at 180°. We have prepared tens of grams of pure VIII by this procedure. Preparation of IX is by the route indicated in reactions (7) and (8), and the pale yellow solid IX can be purified by column chromatography



IX

in air. The thermolysis of IX apparently proceeds cleanly according to reaction (9) giving VIII in good yield along with bibenzyl. Reaction (9) gives VIII in



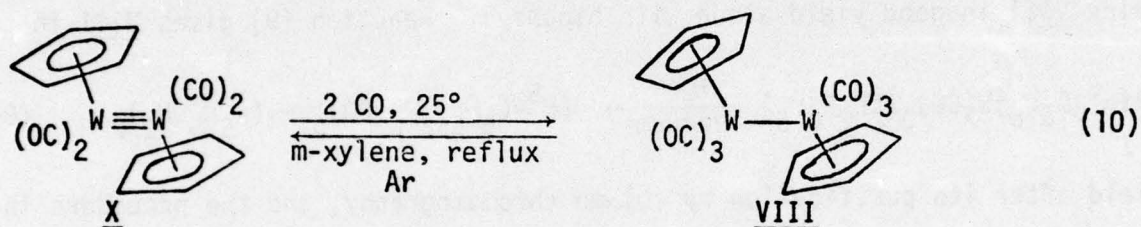
~95% yield after its purification by column chromatography, and the procedure in (7) and (8) gives IX in >98% yield. The overall yield, then, of VIII is >90%. This yield represents a substantial improvement compared to other routes to VIII, and the key precursor to VIII, compound IX, is isolable, inert at room temperature, and not very air sensitive. The detailed procedure for the synthesis of VIII is given in the Experimental.

b. Generation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$, X. In strict analogy to the chemistry of the Mo species III and IV,^{2,3} complex X results from refluxing VIII in m-xylene with a slow Ar purge. The reaction can be monitored by infrared spectral changes in the CO stretching region. Peaks at 1950 and 1900 cm⁻¹ associated with VIII decline, and peaks grow at 1885 and 1830 cm⁻¹ which we associate with the formation of X. From the compilation of spectroscopic data given in Table I for the relevant complexes, the spectral changes for the conversion of VIII to X are similar to those for the IV to III conversion.

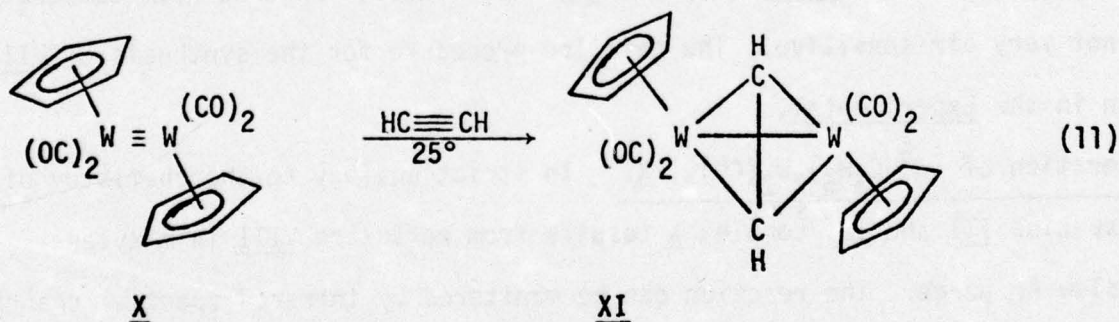
Conversion of VIII to X is also accompanied by substantial changes in the uv-vis absorption spectra. Most notably, the intense near-uv band at ~360nm ($\epsilon \approx 17,000 \text{ l mol}^{-1} \text{ cm}^{-1}$) associated with a $\sigma_b \rightarrow \sigma^*$ transition⁶ in the single

bonded complex VIII disappears upon conversion to the triple bonded species, X. Consistent with its formulation, X exhibits a singlet pmr signal at 4.78 τ compared to 4.67 τ for VIII, both in CDCl_3 .

Owing to its air sensitivity, we have been unsuccessful in obtaining rigorously pure samples of X. But in addition to the spectroscopic evidence cited above, two chemical reactions of X are consistent with its formulation as a species containing a metal-metal triple bond. First, VIII can be regenerated from X quantitatively and rapidly (half-times < minute) at 25° by the passage of CO through solutions of X. That is, reaction (10) appears to obtain just as for the



analogous Mo species in reaction (2). Second, X reacts with acetylenes according to reaction (11). The addition of C_2H_2 to X occurs to yield XI with



half-times < minute. Species XI has a "tetrahedrane-like" core.¹² Spectroscopic data for the acetylene adducts of X are given in Table II, and there is a good resemblance to the data shown for analogous Mo complexes.³ Clean, spectroscopic data for reactions of the triple bonded species are given below.

Thus, in all respects (generation, spectroscopy, reaction chemistry) the species designated here as X appears analogous to the corresponding Mo complex, III. Complex X completes the set of three $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes.

There are few well characterized W-W triple bonded complexes. Indeed, recently the $W_2(NR_2)_6$ complex has been characterized by X-ray crystallography, the first for a $W \equiv W$ triple bonded complex.¹³ For the $W_2(NR_2)_6$ complex though, no simple ligand additions to the triple bond have yet been reported.

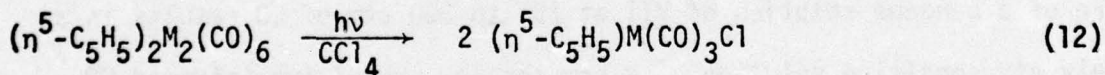
c. Reactions of $(\eta^5-C_5H_5)_2Cr_2(CO)_4$, VIa, and $(\eta^5-C_5(CH_3)_5)_2Cr_2(CO)_4$, VII.

The ready conversion of complexes Va and Vb to their triple bonded analogues, VIa and VIb, reaction (3)⁵, prompted us to compare the Cr complexes with the Mo and W species. In fact, hoping to synthesize $[(\eta^5-C_5(CH_3)_5)Cr(CO)_3]_2$, we first passed CO through a solution of compound VII at 25°. No reaction was observed. Nor do acetylenes react at 25° with VII. We then turned our attention to the simple cyclopentadienyl Cr complexes, Va and VIa. Passing CO through a solution of VIa leads to no detectable reaction, and in particular, complex Va could not be generated. As for VII, no 25° reaction with acetylenes is found. Convinced that one should be able to generate Va by addition of CO, we attempted the reaction of VIa and CO under more forcing conditions. Indeed, exposure of a benzene solution of VIa at 25° to 100 atm of CO does lead to the generation of Va. This interesting result led us to attempt the high pressure reaction of CO with compound VII. Exposure of a benzene solution of VII at 25° to 300 atm of CO results in an extremely air sensitive solution of a new complex exhibiting infrared CO stretching frequencies at 1985 and 1900 cm^{-1} . These new bands grow at the expense of the two bands at 1876 and 1857 cm^{-1} associated with VII. We associate the product bands to $(\eta^5-C_5(CH_3)_5)_2Cr_2(CO)_6$, but the air sensitivity of the complex has precluded a complete characterization of the compound. There remains no doubt that the product does result from the addition of CO to the $Cr \equiv Cr$ triple bond, and based on the high pressure conversion of VIa to Va we are confident of the reaction of CO with VII. It is possible, though, that there is an extremely weak Cr-Cr single bond in $(\eta^5-C_5(CH_3)_5)_2Cr_2(CO)_6$ and that it dissociates

thermally to yield $(\eta^5\text{-C}_5\text{(CH}_3)_5\text{)Cr(CO)}_3$ radicals. Even for Va it is believed^{7e,14} that thermal dissociation to yield $(\eta^5\text{-C}_5\text{H}_5\text{)Cr(CO)}_3$ radicals occurs at room temperature or slightly above.

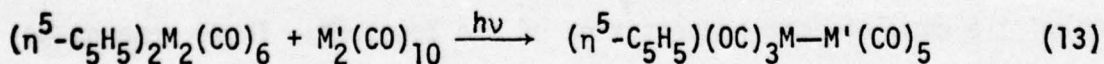
The CO addition experiments with the Cr triple bonded complexes now provides a complete picture for the triad Cr, Mo, W. The lack of ready reactivity of CO with the $\text{Cr}\equiv\text{Cr}$ species indicates a large activation energy compared to the $\text{Mo}\equiv\text{Mo}$ and $\text{W}\equiv\text{W}$ species. This may be a consequence of a larger degree of structural change in adding CO to the $\text{Cr}\equiv\text{Cr}$ bond. These speculations could be tested by thermochemistry and an X-ray structural investigation of Vla.

d. Photogeneration of Metal-Metal Triple Bonded Species and Mechanism of Triple Bond Formation. We mentioned in our earlier note² that it is possible to generate species I from II and III from IV by irradiation of II and IV, respectively, in N_2 purged solutions at 25° . We now assert that the photogeneration procedure is a valuable synthetic technique in these systems, and that one can learn some valuable information concerning the mechanism of triple bond formation. It has been established in these laboratories that near-uv or vis irradiation of species IV and VIII results in cleavage of the metal-metal single bond.⁶ Indeed, reaction (12) occurs⁶ with a quantum efficiency in the range of 0.12 - 0.45. Also,



M=Mo, W

reactions like (13) have been found⁶ to occur quite efficiently. Thus, our



attempts to photogenerate triple bonded complexes from II, IV, Va, and VIII were undertaken with the knowledge that the primary photoproduct is very likely the 17-electron species $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ or $(\eta^5\text{-C}_5\text{(CH}_3)_5\text{)Mo(CO)}_3$.

I. Photogeneration of I, III, VIa, and X. Near-uv or vis irradiation at 25° of rigorously deoxygenated, continuously Ar purged solutions of II, IV, Va, or VIII cleanly yields the analogous triple bonded species I, III, VIa, or X, respectively. Chemical and spectroscopic properties of the photogenerated triple bonded complexes are identical to the thermally generated species.

Irradiation of Va works particularly well, and we note, qualitatively, that the conversion of Va to VIa is more rapid than for the other (Mo, W) complexes. This is reasonable, since there is no possible back reaction of VIa with released CO at ambient pressures whereas all of I, II, and X back react rapidly under the reaction conditions. Since VIa is not particularly reactive, we wish to emphasize the value of the photogeneration procedure with the Mo and W species.

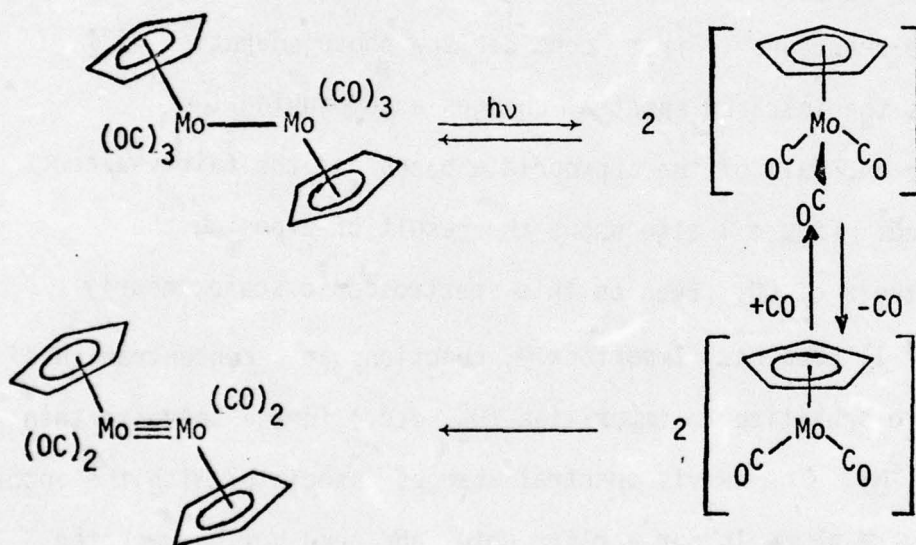
The quality of the photogeneration procedure is reflected in the spectral changes accompanying the reactions. First, consider the photogeneration of I from II. Figure 1 shows the infrared spectral changes accompanying the reaction. Note the rise and fall of the appropriate bands and the fairly decent isosbestic point obtained. Figure 1 also shows the result of exposing the photogenerated I to a stream of CO. Even on this spectroscopic scale, nearly complete regeneration of II obtains. Importantly, reactions at a concentration of $\sim 10^{-4}$ - 10^{-5} M are much more sensitive to impurities (O_2 , etc.) in the solvents than high concentration ($\sim 10^{-2}$ M). The uv-vis spectral changes associated with the inter-conversion of I and II were shown in our earlier note² and need not be repeated here. However, it is of value to note that the generation of I from II can be carried out quite cleanly on a 10^{-4} M scale by the photochemical procedure.

Uv-vis spectral changes accompanying the addition of CO to thermally generated III are shown in Figure 2. Figure 3 shows the spectral changes in a similar region for the photoconversion of IV to III. Note that in both thermal regeneration, Figure 2, and photoconversion, Figure 3, isosbestic points are at the same position. Likewise, in the photoconversion of VIII to X, Figure 4, and the regeneration of VIII from X, Figure 5, isosbestic points are found at the same wavelengths. Spectra shown in Figures 1-5 testify to the fact

that the chemistry claimed here is clean.

Spectral changes in the near-uv and vis region accompanying the reaction of 1-pentyne with photogenerated III and X are shown in Figures 6 and 7. Figure 8 shows the electronic spectrum of purified XI from thermally generated X. These spectral data show that addition of acetylenes to the photogenerated triple bonds occurs cleanly and rapidly. Spectroscopic data for all acetylene adducts synthesized are given in Table II.

2. Mechanism of Triple Bond Formation. We speculate that the mechanism for metal-metal triple bond formation is as illustrated in Scheme I for the photoconversion of IV to III. The key feature is that the photogenerated



Scheme I

17-electron species, $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$, loses CO to generate a 15-electron species which then dimerizes competitively with back reaction with CO to regenerate the 17-electron species. Purging vigorously with Ar or N_2 pushes the equilibrium towards the 15-electron compound and prevents back reaction of the triple bonded species.

One final experiment provides some support for the mechanism outlined in Scheme I. Irradiation of II in the presence of 1.0M CCl_4 with a vigorous Ar purge leads efficiently to only $(\eta^5\text{-C}_5\text{(CH}_3)_5)\text{Mo(CO)}_3\text{Cl}$. In the absence of CCl_4 , of course, irradiation under the same conditions yields I. Importantly, we have shown that I is inert to CCl_4 and does not react at 25° to yield $(\eta^5\text{-C}_5\text{(CH}_3)_5)\text{Mo(CO)}_3\text{Cl}$ in the presence of 1.0M CCl_4 . This result strongly suggests that the 17-electron intermediate proposed in Scheme I is present in the solution and can be scavenged

with 100% efficiency by the CCl_4 .

Our mechanism for the photogeneration gains support from the claims of Byers and Brown¹⁵ concerning the lability of 17-electron $\text{Mn}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$ photogenerated from $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, respectively. Apparently, dissociative loss of CO from $\text{M}(\text{CO})_5$ obtains to yield the 15-electron $\text{M}(\text{CO})_4$. The crucial step in Scheme I is the loss of CO from a 17-electron species to generate the 15-electron species.¹⁶ Dimerization of photogenerated coordinatively unsaturated complexes to yield a metal-metal triple bonded species has precedence in the preparation of $(\eta^5\text{-C}_4\text{H}_4)_2\text{Fe}_2(\text{CO})_3$.¹⁷

It is tempting to adopt Scheme I as the mechanism for the thermal generation of the triple bonded complexes. This adoption depends on the ability to thermally cleave the metal-metal single bonded complexes to generate the 17-electron species. This postulate has gained experimental justification from the work of Klingler and Curtis¹⁸ and is in complete accord with studies¹⁹ of the thermal chemistry of other dinuclear metal-metal bonded complexes which point to metal-metal bond cleavage as a significant thermal reaction.

Summary

Scheme II concisely summarizes the reaction chemistry reported herein. The W and Mo systems are remarkably similar, but the Cr-Cr triple bonded species are exceptional in that they are inert to acetylenes at 25° and require high CO pressure to saturate the triple bond. Photogeneration or thermal generation of the triple bonded complexes from the single bonded species is possible, but the photogeneration procedure can be most conveniently carried out on a spectroscopic scale for mechanistic and reactivity studies.

Acknowledgment. This work was supported by the Office of Naval Research and the National Science Foundation.

Experimental Section

Spectra. All uv-vis absorption spectra were obtained using a Cary 17 uv-vis-nir spectrophotometer. All pmr data in CDCl_3 with TMS reference were acquired using a Varian 1-60, and infrared spectral data were acquired using either a Perkin-Elmer 521 or 337 grating infrared spectrometer.

General Synthetic Procedures.

All synthetic reactions were done under N_2 or Ar, and all solvents were dried and deoxygenated prior to use. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

Materials. $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were obtained from either Strem or Pressure Chemical Company. Hexamethylbicyclo[2,2,0]-hexadiene, *m*-chloroperoxybenzoic acid, phenyl- and diphenylacetylene and benzylbromide were obtained from Aldrich Chemical Company. Acetylene was purchased from Matheson Gas Products. CDCl_3 was obtained from Merck, Sharp, and Dohme. All solvents for ir and uv-vis spectra were obtained commercially in spectro-grade quality.

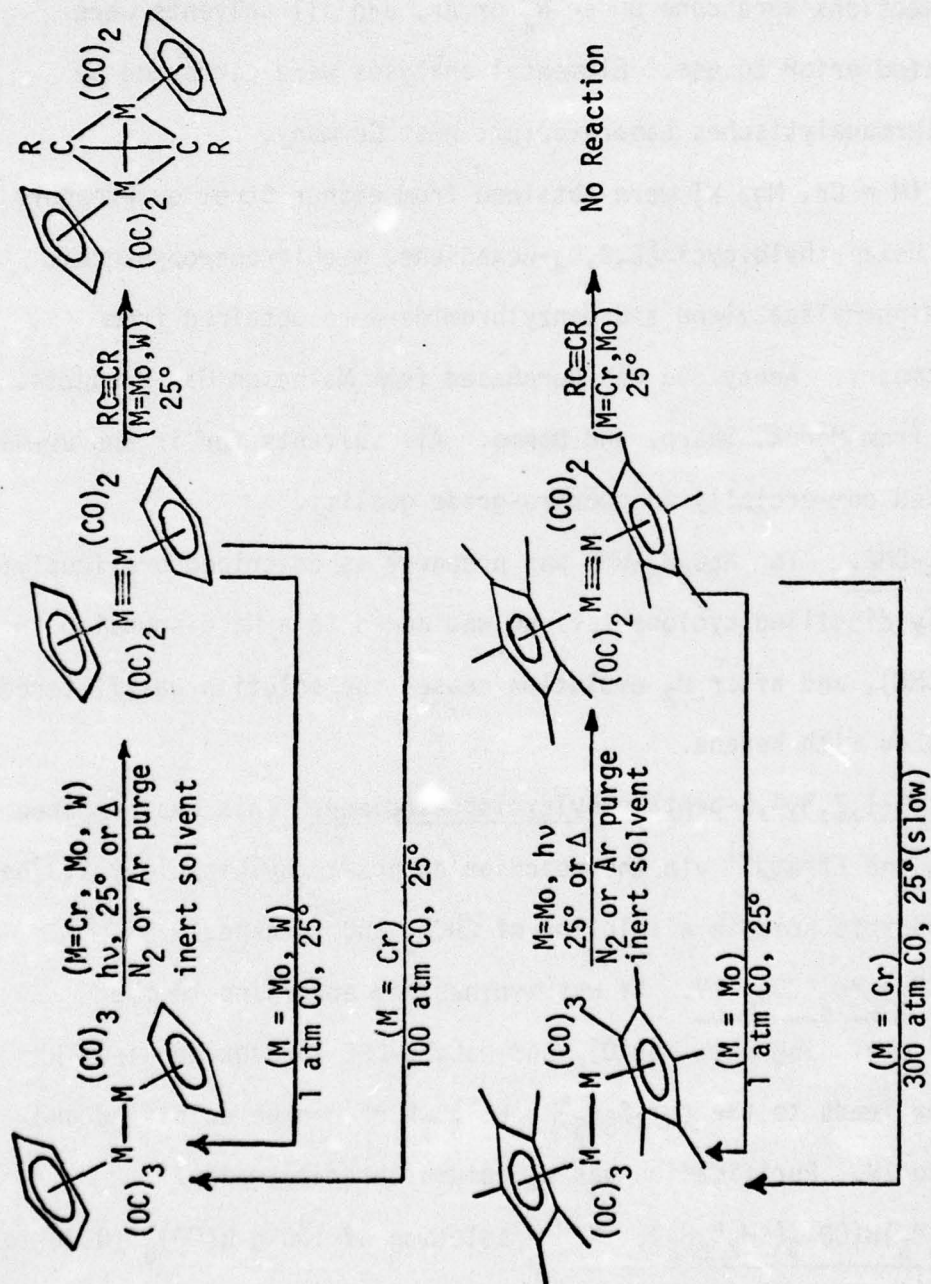
Synthesis of NaC_5H_5 -DME. The NaC_5H_5 -DME was prepared as described previously:²⁰ an excess of freshly distilled cyclopentadiene was added to a Na dispersion in dimethoxyethane (DME), and after H_2 evolution ceased the solution was filtered and the product washed with hexane.

Synthesis of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene. This was prepared as reported by King and Efraty²¹ via the reaction of hexamethylbicyclo[2,2,0]hexadiene and *m*-chlorobenzoic acid in a solution of CHCl_3 and toluene.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$, IV. IV was synthesized according to the established route¹¹ beginning with $\text{Mo}(\text{CO})_6$ and NaC_5H_5 -DME in deoxygenated THF solution. Refluxing leads to the $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$ which can be acidified and then air oxidized to IV. Purification was by column chromatography.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$, IX. A solution of 100 g $\text{W}(\text{CO})_6$ (0.28 mol) and 55 g NaC_5H_5 -DME (0.31 mol) in THF was refluxed in a three-neck flask for

Scheme II



48 hr or until an ir spectrum showed no remaining $W(CO)_6$ (ir band maximum at 1980 cm^{-1}). After cooling the solution to room temperature, 51 g of $C_6H_5CH_2Br$ (0.30 mol) was added to the solution. The mixture was then stirred for three hours. At 50° and 22 mm the solvent was removed by rotary evaporation. The crude product can be purified by chromatography on grade #3 alumina. Elution is first with isooctane to remove any unreacted $W(CO)_6$. Elution with CH_2Cl_2 then moves the desired complex. Rotary evaporation of the solvent yields 111.95 g (94%) of IX which is yellow in color and has ir band maxima in the CO stretching region at 2020 and 1920 cm^{-1} in $CDCl_3$. Proton magnetic resonances are at 3.07τ (phenyl), 4.81τ (cyclopentadienyl), and 7.05τ (CH_2-) with integration of 5:5:2 in $CDCl_3$. The C, H analysis is satisfactory: calculated, C, 42.53; H, 2.86; found, C, 42.83; H, 2.97.

New Synthesis of $(\eta^5-C_5H_5)_2W_2(CO)_6$, VIII. In 25g batches, IX was loaded into 20mm x 200mm heavy wall glass tubing fitted with a $\frac{3}{4}$ 24/40 male joint. A vacuum stopcock on a $\frac{3}{4}$ 24/40 female joint was attached to the pyrolysis tube, and the sample was pumped down to ≤ 0.05 mm. Pyrolysis of the sample was then carried out in an oven at 180° for 16 hr. The yellow solid turns red-purple evidencing the conversion to the desired product. VIII is only sparingly soluble in hexane; repeated washing of the solid with cold hexane removes nearly all of the bibenzyl. Purification of VIII is by chromatography on grade #1 alumina. The compound was added to a column as a hexane slurry. Elution with hexane serves to remove remaining bibenzyl, and VIII is eluted with CH_2Cl_2 . Rotary evaporation of the solvent yields the red-purple solid. A total of 86g (91%) (overall from $W(CO)_6$) of VIII was obtained. The known complex¹⁰ has a MP of $240-242^\circ$ with decomposition and ir bands in the CO stretching region at 1958 and 1910 cm^{-1} in isooctane.

Synthesis of $[(\eta^5-C_5(CH_3)_5)M(CO)_2]_2$ (M = Cr, Mo), I and VII. Complexes I and VII were prepared by the method of King and Efraty²¹ via the direct reaction of

acetylpentamethylcyclopentadiene with $\text{M}(\text{CO})_6$ and subsequent purification by sublimation. The yield of the Mo derivative could be enhanced by a continuous N_2 purge of the refluxing octane solution.

Synthesis of $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Mo}(\text{CO})_3]_2$, II. A mixture of 9 g (0.034 mole) $\text{Mo}(\text{CO})_6$ and 7 g (0.034 mole) acetylpentamethylcyclopentadiene and 200 ml of dry degassed *n*-octane is refluxed for 36 hrs. The solution is then purged with CO to convert any I to II. Filtration, then chromatography on a grade #1 alumina column will separate any $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Mo}(\text{CO})_3\text{CH}_3$ from the desired product. Elution with isooctane removed the methyl complex as a yellow band, then elution of II with CH_2Cl_2 and subsequent removal of the CH_2Cl_2 (35 mm, 50°C) yields 3.45 g of deep red-purple crystalline II (yield 32%). Elemental analysis: calc. C, 49.5; H, 4.8; O, 15.2. Found, C, 48.33; H, 5.03; O, 14.7.

Synthesis of $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Mo}(\text{CO})_3\text{Cl}$. 2 g (3.1 mmole) of II in degassed, N_2 Purged CCl_4 solution was irradiated for 1.5 hr or until the ir showed no more Mo dimer remaining. The CCl_4 was removed under reduced pressure and the chloride could be purified by recrystallization from CH_2Cl_2 :isooctane. (Yield 80%, 1.73 g). The product was identified by ir (bands 2030, 1960, 1925 cm^{-1}) and by spectral analogy to $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}^6$ (M = Mo, W).

Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$, Va. Va was prepared generally by one of the methods previously described by Wilkinson²² or Fischer.²³ For example, one typical procedure will be given. 20g (0.09 mole) $\text{Cr}(\text{CO})_6$ and 18g (0.1 mole) $\text{NaC}_5\text{H}_5 \cdot \text{DME}$ are refluxed in 500 ml THF until the ir no longer shows the presence of $\text{Cr}(\text{CO})_6$. After cooling to room temperature, 6 g (0.1 mole) of degassed glacial acetic acid are added and the solution stirred for 2 hrs. The solvent is removed under reduced pressure (0.05 mm, 40°C) and the residue transferred to a sublimation apparatus in a dry box. The $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ sublimes after the residual $\text{Cr}(\text{CO})_6$ at 0.001 mm and 45°C . Approximately 4 g of the hydride were transferred in the dry box to a 1 liter flask with a female $\text{\text{3}} 24/40$ joint; to this was attached a male $\text{\text{3}} 24/40$ joint with a high vacuum valve. The flask was evacuated to 10^{-3} Torr and then thermalized at 160°C for 6 hrs. The residue

was transferred to a sublimation apparatus in the dry box and sublimation (10^{-3} Torr and 65° C) produced 2.4 g $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ (13% yield) as dark green needles identified by ir and nmr.

Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2$ (M = Mo, W, Cr), III, X, and VIa. The synthesis of the Cr, Mo, and W triple-bonded compounds could be effected in two ways: by a photochemical route and by a thermal route. For the photochemical synthesis, 0.1 - 0.2 g of the hexacarbonyl dimers were dissolved in 100 ml of benzene in a 32 x 200 mm test tube, with a constant Ar-purge. The solution was irradiated with a broad band ultraviolet source until the ir had only bands for the tetracarbonyl dimer, (1 hr, Cr, 5-20 hr, Mo, W). The benzene was then removed under reduced pressure (30 mm, 50°C) and the compounds could be purified by extracting the residue with cold, degassed pentane. This method proved to be the best for the production of the air-stable $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$ dimer with yields of 90% observed.

For the thermal route 0.1 - 0.6 g of the hexacarbonyl dimers were dissolved in 150 ml of m-xylene under a constant Ar-purge. The solution was heated to reflux until the ir showed only bands for the tetracarbonyl dimers (3-5 hrs). The solvent was removed under reduced pressure (30 mm, 75°C) and the product could be extracted with cold degassed pentane. Yields on the order of 60-70% were obtained for all compounds but it was observed in the case of the air-sensitive Mo and W compounds that small amounts of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ were always found as impurities.

Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$, VIa, and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Cr}(\text{CO})_2]$, VII, with CO.

In the dry box, solutions of the tetracarbonyl dimers in benzene, CDCl_3 or isooctane were prepared and zero time spectra were taken. The solution was then loaded into a 13 x 100 mm test tube which was used as the liner in an American Instruments Co. 125 ml high pressure bomb apparatus. This apparatus was then attached to the inlet system and filled and vented with N_2 (3 cycles)

and CO (2 cycles). The bomb was then pressurized to 100 atm (new tank pressure) for VIIa and 300 atm (boosted pressure) for VII, and sealed off. After 18 hrs for VIIa and 72 hrs for VII the bomb was vented to 200 psig and loaded into the dry box. Then the bomb was opened and the solutions analyzed by ir, uv, and nmr. Nearly quantitative generation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ was found and 50% conversion to the presumed $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Cr}(\text{CO})_3]_2$ was found.

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2$ (M = Mo, W) with Acetylenes.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4\text{C}_2\text{H}_2$ (M = Mo, W) were both made in nearly quantitative yields by performing the thermal synthesis for the triple-bonded compounds detailed above under an acetylene purge. This synthesis also works well if a solution of the triple bonded complexes at 25° is reacted with acetylene.

Reaction with the liquid substituted acetylenes C_2R_2 (R = H or Ph) was performed in the same fashion.

These air-stable compounds were purified by elution from a grade #1 alumina column with CH_2Cl_2 . The acetylene complexes were identified by uv-vis, ir, and pmr, Table II, and have the same features as those prepared by Curtis.³

Satisfactory elemental (C,H) analyses for $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ (M=Mo and W) were obtained: for M=Mo, calcd: C, 41.8; H, 2.6; Found: C, 42.0, H, 3.0 and for M=W, calcd: C, 30.2, H, 1.9; Found: C, 30.2; H, 1.9.

Photogeneration Procedures. The photogeneration of the metal-metal triple bonded species was carried out by near-uv and vis irradiation of the single bonded species. Isooctane, pentane, or benzene solutions of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ or $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Mo}(\text{CO})_3]_2$ at 25° were purged vigorously with Ar or N_2 . Irradiation was with the output from a (i) 9x beam expanded Spectra Physics Model 164 argon ion laser, (ii) a Pyrex filtered 200 W super-pressure Hg lamp source from Bausch and Lomb, or (iii) a GE Blacklite (300-380nm) equipped with two 15W blacklite bulbs. The spectral changes accompanying irradiation were monitored in the uv-vis, ir, and pmr and corresponded in all cases to consumption

of the single bonded complex and the generation of the triple bonded species. Subsequent airless reactions were carried out with CO or acetylenes to regenerate the single bonded parent complexes or to prepare the acetylene adducts.

References

1. Fellow of the Alfred P. Sloan Foundation, 1974-1976, and a recipient of a Dreyfus Teacher-Scholar Grant, 1975-1980.
2. D.S. Ginley and M. S. Wrighton, J. Amer. Chem. Soc., **97**, 3533 (1975).
3. R. J. Klingler, W. Butler, and M. D. Curtis, ibid., **97**, 3535 (1975).
4. R. D. Adams, D. M. Collins, and F. A. Cotton, Inorg. Chem., **13**, 1086 (1974).
5. P. Hackett, P. S. O'Neil, and A. R. Manning, J. Chem. Soc. Dalton, 1625 (1974).
6. M. S. Wrighton, and D. S. Ginley, J. Amer. Chem. Soc., **97**, 4246 (1975).
7. (a) K. W. Barnett, J. Organometal. Chem., **44**, 1 (1972); (b) A. R. Burkett, T. J. Meyer, and D. G. Whitten, ibid., **67**, 67 (1974); (c) J. L. Hughey, IV, C. R. Bock, and T. J. Meyer, J. Amer. Chem. Soc., **97**, 4440 (1975); (d) J. L. Hughey, IV, and T. J. Meyer, Inorg. Chem., **14**, 947 (1975); (e) R. D. Adams, D. E. Collins, and F. A. Cotton, J. Amer. Chem. Soc., **96**, 749 (1974); (f) R. D. Adams, F. A. Cotton, Inorg. Chim. Acta, **7**, 153 (1973).
8. J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, Inorg. Chem., **13**, 2540 (1974).
9. R. B. King, A. Efraty, and W. M. Douglas, J. Organometal. Chem., **60**, 125 (1973).
10. G. Wilkinson, J. Amer. Chem. Soc., **76**, 209 (1954).
11. E. O. Fischer and R. L. Pruett, Inorg. Syn., **7**, 136 (1963).
12. The acetylene complexes have been obtained previously by a different synthetic procedure involving thermolysis of mononuclear metal carbonyl in the presence of an acetylene: A. Nakamura and N. Hagiwara, Nippon Kagaku Zasshi, **84**, 344 (1963); Chem. Abstr., **39**, 14021d (1963). The x-ray structural results for complex XI show it to have the tetrahedrane-like core: R. Bau, B. Fischer, M.S. Wrighton, and D.S. Ginley, in preparation.
13. F. A. Cotton, B. R. Stults, J. M. Troup, M. H. Chisholm, and M. Extine, J. Amer. Chem. Soc., **97**, 1242 (1975), and references therein.
14. H. J. Keller, Z. Naturforsch. B., **23**, 133 (1968).
15. B. H. Byers and T. L. Brown, J. Amer. Chem. Soc., **97**, 3260 (1975).
16. Cf. also M. Wrighton, Chem. Rev., **74**, 401 (1974) and M. S. Wrighton and D. S. Ginley, J. Amer. Chem. Soc., **97**, 2065 (1975) for a discussion of thermally substitution labile photogenerated metal radicals.
17. I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, Angew. Chem. Int. Ed., **14**, 54 (1975).
18. R. J. Klingler and M. D. Curtis, private communication and submitted for publication.
19. J. P. Fawcett, A. Poe, and K. R. Sharma, J. Amer. Chem. Soc., **98**, 1401 (1976), and references therein.

References, continued

20. J. C. Smart, Ph.D. Thesis, M. I. T., 1973.
21. R. B. King and A. Efraty, J. Amer. Chem. Soc., 93, 4950 (1971) and 94, 3773 (1972).
22. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3, 104 (1956).
23. E. O. Fischer and W. Hafner, Z. Naturforsch. B, 18, 157 (1963).

Table I. Spectroscopic Data for Single and Triple Bonded Complexes

Complex	Infrared, cm^{-1} ^a	PMR, τ ^b	uv-vis, nm (ϵ) ^{a,c}
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$	2008; 1945; 1922; 1912	3.77 (broad singlet)	590 (<u>0.05</u>); 488 (<u>0.70</u>)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4$	1900; 1880	4.82 (singlet)	615 (300; 390 (19,200))
$(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Cr}_2(\text{CO})_6$	1985; 1900 ^d	—	—
$(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Cr}_2(\text{CO})_4$	1876; 1857 ^d	8.37 (singlet)	590 (240); 402 (9020)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$	1960; 1915	4.80 (singlet)	512 (1720); 388 (20,400)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$	1889; 1859	4.91 (singlet)	380 sh; 325 (13,800); 280 sh
$(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Mo}_2(\text{CO})_6$	1940; 1907	7.95 (singlet)	495 (2500); 409 (9500)
$(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Mo}_2(\text{CO})_4$	1874; 1846	8.05 (singlet)	395 sh; 326 (13,200); 280 sh
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$	1958; 1910	4.67 (singlet)	493 (2450); 362 (20,200)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$	1885; 1830	4.78 (singlet)	—

^a Ir. isoctane unless noted otherwise.^b In CDCl_3 .^c Underlined values in parentheses are relative absorbances.^d In benzene.

Figure Captions

Figure 1. Infrared spectral changes accompanying the photoconversion of $[(\eta^5\text{-C}_5\text{(CH}_3)_5)\text{Mo(CO)}_3]_2$ to $[(\eta^5\text{-C}_5\text{(CH}_3)_5)\text{Mo(CO)}_2]_2$ in Ar-purged benzene solution at 25° irradiating with near-uv light. Curve 0 is the starting spectrum of the single bonded complex and curves 1 and 2 are after irradiation periods of 10 and 15 minutes, respectively. Curve 3 is the result of exposing the solution to CO showing the regeneration of the initial complex.

Figure 2. Spectral changes accompanying the conversion of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2]_2$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ by adding CO to the pentane solution. Curves 0, 1, and 2 are 0, 1, and 5 sec of CO purge, respectively. The band at 325 nm is due to the triple bonded species, and the bands which grow at 512 and 388 nm are those for the single bonded complex. The reaction is carried out in a cell with an optical path length of 1.0 cm.

Figure 3. Spectral changes accompanying the photoconversion of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2]_2$ in Ar-purged pentane solution at 25° irradiating with near-uv light. Curves 0, 1, and 2 are 0, 45, and 75 sec of irradiation, respectively. The reaction is carried out in a cell with an optical path length of 1.0 cm.

Figure 4. Spectral changes accompanying the photoconversion of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3]_2$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2]_2$ in Ar-purged isooctane solution at 25° in a cell having a 1.0 cm optical path length. Curves 0, 1, and 2 are 0, 60, and 240 sec of near-uv irradiation, respectively. The bands at 493 and 362 nm are due to the starting material, and the new shoulder at ~290 nm is due to $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2]_2$.

Figure 5. Uv-vis spectral changes accompanying the conversion of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2]_2$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3]_2$ by addition of CO to an isooctane solution at 25°. Curves 0, 1, and 2 are after 0, 1, and 5 sec of CO purge, respectively.

Figure 6. Uv-vis spectral changes accompanying reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2]_2$ with 1-pentyne in Ar-purged pentane solution at 25°. Curve 0 is the

Table II. Spectroscopic Data for Acetylene Complexes.

Complex	Infrared, cm^{-1} ^a	PMR, τ ^b	uv-vis, nm (ϵ) ^a
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{H}_2)$	1994; 1927; 1847	4.68; 5.18 (singlets 5:1 ratio)	530 (845); 360 (7740)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{HCCPh})$	1995; 1931; 1848	2.86; 4.68; 4.5 (6:10:1 ratio)	543 (809); 362 (8000)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{HCCCH}_3)$	1990; 1928; 1919; 1848	4.53; 4.80; 7.5 (singlets 1:10:3 ratio)	538 (770); 360 (6600)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{HCCC}_3\text{H}_7)$	1990; 1928; 1916; 1845	4.10, 4.85; 7.40; 8.95 (1:10:2:5 ratio)	535 (903); 360 (7200)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$	1990; 1922 1835	4.64; 6.11 (singlets 5:1 ratio)	520 (950); 348 (6180)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{HCCC}_3\text{H}_7)$	1988; 1920; 1911; 1833	4.65; 4.7; 7.45; 9.0 (~1:10:2:5)	528 (1070); 353 (6000)

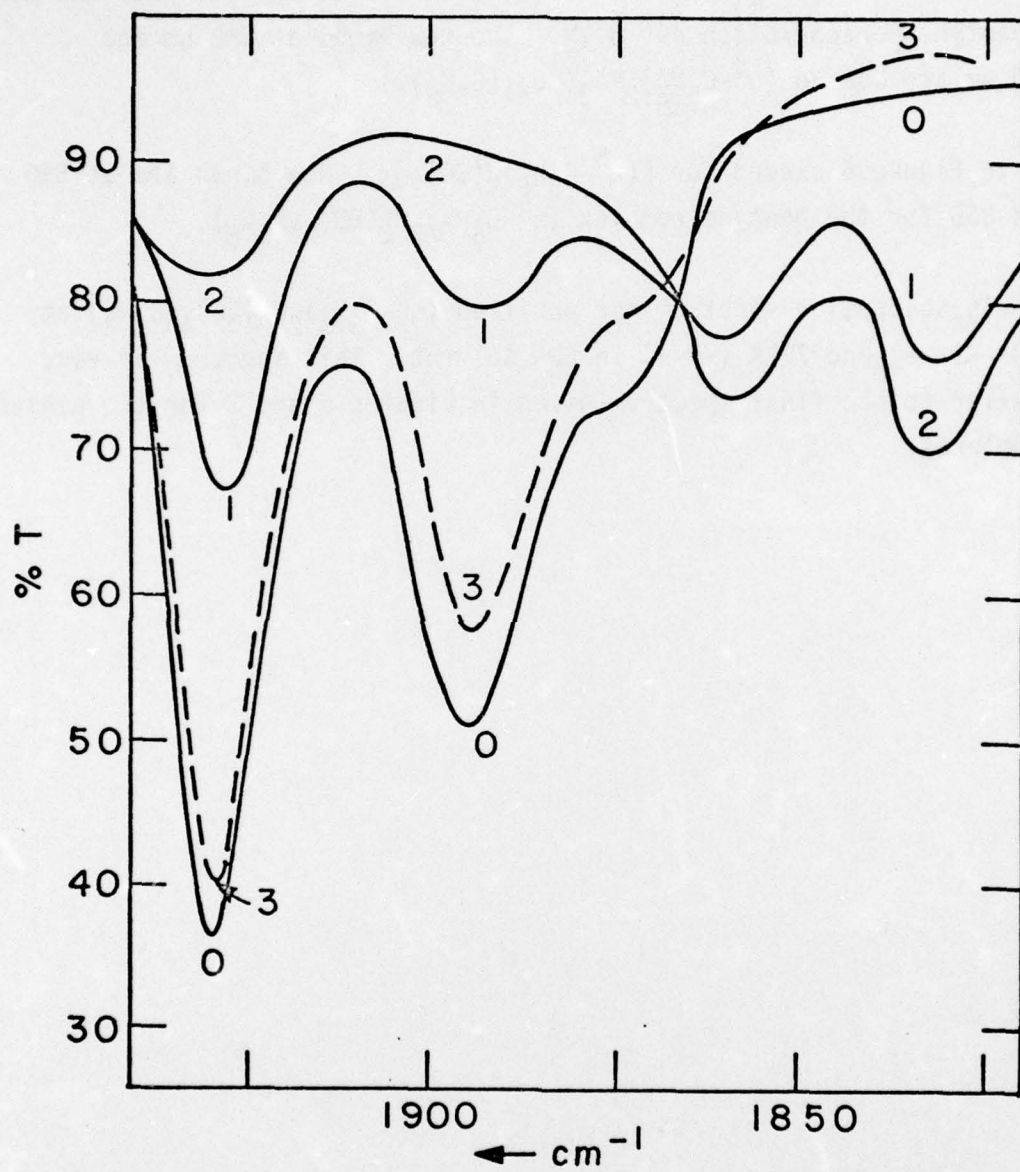
^aIn isooctane at 25°.

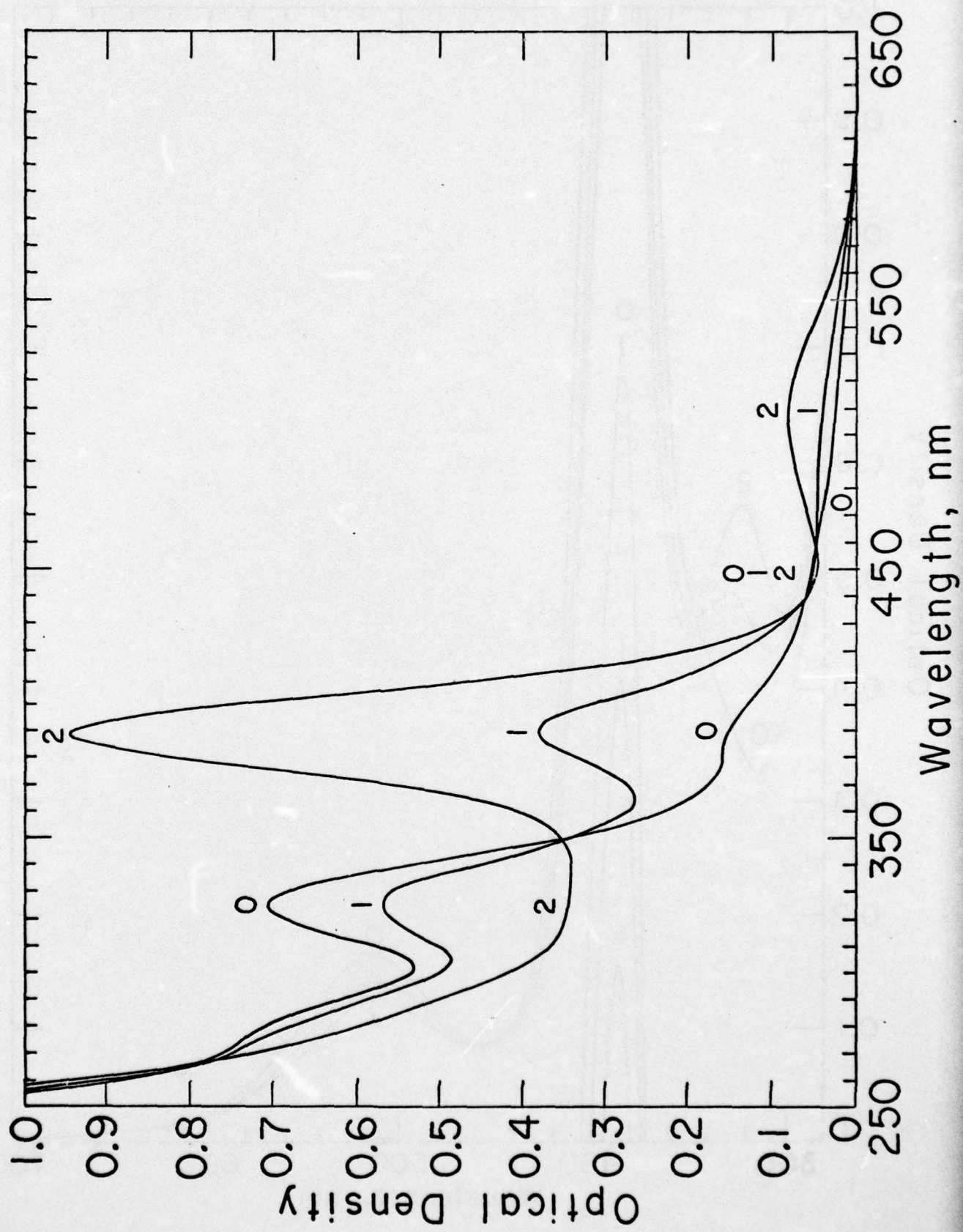
^bIn CDCl_3 .

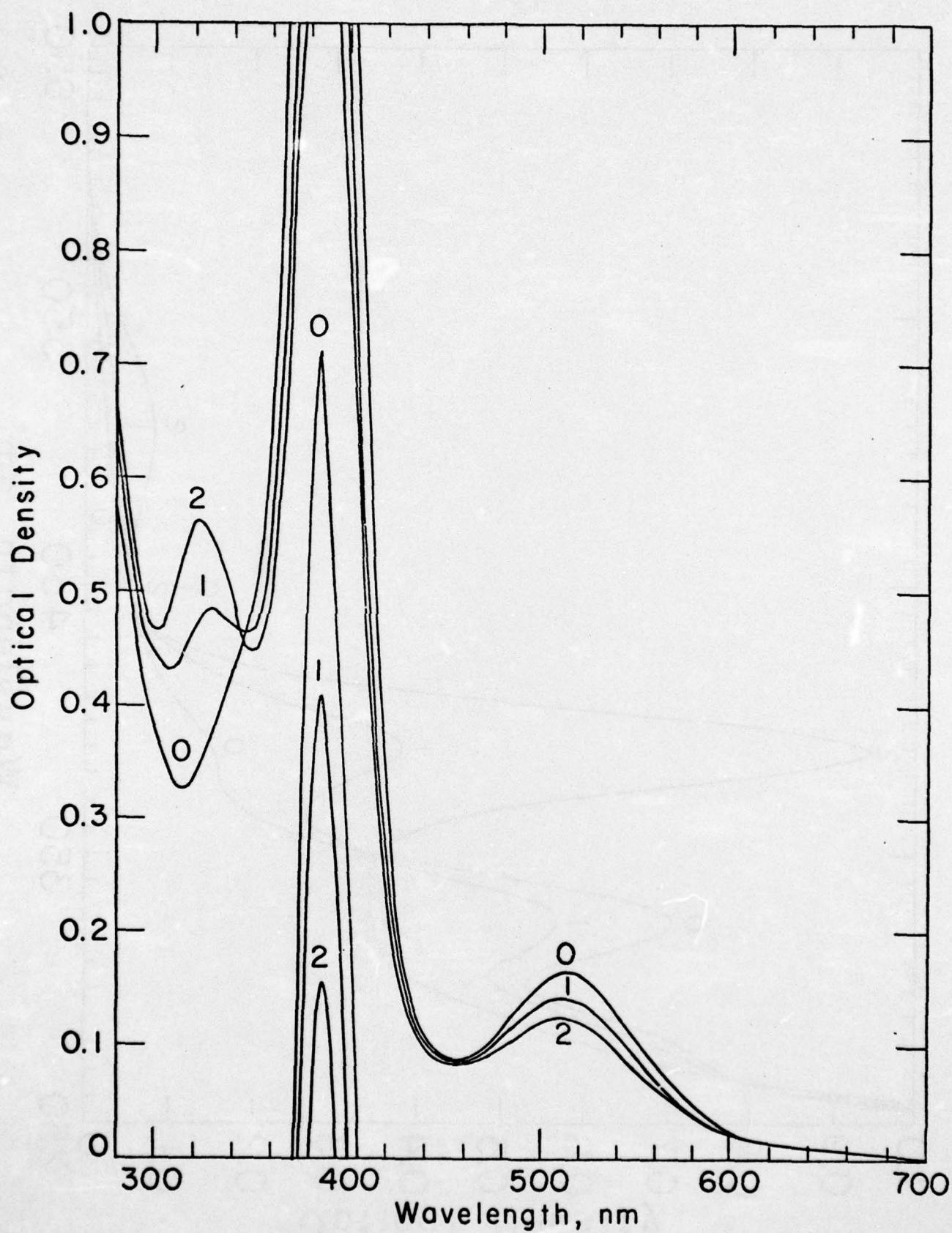
initial spectrum; curve 1 is after 1 min reaction; and curve 2 is after ~3 minutes when no further spectral changes occurred. The reaction was carried out in a cell with a 1.0 cm optical path and at a 1-pentyne concentration of ~0.1M. The new bands at 538 nm and 360 nm are due to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_5\text{H}_8)$.

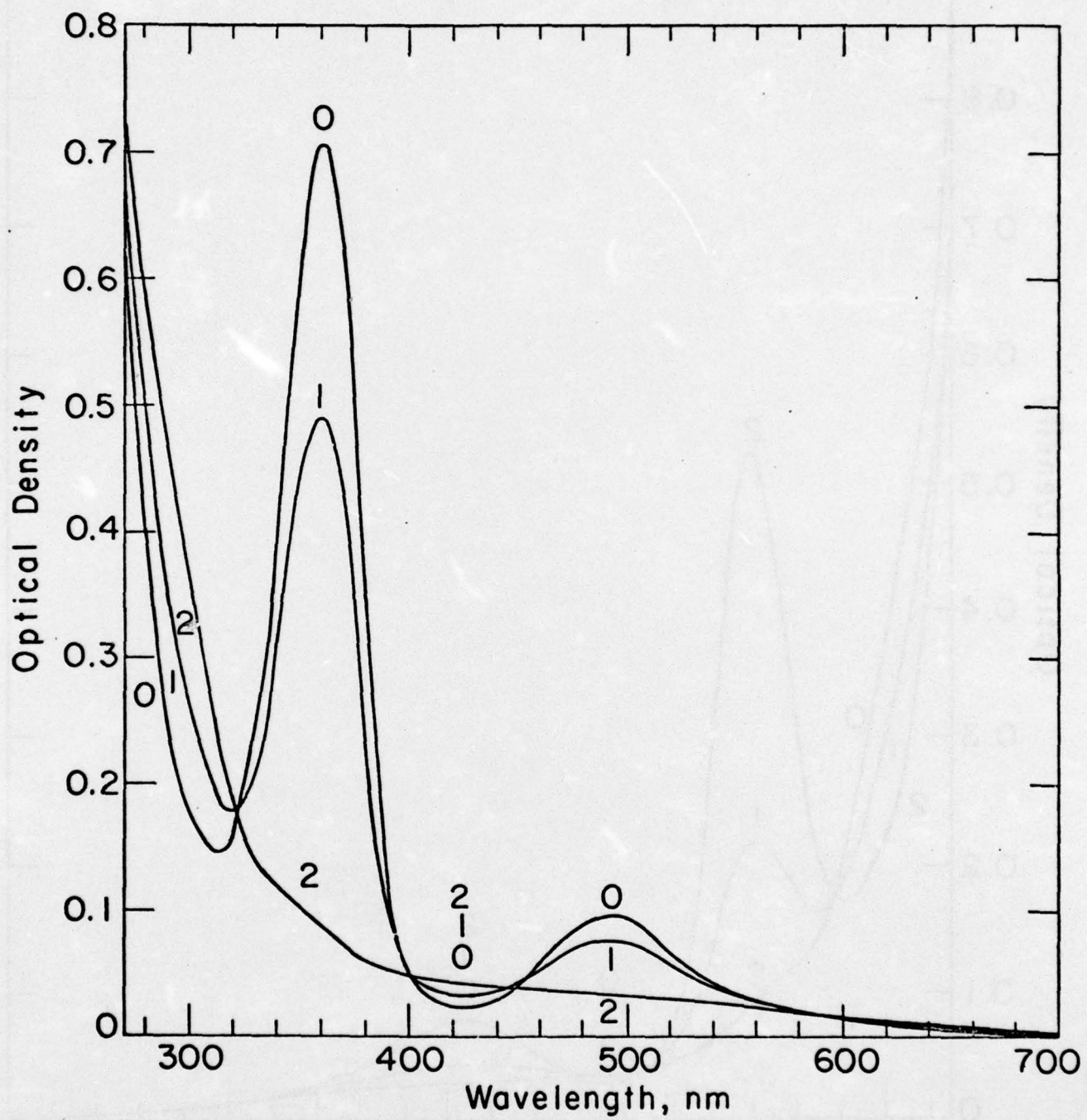
Figure 7. As in Figure 6 except for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2]_2$. New bands are at 530 and 355 for the pentyne complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_5\text{H}_8)$.

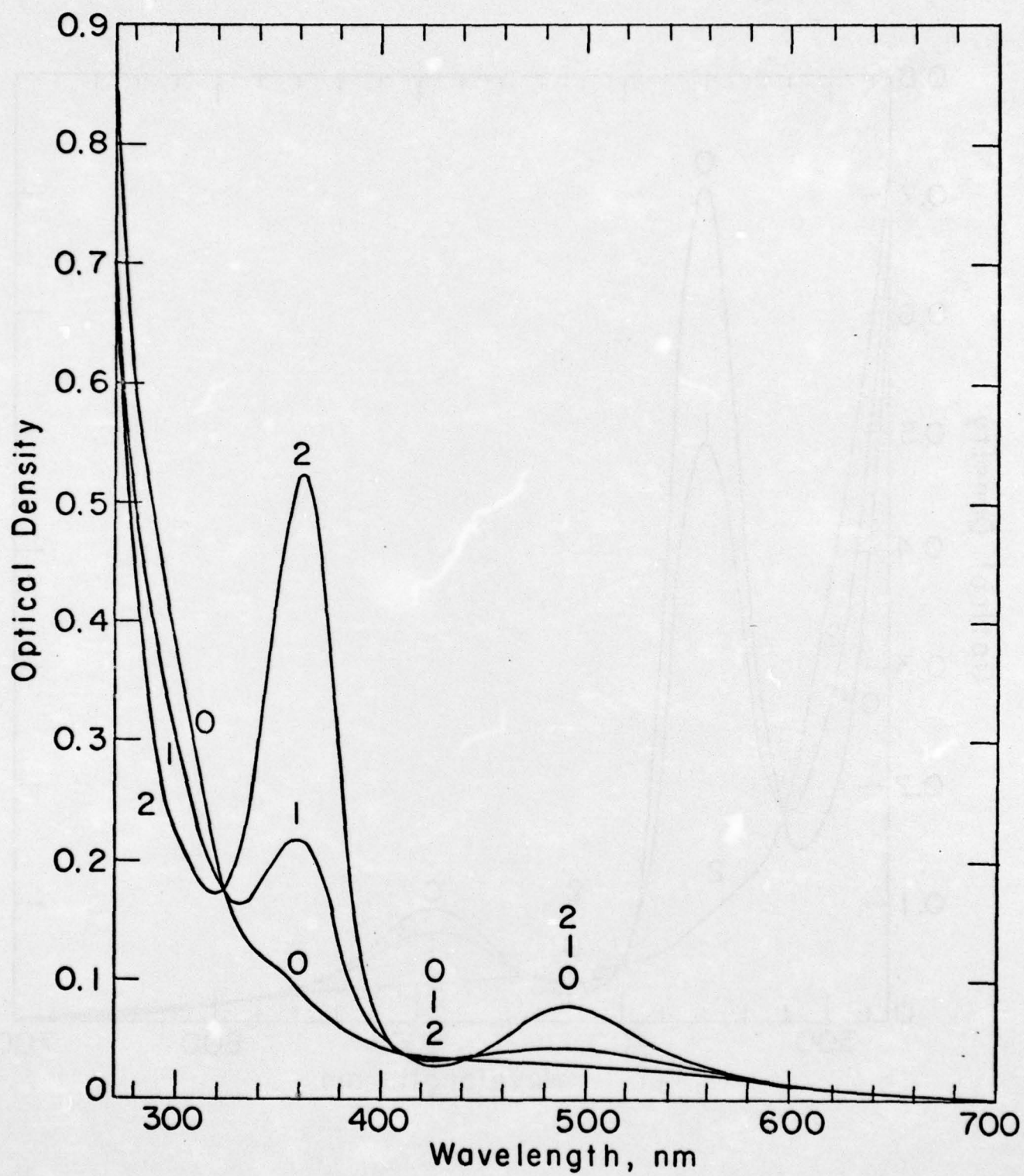
Figure 8. Uv-vis absorption spectrum for purified $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ at 298° K(—) and 77°K (----) in EPA solvent. This spectrum is very similar to the final spectrum given in Figures 6 and 7 for the pentyne complexes.

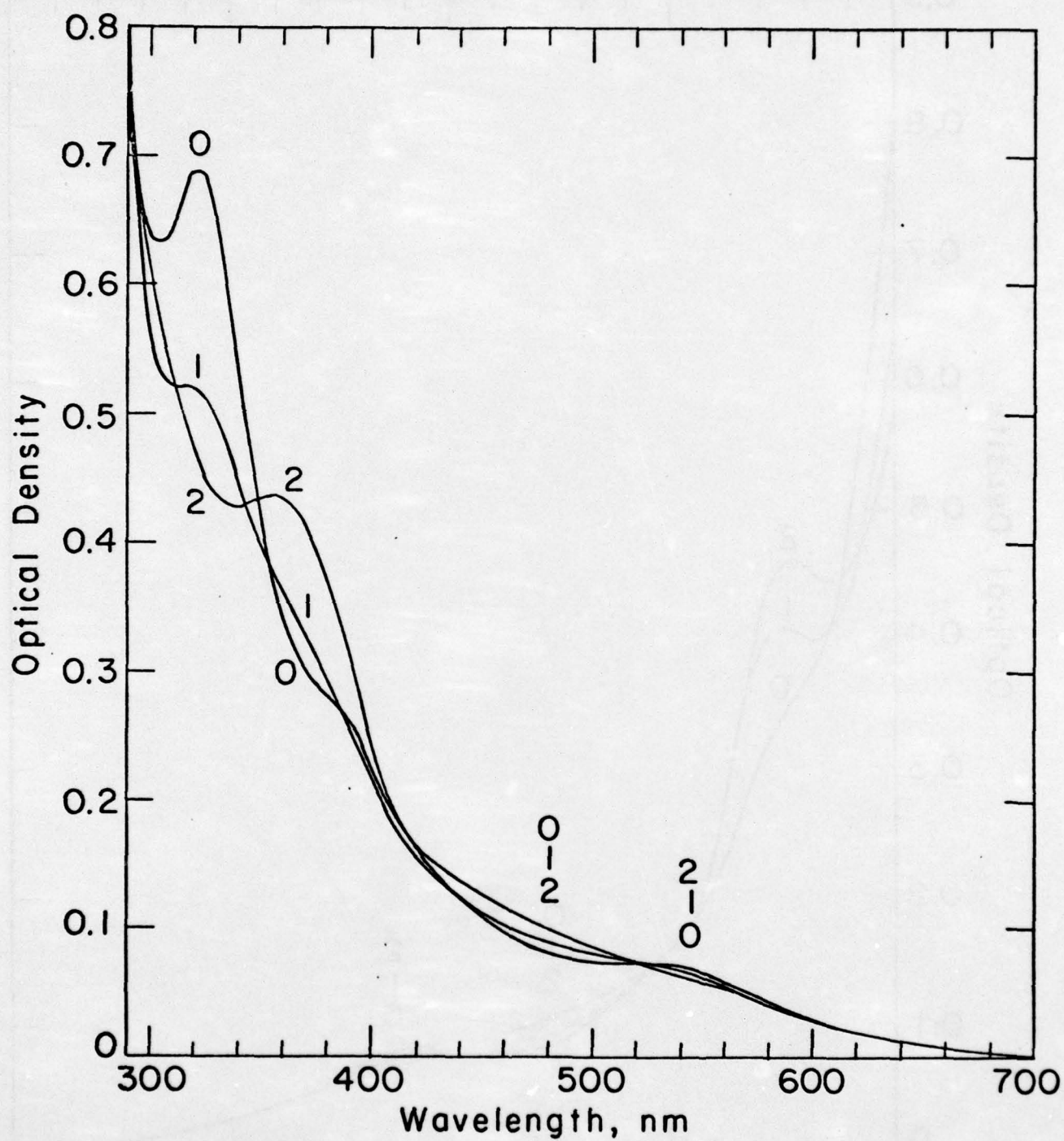


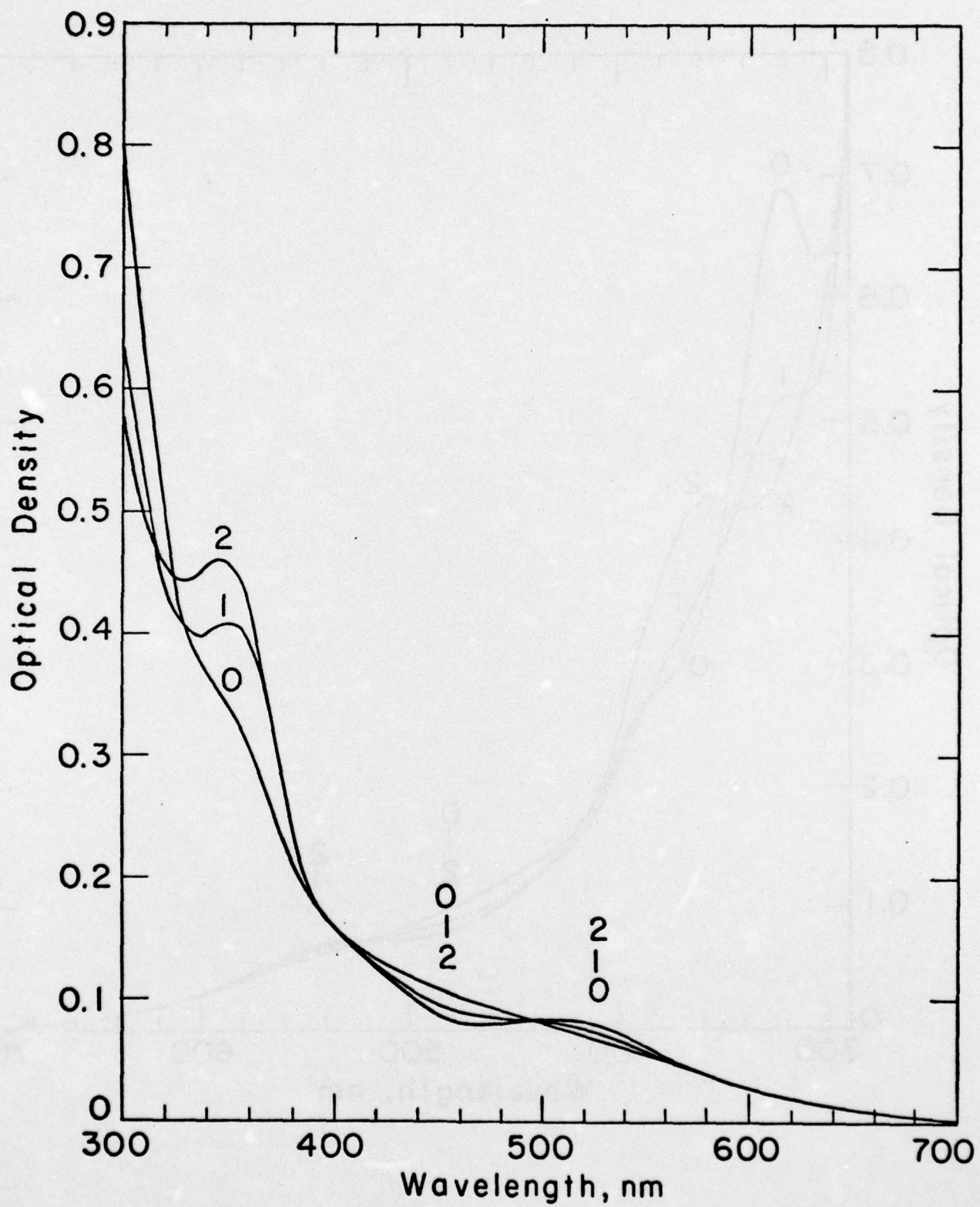


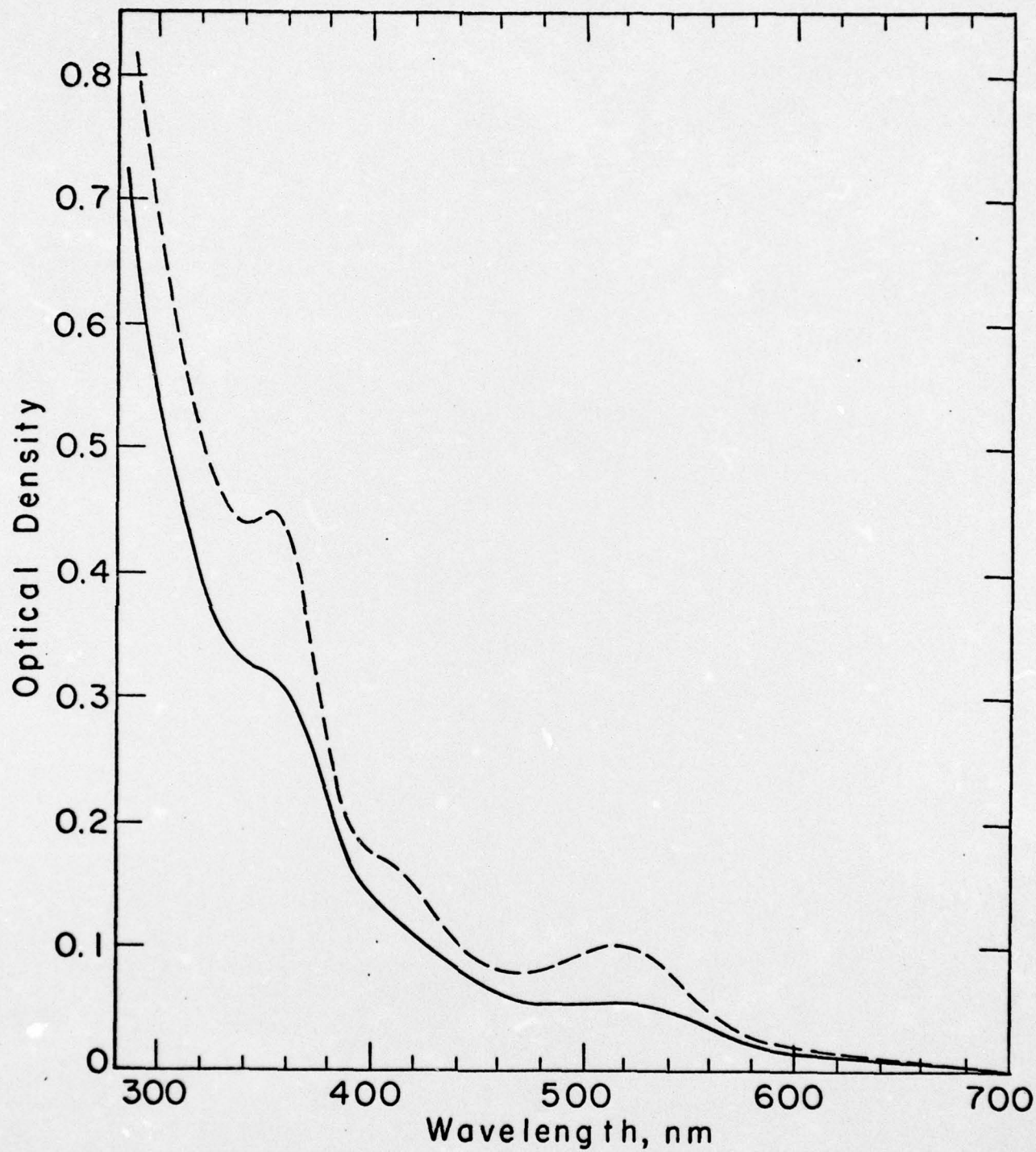












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