vent cage to undergo secondary radical reactions (eq 9 and 10). However, the possibility of producing monoselenide (II) and selenium by a cage process cannot definitely be ruled out. Reported observations on benzylic species[17,18] indicate that both cage and noncage reactions may occur when benzyl radicals are generated photochemically or thermally, although noncage processes are likely to be favored, particularly in photoreactions.

The presence of benzyl in our photolysis mixture is substantiated by the formation of benzyl chloride upon irradiation of I in carbon tetrachloride. Furthermore, irradiation of a solution of I in oxygenated acetonitrile gives benzaldehyde. These results confirm the importance of C–Se cleavage and the formation of benzyl radicals.

The generation of benzyl radicals further indicates the concomitant formation of the benzylselenoselenyl radical (eq 7) as an essential step leading to deposition of elemental selenium.

Photosensitization and quenching experiments as well as various scavenging reactions on the intermediate organoselenyl radicals are in progress and will be reported in full.

Acknowledgment. J. Y. C. Chu wishes to acknowledge Professors J. A. Kampmeier and J. C. Dalton for helpful discussions.

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Photochemistry of Metal–Metal Bonded Complexes. IV. Generation of d^5 and d^7 Mononuclear Fragments via Homolytic Cleavage in Heterodinuclear Metal Carbonyls

David S. Ginley and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 4, 1974*

Abstract: The flash photolysis of $(OC)_5M'{-}M(CO)_3(\eta^5\text{-}C_5H_5)$ in degassed isooctane solution yields $M'_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ in nearly a 1:1 ratio with high chemical yield ($\geq$65%) for M = W, Mo and M′ = Mn, Re. Photolysis at 366 nm of the $(OC)_5M'{-}M(CO)_3(\eta^5\text{-}C_5H_5)$ complexes in degassed CCl_4 yields $M'(CO)_5Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ with a M–M′ disappearance quantum yield in the range of 0.23–0.56. Photolysis at 436 nm gives the same products, but the quantum yields are substantially less. The electronic spectra of the M–M′ species exhibit absorptions which can be ascribed to transitions resulting in population of a σ-antibonding orbital with respect to the M–M′ bond. Such transitions apparently result in efficient homolytic cleavage despite the fact that heterolytic cleavage to yield $M'(CO)_5{}^+$ and $(\eta^5\text{-}C_5H_5)M(CO)_3{}^-$ would give diamagnetic fragments of the stable d^6 electronic configuration.

The photochemistry of metal carbonyls containing metal–metal bonds has involved complexes where the metals are the same, or at least of the same formal d^n configuration. In every case to date the chemistry following photoexcitation is consistent with homolytic cleavage of the metal–metal bond as the primary excited state decay path. Specific examples are $M_2(CO)_{10}$ (M = Mn, Re),[1-3] $MnRe(CO)_{10}$,[2] $Mn_2(CO)_n(PPh_3)_{10-n}$[2] (n = 9, 8), $[Mn(CO)_3(phen)]_2$,[4] $(OC)_5Mn{-}Re(CO)_3(phen)$,[4] and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W).[5] Phenomenologically, at least, it may also be said that the $Re_2Cl_8{}^{2-}$ undergoes $Re{\equiv}Re$ homolysis upon photoexcitation in CH_3CN,[6] and $Ru_3(CO)_{12}$ undergoes Ru–Ru homolysis upon photolysis in the presence of CO to quantitatively yield $Ru(CO)_5$.[7]

Heterodinuclear complexes having metals of differing d^n configuration seemingly have the best a priori chance of yielding efficient photoinduced heterolytic cleavage. This would be especially true if the resulting cations and anions could have stable electronic configurations. Such a series of heterodinuclear compounds are the $(OC)_5M'{-}M(CO)_3(\eta^5\text{-}C_5H_5)$ (M′ = Mn, Re; M = Mo, W) complexes which are thermally stable, well-characterized species.[8] Here heterolytic splitting could yield $(OC)_5M'^+$ and $(\eta^5\text{-}C_5H_5)M(CO)_3{}^-$ which are both of the d^6 electronic configuration. Homolytic cleavage would give the metal radicals which can be photogenerated from appropriate homodinuclear metal carbonyls.[1-3,5] In this short paper we report electronic spectral properties and photochemistry of the $(OC)_5M'{-}M(CO)_3(\eta^5\text{-}C_5H_5)$ complexes.

Results

a. Spectra of the Complexes. The $(OC)_5M'{-}M(CO)_3(\eta^5\text{-}$

Table I. Electronic Absorption Spectral Data for $(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5)$ at 25°

M	M'	Solvent	Bands, nm $(\epsilon)^a$
Mn	Mo	CCl_4	458 (1930), 377 (18,550)
		Isooctane	450 (1400), 373 (14,000)
		EPA	452 (0.04), 372 (0.40)
		EtOH	450 (0.05), 372 (0.71)
Mn	W	CCl_4	440 (1620), 363 (15,830)
		Isooctane	450 (1460), 362 (14,900)
		EPA	445 (0.05), 360 (0.44)
		EtOH	450 (0.05), 360 (0.63)
Re	Mo	CCl_4	453 (1100), 375 (7000)
		Isooctane	454 (642), 365 (6500)
		EPA	430 (0.11), 352 (1.15)
Re	W	CCl_4	412 (2000), 342 (12,600)
		Isooctane	411 (1400), 331 (9000)
		EPA	410 (0.11), 340 (0.80)
		EtOH	408 (0.04), 341 (0.41)

[a] Underlined values in parentheses are relative absorptivities.

C_5H_5) complexes (M' = Mn, Re; M = Mo, W) all have remarkably similar electronic absorption spectra in the near-uv and visible region of the spectrum. Spectra at 298 and 77 K are given in Figure 1, and the data at 298° K in several solvents are summarized in Table I. The spectra consist of two bands: one in the near-uv (340–375 nm) which is ca. ten times more intense than the lower energy absorption which falls between 410 and 460 nm. Importantly, the band positions are not significantly influenced by either solvent or temperature.

Analysis of the photoreactions of $(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5)$ has been carried out by ir spectroscopy. Ir band intensities and maxima are those determined and used previously.[2,5]

b. Photochemistry. Two series of experiments have been carried out with the $(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5)$ complexes. First, the flash photolysis of these complexes has been investigated, and in degassed isooctane we find that net photochemistry does obtain, yielding $M'_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ in nearly a ~ 1:1 ratio. Some representative data are given in Table II for two of the M–M' complexes. Ir spectral changes accompanying this flash photolysis are given in Figures 2 and 3. Qualitatively, flash photolysis of $(OC)_5Mn-Mo(CO)_3(\eta^5\text{-}C_5H_5)$ in THF purged with CO leads to substantial amounts of $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.

Photolysis of the M'–M species at 366 or 436 nm in degassed CCl_4 solution at 298 K leads to efficient disappearance of the M'–M species. Quantum yields are given in Table III. The analysis of the products is complicated by the large number of CO stretching frequencies associated with the starting materials and products. Typical uv-visible and ir spectral changes accompanying photolysis of M'–M species in CCl_4 are shown in Figure 4. Subsequent to photolysis in each case we find ir spectral maxima which reflect the presence of $M'(CO)_5Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$. For M' = Mn and M = W or Mo the $Mn(CO)_5Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ have been determined to be the *only primary products* resulting from the photolysis of the M'–M species.

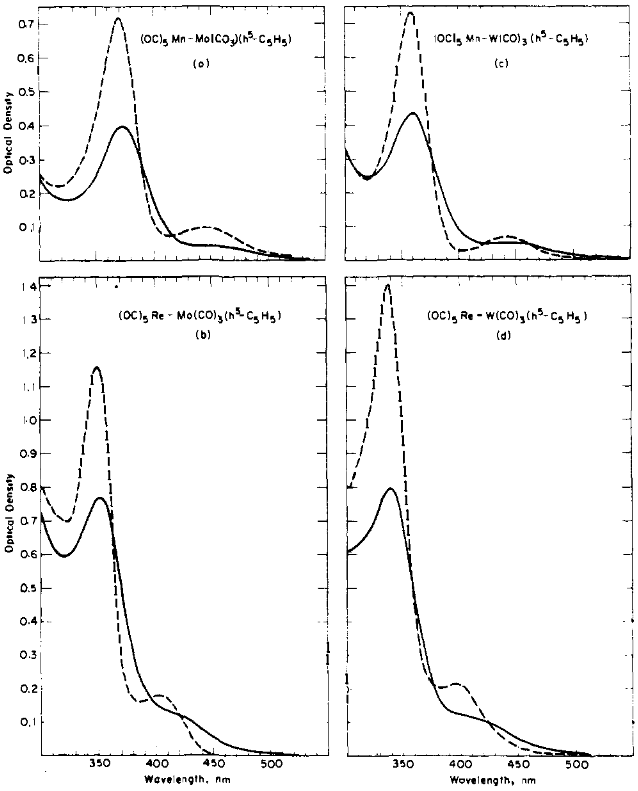


Figure 1. Electronic absorption spectra of $(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5)$ in EPA at 298 (—) 77 K (- - -). Spectral changes upon cooling from 298 to 77 K shown here are not corrected for solvent contraction. Band positions and absorptivities are given in Table I.

Discussion

The electronic spectral and photochemical results for the four M'–M species investigated here supports the conclusion that efficient homolytic M'–M cleavage is the primary result of photoexcitation, reaction 1. Subsequent cross-coupling of the mononuclear fragments leads to formation of the homodinuclear products obtained in flash photolysis, reaction 2, and reaction of the mononuclear fragments with

$$(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5) \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} M'(CO)_5 + (\eta^5\text{-}C_5H_5)M(CO)_3 \quad (1)$$

$$M' = Mn, Re$$

$$M = Mo, W$$

$$2M'(CO)_5 + 2(\eta^5\text{-}C_5H_5)M(CO)_3 \longrightarrow M'_2(CO)_{10} + [(\eta^5\text{-}C_5H_5)M(CO)_3]_2 \quad (2)$$

$$M'(CO)_5 + (\eta^5\text{-}C_5H_5)M(CO)_3 + 2CCl_4 \longrightarrow M'(CO)_5Cl + (\eta^5\text{-}C_5H_5)M(CO)_3Cl \quad (3)$$

Table II. Cross-Coupling Products via Flash Photolysis of $(OC)_5M'-M(CO)_3(\eta^5\text{-}C_5H_5)^a$

Starting complex (moles)	No. of Flashes	Moles reacted	Products (moles formed)
$(OC)_5Mn-Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (2.91×10^{-6})	1	7.30×10^{-7}	$Mn_2(CO)_{10}$ (3.23×10^{-7}) + $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (4.42×10^{-7})
$(OC)_5Mn-W(CO)_3(\eta^5\text{-}C_5H_5)$ (8.64×10^{-7})	1	3.11×10^{-7}	$Mn_2(CO)_{10}$ (1.06×10^{-7}) + $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (1.36×10^{-7})

[a] Flash photolysis of 3-ml degassed isooctane solutions of the M'–M complex in Pyrex ampules. Flashes were at 300 J and analyses were carried out by ir spectral changes.

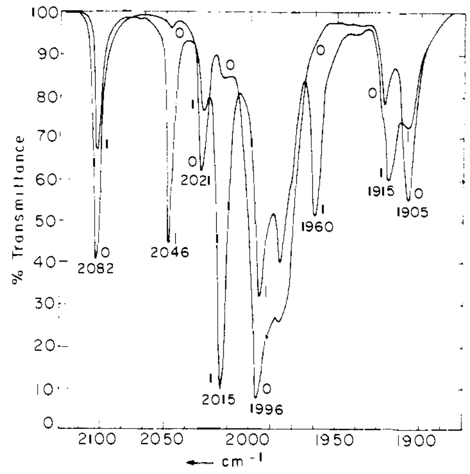


Figure 2. Infrared spectral changes accompanying flash photolysis of $(OC)_5Mn-Mo(CO)_3(\eta^5-C_5H_5)$ in degassed isooctane solution. Curve 0 is the initial spectrum and curve 1 is after one flash. Bands at 2082, 2021, 1996, and 1905 cm^{-1} are characteristic of the starting complex. Bands at 1960 and 1915 cm^{-1} are due to the $[(\eta^5-C_5H_5)Mo(CO)_3]_2$, and those at 2015 and 2046 cm^{-1} are due to $Mn_2(CO)_{10}$. Quantitative concentration changes are given in Table II.

Table III. Disappearance Quantum Yields for $(OC)_5M'-M(CO)_3(\eta^5-C_5H_5)$ in CCl_4[a]

M	M'	$\Phi_{366nm} \pm 10\%$	$\Phi_{436nm} \pm 10\%$
Mo	Mn	0.51	
Mo	Re	0.56	
W	Mn	0.35	0.05_6
W	Re	0.23	0.05_1

[a] Photolysis in degassed CCl_4 solution at 25°. Analysis by uv and ir spectral changes. The products of the photolysis are $M(CO)_5Cl$ and $(\eta^5-C_5H_5)M(CO)_3Cl$.

CCl_4 yields the corresponding mononuclear metal carbonyl chlorides, reaction 3. The apparent one to one ratio of the homodinuclear products, and the stoichiometry and efficiency of the reactions in CCl_4, is just the type of convincing data that has led to the establishment of the photoinduced homolytic cleavage in other metal-metal bonded carbonyls.[1-3,5] The lack of substantial changes in the electronic absorption spectrum of the M-M′ complexes with variation in solvent polarity suggests that the mode of primary excited state decay will not change to heterolytic cleavage in polar media. Our qualitative results upon flash photolysis of the Mn-Mo complex in THF support this notion.

Examination of the electronic spectra of the M′-M complexes alone points to a mechanism for photoinduced M′-M cleavage like that found in M-M and M′-M′ complexes, i.e., homolytic cleavage. This remark is based upon the totally analogous spectra of M-M′ and the M-M and M′-M′ species. The simple orbital diagram in Scheme I accounts for all of the facts. In M′-M the near-uv absorption is associated with the $\sigma_b \rightarrow \sigma^*$ transition, and the visible absorption band is associated with the π-d $\rightarrow \sigma^*$ transition by analogy to $Mn_2(CO)_{10}$[9] and $[(\eta^5-C_5H_5)M(CO)_3]_2$.[5] As found[5] in the $[(\eta^5-C_5H_5)M(CO)_3]_2$, the $\sigma_b \rightarrow \sigma^*$ transition results in a higher M′-M cleavage efficiency than the π-d $\rightarrow \sigma^*$ transition.

The similarity of the spectra for the M′-M complexes reported here and the homodinuclear complexes is so striking that heterolytic cleavage would be unlikely. Thus, the expected requirements for heterolytic cleavage to obtain should include the statement that the electronegativity of the two incipient mononuclear fragments must be substantially different. Empirically, the more or less averaged ener-

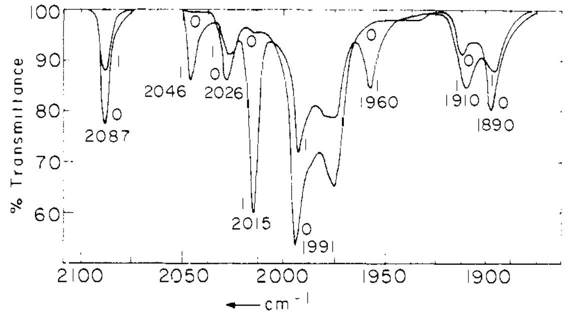


Figure 3. Infrared spectral changes accompanying flash photolysis of $(OC)_5Mn-W(CO)_3(\eta^5-C_5H_5)$ in degassed isooctane solution. Curve 0 is the initial spectrum and curve 1 is after one flash. Bands at 2087, 2026, 1991, and 1890 cm^{-1} are characteristic of the starting complex. Bands at 1960 and 1910 cm^{-1} are due to $[(\eta^5-C_5H_5)W(CO)_3]_2$, and those at 2046 and 2015 cm^{-1} are due to $Mn_2(CO)_{10}$. Quantitative concentrations changes are given in Table II.

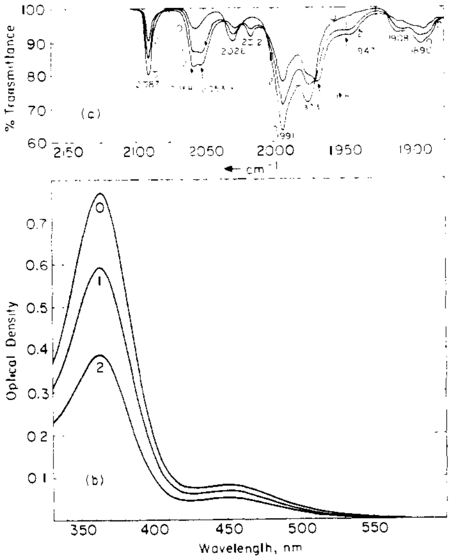
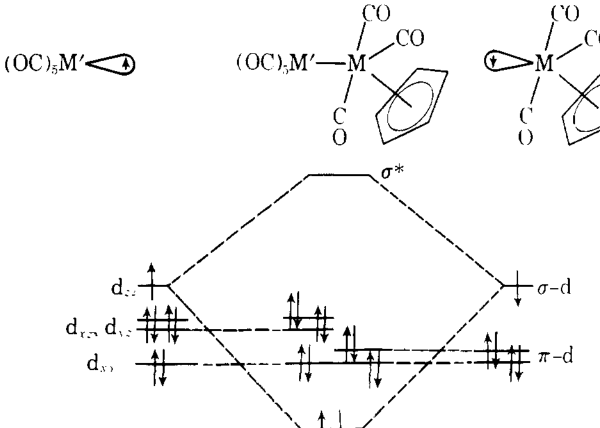


Figure 4. Infrared (a) and uv-visible (b) spectral changes accompanying 366-nm (~10^{-7} einstein/min) photolysis of $(OC)_5Mn-W(CO)_3(\eta^5-C_5H_5)$ in degassed CCl_4 solution. Infrared bands at 2087, 2026, 1991, 1908, and 1890 cm^{-1} are characteristic of the starting complex. The band at 2058 cm^{-1} is characteristic of $Mn(CO)_5Cl$ and the band at 2012 cm^{-1} reflects some formation of $[Mn(CO)_4Cl]_2$ via a secondary thermal reaction. Bands at 2053, 1968, and 1947 cm^{-1} reflect the formation of $(\eta^5-C_5M_5)W(CO)_3Cl$. Curves 0, 1, and 2 are after 0, 15, and 25 min of photolysis, respectively.

Scheme I



getic position of the $\sigma_b \rightarrow \sigma^*$ transition in M′–M compared to the M–M and M′–M′ is an indicator that reaction will follow a homolytic cleavage path. The insensitivity of the optical spectra to polar media is consistent with this conclusion. Naturally, observation of heterolytic cleavage products depends on the ability of the ions to undergo cage escape, but the absolute efficiency of the radical cross-coupling reactions argues against formation of caged ions. Experiments are now in progress with other dinuclear metal-metal bonded complexes to test and extend these propositions, and further, for the systems at hand, and in other cases where homolytic cleavage of a heterodinuclear system obtains, we have suitable conditions for investigation of the relative reactivity of the metal radicals toward various substrates.

Experimental Section

Materials. The $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were obtained from Pressure Chemical Co. and were used after purification by sublimation. The $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W) were synthesized by the established route[10] and were used after chromatography on grade no. 1 alumina. All solvents used were of a spectroscopic grade and were used without further purification.

Spectra. All uv-visible spectra were obtained using a Cary 17 uv-vis-nir spectrophotometer. All ir spectra were recorded using a Perkin-Elmer 521 grating infrared spectrometer. Low temperature uv-visible spectra were obtained in EPA solution with a quartz liquid nitrogen dewar fitted with quartz optical flats for windows. Quantitative ir measurements were made using matched 0.1- or 1.0-mm path length NaCl cells obtained from Perkin-Elmer Corp.

Synthesis of $(OC)_5M\text{–}M'(CO)_3(\eta^5\text{-}C_5M_5)$ (M = Mn, Re; M′ = Mo, W).[5] The method of synthesis for all four possible M–M′ compounds was the same and can be illustrated by that for the Mn–Mo compound. An N_2 purged 100 ml benzene solution of 0.5 g (1.2 mmol) of $Mn_2(CO)_{10}$ and 0.6 g (1.23 mmol) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ was photolyzed with a 450-W Hanovia medium pressure Hg lamp with a broad band uv filter (300–400 nm) until the ir showed that the rate of product formation had slowed demonstrably (about 1.5–2 hr). Then the solution was rotary evaporated to dryness (35°, 40 mm) and redissolved in a minimum amount of CH_2Cl_2. The reactants and products were separated from this solution by chromatography, in the dark, on grade no. 1 alumina. The unreacted $Mn_2(CO)_{10}$ was eluted with pure isooctane, the $(OC)_5Mn\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ was then eluted with a 25% solution of CH_2Cl_2 in isooctane, and finally unreacted $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ was eluted with pure CH_2Cl_2. The product was identified by ir[8] and the yield (0.115 g 85%) was based on Mn_2CO_{10} disappearance. Photolyses in the cases where $Re_2(CO)_{10}$ was used were carried out in Vycor tubes. Synthetic yields based on recovered reactants for the other compounds were Mn–W (70%), Re–Mo (25%), and Re–W (40%). The ir bands and the melting points agree with those in the literature:[8] Re–W (mp 109–110°, lit. 110–11.5°), Mn–W (mp 89.5–90°, lit. 90–91°), Mo–Mn (mp 78.5–80.5°, lit. 80.5–81.5°).

Flash Photolysis of $(OC)_5M'\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$. Degassed solutions of the metal carbonyl (1×10^{-3} *M*) in isooctane were flashed using a Xenon Corp. Model F-710 flash photolysis apparatus as the light source. The disappearance of starting material and the appearance of the products were monitored by ir. The ir spectra of the M′–M and M–M products and band intensities have been previously reported.[2,5]

Photolysis of $(OC)_5M'\text{–}M(CO)_3(\eta^5\text{-}C_5H_5)$ in CCl_4. Solutions of the metal carbonyl (1×10^{-3} *M*) in CCl_4 in 3-ml aliquots were placed in Pyrex test tubes (13 × 100 mm) with constrictions. These solutions were degassed in four freeze-pump-thaw cycles and hermetically sealed. Photolysis was performed with the use of a merry-go-round[11] equipped with a 550-W Hanovia medium pressure Hg source filtered with Corning glass filters to isolate the 366- or 436-nm mercury emissions. Ferrioxalate actinometry[12] was performed for each experiment to measure the light intensity. Disappearance of the metal carbonyl was monitored in the uv-visible, after a 1:5 dilution with CCl_4, and appearance of the metal carbonyl halides was monitored by ir. The ir data for the mononuclear metal carbonyl halides have been reported earlier.[2,5]

Acknowledgments. We thank the National Science Foundation for support of this research. M.S.W. acknowledges support as a Fellow of the A. P. Sloan Foundation and D.S.G. thanks the Department of Chemistry, M.I.T., for support as a Uniroyal Fellow.

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