"peripheral steric interaction" might interfere with O_2 binding in these models. Chang[23] has made a comparison between two iron(II)-copper(II) cofacial dimeric porphyrins and "chelated mesoheme" and found that increased steric encumbrance led to both reduced O_2 and CO affinities. A degree of steric differentiation was noted in the dimeric system; the CO affinities were reduced to a ca. 4-fold greater extent than the O_2 affinities.

It remains of interest that these other workers, using other model systems, fail to observe the same degree of discrimination that we do. At present there is no simple explanation, structural or otherwise, for why this should be so. Certainly, our own experience indicates that extreme caution must be used in making comparisons—even among ostensibly similar heme systems—since many factors can serve to influence O_2 and CO binding behavior.

Summary

Derivatives of the iron(II) "pocket" and "picket fence" porphyrins constitute a series of congruent complexes with which the effects of distal-side steric interactions on gaseous ligand binding can be explored. The "pocket" porphyrins have been designed to possess the same electronic nature and polarity in their binding cavity as that found in the "picket fence" complexes. Further, because both sets of models have one protected face, solvation is thought to be similar. Whereas the O_2 affinities for the iron(II) "pocket" porphyrins are similar to those of the iron(II) "picket fence" porphyrins, the CO affinities of the "pocket" complexes are substantially lower than those of the "picket fence" analogues. We attribute this behavior to the design of the "pocket", which should not substantially effect the intrinsically bent FeO_2 unit, yet still present steric hindrance sufficient to distort the FeCO moiety from its favored linear binding geometry. Our results therefore indicate that it *is* possible to discriminate between CO and O_2 binding in model iron(II) porphyrins. We suggest on this basis that distal-side interactions *may* play a role in regulating ligand binding to natural hemoproteins.

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Registry No. I, 75597-81-8; I(O_2), 74171-97-4; II, 75557-97-0; IIIa, 77338-87-5; IIIa(CO), 78694-32-3; IIIb, 77338-86-4; IVa, 85293-87-4; IVa(CO), 85293-92-1; IVb, 85293-88-5; V, 85293-89-6; FeTPP4CIm, 75529-05-4; FeTPP(2-MeIm), 48243-44-3; FeTPP(1,2-Me_2Im), 72186-60-8; FeOEP(1,2-Me_2Im), 75811-16-4; Fe(T(*p*-Cl)PP)(1,2-Me_2Im), 85293-90-9; FeTMesP(1,2-Me_2Im), 85293-91-0; FeAmPoc(1,2-Me_2Im), 85304-55-8; O_2, 7782-44-7; CO, 630-08-0; Fe "ether" "hanging base", 85293-93-2.

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(81) Wang, M. R.; Hoffman, B. M.; Shire, S. J.; Gurd, F. R. N. *J. Am. Chem. Soc.* **1979**, *101*, 7394-7398.

Photochemistry of $[W(CO)_5\{C(OMe)Ph\}]$. Formation of Alkyne-Carbene Complexes and Studies of Their Decomposition Reactions

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Abstract: The photochemistry of $[W(CO)_5\{C(OMe)Ph\}]$ has been examined and been shown to involve CO loss as the only detectable photoreaction. Irradiation in acetonitrile solution leads smoothly to the formation of $[W(CO)_4(CH_3CN)\{C(OMe)Ph\}]$ in quantitative yield. The 366- and 313-nm quantum yields for disappearance of $[W(CO)_5\{C(OMe)Ph\}]$ in CH_3CN solution are 0.009 and 0.011, respectively, but the quantum yield drops to $\leq 10^{-4}$ at 436 nm, even though the complex absorbs strongly at the latter wavelength. The lowest intense absorption band (λ_{max} 402 nm) (ϵ_{max} 10 560 L mol^{-1} cm^{-1}) has been assigned as a W → carbene(π^*) charge-transfer transition with ligand field bands lying at higher energy. The low-lying W → carbene charge-transfer state is inactive with respect to CO loss, with the latter occurring from ligand field excited states. Low-temperature photolysis in the presence of $PhC\equiv CPh$, $MeC\equiv CPh$, $MeC\equiv CMe$, $PhC\equiv CH$, and n-$BuC\equiv CH$ leads to spectroscopically observable alkyne-carbene adducts, with the diphenylacetylene complex $[W(CO)_4(PhC\equiv CPh)\{C(OMe)Ph\}]$ isolated as a crystalline solid. None of the alkyne adducts are stable at 25 °C in solution, and they decompose to give products that depend markedly upon the nature of the alkyne. With terminal alkynes, only polyacetylenes form, whereas the $PhC\equiv CPh$ and $PhC\equiv CMe$ adducts decay exclusively to form 1-methoxy-2,3-diphenylindene and 1-methoxy-2-methyl-3-phenylindene, respectively. The $MeC\equiv CMe$ adduct leads to both poly-2-butyne and 1-methoxy-2,3-dimethylindene.

Much attention has been given to studies of the thermal reactivity of transition-metal carbene complexes, because of their important role in a number of catalytic and stoichiometric transformations.[1] In contrast, relatively little attention has been devoted to the photochemical properties of this class of compounds,[2-10] even though photolysis might be expected to substantially alter the reactivity of the carbene ligand through population of charge-transfer excited states which involve that ligand. The compounds that have had their photochemistry most extensively studied are the pentacarbonyl carbene complexes of Cr and W, but even here a somewhat confusing pictue emerges concerning

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(1) (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (c) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (d) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487. (e) Casey, C. P. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 189.

(2) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

(3) (a) Neumann, S. M. Ph.D. Dissertation, University of Wisconsin, Madison WI, 1978. (b) Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1970**, *8*, 1. (c) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *Fundam. Res. Homogenous* **1979**, *3*, 141. (d) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417.

(4) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.

(5) Edwards, B. H.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *210*, 91.

(6) (a) Öfele, K.; Herberhold, M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1973**, *28*, 306. (b) Öfele, K.; Roos, E.; Herberhold, M. *Ibid.* **1976**, *31*, 1070. (c) Rieke, R. D.; Kojiana, H.; Öfele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735.

(7) (a) Fischer, E. O.; Beck, H. J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 72. (b) *Chem. Ber.* **1971**, *104*, 3101. (c) Fischer, E. O.; Besl, G. *J. Organomet. Chem.* **1978**, *157*, C33.

(8) Wright, R. E.; Vogler, A. *J. Organomet. Chem.* **1978**, *160*, 197.

(9) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486.

(10) McCormick, F. B.; Kiel, W. A.; Gladsyz, J. A. *Organometallics* **1982**, *1*, 405.

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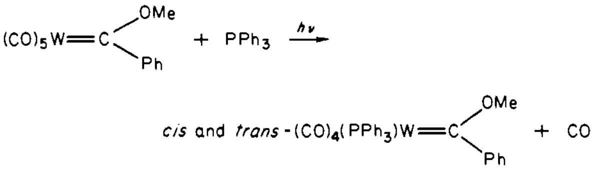
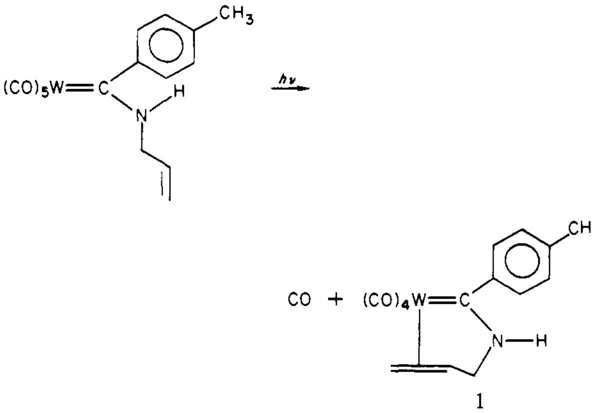
the primary photochemical reaction.[2-5] Most of the literature data indicate that photolysis leads to loss of CO although other studies appear to argue against this conclusion. In early work Fischer and co-workers[2] noted that irradiation of several [M(CO)$_5${C(OR)R′}] (M = Cr, W) complexes in the presence of phosphines leads to cis and trans tetracarbonyl carbene phosphine complexes, with low-temperature studies indicating the cis complexes to be the primary photoproducts, e.g., eq 1. These substitution reactions presumably proceed through photoinduced CO loss. A similar conclusion can be drawn from reactions reported by Casey and co-workers,[3] who noted that exchange of ^{13}CO for ^{12}CO in [W(CO)$_5$(CPh$_2$)] and [W(CO)$_5${C(OMe)Ph}] can be photoinduced[3a] and who observed the interesting conversion shown in eq 2.[3d]



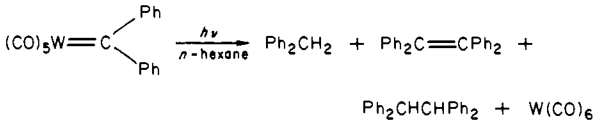
$$(CO)_5W{=}C(OMe)Ph + PPh_3 \xrightarrow{h\nu} cis\text{ and }trans\text{-}(CO)_4(PPh_3)W{=}C(OMe)Ph + CO \quad (1)$$



(2)

1

However, other workers[4] have noted that [W(CO)$_5${C(OMe)Ph}] and [W(CO)$_5${C(OMe)Me}] are relatively inactive photochemically when irradiated at 405 nm and that photolysis in the presence of PPh$_3$ does not lead to [W(CO)$_4$(PPh$_3$){C(OMe)R}] products, in contrast to the results of Fischer and Fischer,[2] who used higher energy irradiation. Irradiation in the presence of CO was reported to lead to carbene photoreplacement and to the formation of [W(CO)$_6$] with a very low quantum yield ($\phi_{405} < 10^{-2}$).[4] Furthermore, a recent report of the photodegredation reaction of [W(CO)$_5$(CPh$_2$)] to give the products shown in eq 3 stated that photolysis under 2–5 atm of CO did not substantially inhibit the photodecomposition, suggesting a pathway not involving CO loss.[5] This observation contrasts with Casey and Neumann's[3a] observation of facile photoinduced ^{13}CO/^{12}CO exchange in [W(CO)$_5$(CPh$_2$)]. However, different irradiation wavelengths were used in these two studies, with quartz-filtered medium-pressure Hg irradiation used in the former (eq 3).



$$(CO)_5W{=}CPh_2 \xrightarrow[n\text{-hexane}]{h\nu} Ph_2CH_2 + Ph_2C{=}CPh_2 + Ph_2CHCHPh_2 + W(CO)_6 \quad (3)$$

The objectives of the study described herein were twofold. We first wish to clearly define the primary photochemical properties of [W(CO)$_5${C(OMe)Ph}] in order to place our understanding of the photochemistry of this compound on sound footing. Following the stronger literature indications that photoinduced CO loss would occur, we also wished to try to trap the coordinatively unsaturated photogenerated intermediate with potentially interesting alkyne ligands. We report herein definitive experiments which show that photolysis of [W(CO)$_5${C(OMe)Ph}] does indeed lead to CO loss as the only detectable photoreaction when suitable trapping substrates are available. Low-temperature irradiation in the presence of alkynes leads to spectroscopic observation and, in one case, isolation of carbene–alkyne complexes [W(CO)$_4$(RC≡CR′){C(OMe)Ph}]. The thermal decomposition modes of these adducts have been studied. With internal alkynes, a photochemical route has been developed for the synthesis of potentially interesting indenyl ethers.

Experimental Section

General Procedures. [W(CO)$_5${C(OMe)Ph}][11] and [W(CO)$_5$(CPh$_2$)][12] were prepared by literature procedures. Solvents were dried by stirring over Na/benzophenone (THF, hexane, benzene, toluene, Et$_2$O) or CaH$_2$ (CH$_3$CN) and freshly distilled under N$_2$ prior to use. Solutions were prepared either on a vacuum line by transferring solvent in vacuo to the reaction flask or in a Vacuum Atmospheres drybox under an N$_2$ atmosphere. All solutions were rigorously degassed by three freeze–pump–thaw cycles prior to irradiation. Solutions were cooled for low-temperature photochemical reactions (−30 °C and below) by use of a Neslab Cryocool CC-80II refrigeration unit, and the temperature was measured with a standard low-temperature alcohol thermometer.

General Photochemical Procedures. Photolyses which were monitored by electronic absorption spectroscopy were conducted in cells fitted with Kontes quick-release Teflon valves and glass joints for attachment to a vacuum line. For IR and NMR monitoring of photochemical reactions, samples were irradiated in 1-mm solution IR cells fitted with NaCl windows and in 5-mm diameter NMR tubes sealed tightly with parafilm-wrapped plastic caps, respectively. All other photolyses were conducted in standard Pyrex Schlenk glassware. Photolyses were conducted with broad-band irradiation from a 100-W Blak Ray B100 A lamp filtered through Pyrex or through a 366-nm narrow band-pass filter, with a Pyrex-filtered 450-W Hanovia medium-pressure Hg lamp, or with a Rayonet photoreactor equipped with 254-nm low-pressure Hg vapor tubes. Quantum yield measurements at 313, 366, and 436 nm were conducted as previously described.[13] Light intensities ($I_{436} = 4.33 \times 10^{-8}$ einsteins/min; $I_{366} = 1.6 \times 10^{-7}$ einsteins/min; $I_{313} = 1.28 \times 10^{-7}$ einsteins/min) were measured by ferrioxalate actinometry,[14] modified according to the recommendations of Bowman and Demas.[14b]

Photolysis of [W(CO)$_5${C(OMe)Ph}] in CH$_3$CN Solution. Freshly dried and degassed CH$_3$CN (60 mL) was transferred in vacuo into a 100-mL Schlenk flask charged with [W(CO)$_5${C(OMe)Ph}] (250 mg, 0.56 mmol). This solution was irradiated under reduced N$_2$ pressure at 25 °C for 20 h by using the Blak Ray 100-A lamp filtered through Pyrex, during which time the solution changed color from light to dark red. The CH$_3$CN solution was reduced to 75% of its original volume and cooled to −25 °C. After 3 days, a dark burgundy solid precipitated. The solution above the precipitate was decanted under N$_2$ and the resultant solid washed with *n*-hexane and dried to give [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] as an impure dark burgundy solid in ~66% yield (170 mg, 0.37 mmol). Anal. Calcd for $C_{14}H_{11}O_5NW$: C, 36.77; H, 2.41. Found: C, 35.87; H, 2.53. Exposure of hexane solutions of the complex to 1 atm CO results in immediate reformation of [W(CO)$_5${C(OMe)Ph}] (by IR).

Photolysis of [W(CO)$_5${C(OMe)Ph}] in THF and Et$_2$O Solutions. These experiments were conducted in a manner analogous to those in CH$_3$CN solution. Photolysis with 366-nm light induces a slow color change from light red to dark red, but IR spectral monitoring showed that the reactions did not proceed to completion. Solid THF and Et$_2$O adducts could not be isolated because of their apparent instability. THF and Et$_2$O solutions of the respective adducts rapidly react with CO to reform [W(CO)$_5${C(OMe)Ph}]. This species also forms upon exposure of these solutions to air, and a small amount of a brown decomposition product deposits.

Photolysis of [W(CO)$_5${C(OMe)Ph}] in the Presence of PhC≡CPh. Dried and degassed hexane (50 mL) was vacuum transferred into a 100-mL Schlenk flask charged with 100 mg (0.24 mmol) of [W(CO)$_5${C(OMe)Ph}] and 40 mg (0.24 mmol) of PhC≡CPh. After dissolution of the starting complex at room temperature, the flask was placed in a 2-propanol bath contained in an unsilvered Pyrex Dewar flask and cooled to −50 °C with the Neslab refrigeration unit. Photolysis was conducted under reduced pressure by placing the Black Ray 100-A lamp equipped with a 366-nm filter next to the Dewar flask. The Schlenk flask was periodically evacuated to remove the released CO. [W(CO)$_4$(PhC≡CPh){C(OMe)Ph}] slowly precipitates from solution during photolysis as a burgundy microcrystalline solid. After ~1 week, the solution above

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[11] Fischer, E. O.; Shubert, V.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164.

[12] Casey, C. P.; Burkhardt, T. J.; Newmann, S. M.; Scheck, D. M.; Tuinstra, H. E. *Inorg. Synth.* **1979**, *19*, 180.

[13] Foley, H. C.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7176.

[14] (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

Table I. Electronic Absorption Spectral Data

complex	λ_{max}, nm	λ_{max}, μm^{-1}	ϵ_{max}, L mol^{-1} cm^{-1}	assignt	ref
$[W(CO)_6]$[a]	353	2.83	1000	LF, $^1A_{1g} \rightarrow {}^3T_{1g}$	16
	334	2.995	1680	LF, $^1A_{1g} \rightarrow {}^1T_{1g}$	
	314	3.185	3250	LF, $^1A_{1g} \rightarrow {}^1T_{2g}$	
	289	3.465	17600	MLCT, $^1A_{1g} \rightarrow {}^1T_{1u}$	
$[W(CO)_5NH_3]$[b]	440	2.273	600	LF, $^1A_1 \rightarrow {}^3E$	17a
	408	2.451	3800	LF, $^1A_1 \rightarrow {}^1E$	
$[W(CO)_5(4\text{-CN-pyridine})]$[c]	456	2.193	7060	MLCT	17b
	404	2.475	5530	LF, $^1A_1 \rightarrow {}^1E$	
$[W(CO)_5\{C(OEt)CH_3\}]$[d]	371	2.696	7300	$(W \rightarrow carbene(\pi^*))^1$	18
	349	2.863	7300	LF, $^1A_1 \rightarrow {}^1B_2$	
$[W(CO)_5\{C(OEt)Ph\}]$[d]	403	2.483	8400	$(W \rightarrow carbene(\pi^*))^1$	18
	356	2.811	1800	LF, $^1A_1 \rightarrow {}^1B_2$	
$[W(CO)_5\{C(OMe)Ph\}]$[d]	521	1.920	576	$(W \rightarrow carbene(\pi^*))^3$	f
	402	2.490	10560	$(W \rightarrow carbene(\pi^*))^1$	
	352	2.840	6080	LF, $^1A_1 \rightarrow {}^1B_2$	
$[W(CO)_5\{CPh_2\}]$[e]	485	2.06	10400	$(W \rightarrow carbene(\pi^*))^1$	19
	373	2.68	7356	LF, $^1A_1 \rightarrow {}^1B_2$	
$[W(CO)_4(CH_3CN)\{C(OMe)Ph\}]$[a]	438	2.28	7560	$(W \rightarrow carbene(\pi^*))^1$	f

[a] CH_3CN solution. [b] C_6H_6 solution. [c] Isooctane solution. [d] Cyclohexane solution. [e] Hexane solution. [f] This work.

the solid was decanted and the resultant solid dried at −30 °C in vacuo to give 14 mg (0.02 mmol, 10% yield) of an isolated sample. Anal. Calcd for $C_{26}H_{18}O_5W$: C, 52.53; H, 3.00. Found: C, 52.86; H, 3.11. The precipitate does not form if solutions are too dilute. When solutions containing $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ are warmed above −20 °C, they rapidly become cloudy as decomposition occurs. IR spectra shows $[W(CO)_6]$ (ν_{CO} = 1978 cm^{-1}) to be the only carbonyl-containing complex present after warmup. Chromatography of these solutions on deactivated Al_2O_3 using hexane as eluant gave a colorless fraction containing $[W(CO)_6]$ followed by a yellow fraction which yielded a small amount of a white solid upon solvent evaporation. The latter showed a parent ion at *m/e* 298 in its mass spectrum and ^1H NMR resonances characteristic of 1-methoxy-2,3-diphenylindene, **1**.

Photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ in the Presence of $PhC{\equiv}CMe$. Irradiation of hexane solutions of $[W(CO)_5\{C(OMe)Ph\}]$ containing a slight molar excess of $PhC{\equiv}CMe$ at −40 °C gave color and IR changes similar to those obtained with $PhC{\equiv}CPh$, but a precipitate did not form. Upon solvent removal at −40 °C or upon warmup to 25 °C, decomposition occurred with a clouding of the solution. IR spectra of these warmed solutions showed only $[W(CO)_6]$ and $[W(CO)_5\{C(OMe)Ph\}]$ to be present. Chromatography of such solution on deactivated alumina using hexane as eluant gave fractions of $[W(CO)_6]$ and $[W(CO)_5\{C(OMe)Ph\}]$ and a yellow fraction which yielded a small amount of a yellow solid upon solvent evaporation. The latter showed a parent ion at *m/e* 236 in its electron-impact mass spectrum, consistent with the presence of 1-methoxy-2-methyl-3-phenylindene, **2**.

Photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ in the Presence of $MeC{\equiv}CMe$, $PhC{\equiv}CH$, and *n*-$C_4H_9C{\equiv}CH$. Color and IR spectral changes that occur upon photolysis of hexane solutions at −40 °C containing $[W(CO)_5\{C(OMe)Ph\}]$ with a slight molar excess of the title alkynes are qualitatively similar to those obtained with $PhC{\equiv}CPh$. Upon warmup of these solutions or upon photolysis at 25 °C, these solutions became viscous, implying polymer formation, and cloudy. A jellylike material is deposited in the case of $MeC{\equiv}CMe$, and the IR spectrum (KBr) of an isolated and dried sample showed bands at 2970 (s), 2920 (s), 2850 (m), 2710 (w), 1440 (m), 1365 (m), 1095 (m), 1040 (sh), and 1030 (m) cm^{-1} similar to those reported for poly-2-butyne.[15b] Chromatography of such solutions on deactivated alumina using hexane as eluant gives a trace amount of a yellow solid which shows a parent ion at *m/e* 174, consistent with the presence of 1-methoxy-2,3-dimethylindene, **3**.

Photolysis of $[W(CO)_5\{C(OMe)(Ph)\}]$ in the presence of $PhC{\equiv}CH$ and 1-hexyne induces a color change from light red to dark red and a marked increase in viscosity of the solutions when concentrated. Chromatography on deactivated alumina gave $[W(CO)_6]$ and $[W(CO)_5\{C(OMe)Ph\}]$ as the only identifiable fractions.

Thermolysis of $[W(CO)_5\{C(OMe)Ph\}]$ with Alkynes. These experiments were conducted in 5-mm ^1H NMR tubes containing an equimolar mixture of $[W(CO)_5\{C(OMe)Ph\}]$ and the alkyne under study dissolved in toluene-d_8. The samples were heated in an oil bath maintained at 100 °C for up to 18 h, and the course of the reactions were monitored by ^1H NMR spectroscopy.

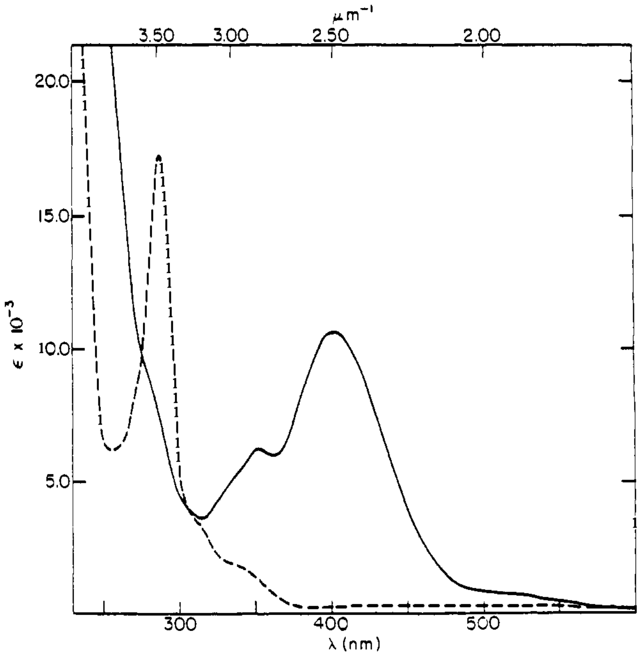

Figure 1. Electronic absorption spectra of $[W(CO)_5\{C(OMe)Ph\}]$ (—) and $[W(CO)_6]$ (---) at 300 K in hexane solution.

Spectral Measurements. IR spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer, and electronic absorption spectra were obtained on either a Cary 17 spectrophotometer or a Hewlett Packard 8450A spectrophotometer equipped with a Hewlett Packard 9875A cartridge tape unit and 7225A plotter. Spectra at 77 K were recorded in a 7:4 methylcyclohexane/pentane glass using a quartz Dewar flask fitted with Suprasil quartz optical windows. Proton NMR spectra were obtained by using a Varian EM-360 NMR spectrometer and Bruker WM360 and WP200 Fourier transform NMR spectrometers. Electron-impact mass spectra were obtained on an AEI-MS9 spectrometer with a source voltage maintained at 70 eV.

Results

Electronic Absorption Spectral Data. The electronic absorption spectra of $[W(CO)_5\{C(OMe)Ph\}]$ and $[W(CO)_6]$, for comparison, are shown in Figure 1. Spectral data for these and related complexes are set out in Table I.[16-19] The complex $[W(CO)_5$-

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(15) (a) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (b) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *Ibid.* **1980**, *102*, 7940. (c) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

(16) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

(17) (a) Wrighton, M. *Inorg. Chem.* **1974**, *13*, 905. (b) Wrighton, M. A.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

(18) Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32.

(19) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833.

Table II. Infrared Spectral Data for *cis-* and *trans-*[M(CO)$_4$L{C(OR)R'}] Complexes

complex	ν_{CO}, cm^{-1} A$_{1g}$	B$_{1g}$	Eu	ref
	Trans Complexes			
trans-[Cr(CO)$_4$(P-*n*-Bu$_3$){C(OMe)Me}]^a	2006 w	1933 vw	1889 vs	2
trans-[Cr(CO)$_4$(PPh$_3$){C(OMe)Me}]^a	2012 vw	1943 vs	1899 vs, br	2

complex	ν_{CO}, cm^{-1} A$_1$	A$_2$	B$_1$	B$_2$	ref
	Cis Complexes				
cis-[Cr(CO)$_4$(P-*n*-Bu$_3$){C(OMe)Me}]^a	2001 m	1920 s	1909 s	1889 vs	2
cis-[W(CO)$_4$(P-*n*-Bu$_3$){C(OMe)Me}]^a	2018 m	1919 s	1912 s, br	1889 vs	2
cis-[W(CO)$_4$(CH$_3$CN){C(OMe)Ph}]^b	2017 m	1900 s	1804 m	1790 m	*c*
cis-[W(CO)$_4$(CH$_3$CN){C(OMe)Ph}]^a	2024 m	1940 s	1912 m	1880 m	*c*
cis-[W(CO)$_4$(THF){C(OMe)Ph}]^d	2024 m	*e*	1898 m, sh	*e*	*c*
cis-[W(CO)$_4$(PhC≡CPh){C(OMe)Ph}]^a	2030 m	1940 s	1915 m	1890 m	*c*
cis-[W(CO)$_4$(PhC≡CH){C(OMe)Ph}]^a	2025	*e*	*e*	1883	*c*
cis-[W(CO)$_4$(PhC≡CMe){C(OMe)Ph}]^a	2025	*e*	*e*	1890	*c*
cis-[W(CO)$_4$(MeC≡CMe){C(OMe)Ph}]^a	2025	*e*	*e*	1863	*c*

^{a} Hexane solution. ^{b} CH$_3$CN solution. ^{c} This work. ^{d} THF solution. ^{e} Bands obscured by [W(CO)$_5${C(OMe)Ph}] absorption.

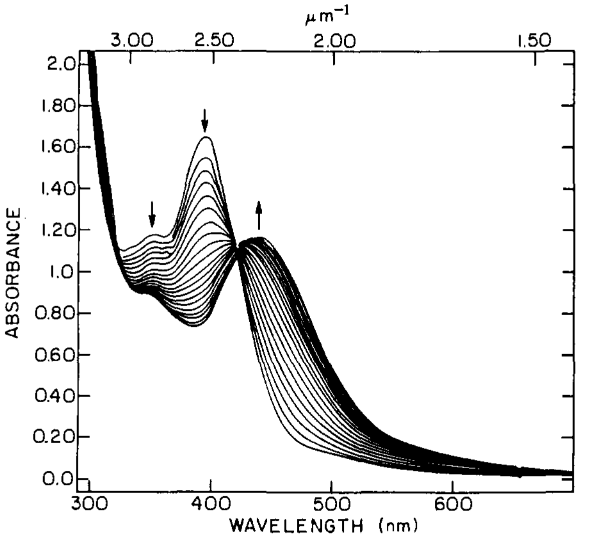
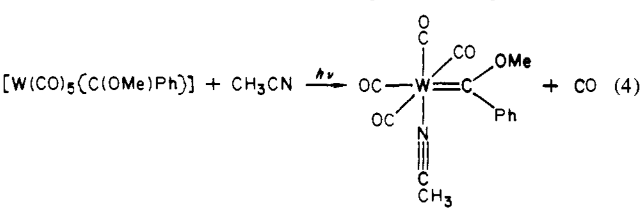


Figure 2. Electronic absorption spectral changes that occur during 366-nm photolysis of a CH$_3$CN solution of [W(CO)$_5${C(OMe)Ph}]. Intervals between successive spectra are approximately 60-s irradiation time. The arrows indicate the direction of change with increasing irradiation.

{C(OMe)Ph}] shows three bands at 521 (ϵ 576 M^{-1} cm^{-1}), 402 (ϵ 10650 M^{-1} cm^{-1}), and 352 nm (ϵ 6080 M^{-1} cm^{-1}) which sharpen but do not shift upon cooling from 300 to 77 K. Similar spectra are shown by other [W(CO)$_5${C(OR)R'}] derivatives[18] (Table I), but [W(CO)$_5$(CPh$_2$)] shows a significant red-shift of the low-energy intense band as compared to the heteroatom-stabilized carbene complexes.[19]

Photolysis of [W(CO)$_5${C(OMe)Ph}] in CH$_3$CN, THF, and Et$_2$O Solutions. Ultraviolet irradiation of [W(CO)$_5${C(OMe)Ph}] in degassed CH$_3$CN solution leads to photosubstitution of CH$_3$CN for CO (eq 4). The UV–vis and IR spectral changes which occur



(4)

during 366-nm irradiation are shown in Figures 2 and 3, respectively. The maintenance of isosbestic points in both spectra shows the conversion to be clean with no indication of competing or secondary photoreactions under these conditions. The spectra further illustrate that the reaction can be driven to completion. The [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] photoproduct was obtained as a burgundy solid following a batch scale photolysis and was characterized spectroscopically. This photoproduct was observed to react with CO to reform the [W(CO)$_5${C(OMe)Ph}] starting complex (eq 5) but otherwise is stable at 25 °C for prolonged

$$[W(CO)_4(CH_3CN)\{C(OMe)Ph\}] + CO \rightarrow [W(CO)_5\{C(OMe)Ph\}] + CH_3CN \quad (5)$$

periods in the absence of air. In solutions exposed to air and in hydrocarbon solutions under N$_2$, it decomposes to give [W(CO)$_5${C(OMe)Ph}] and other unidentified products.

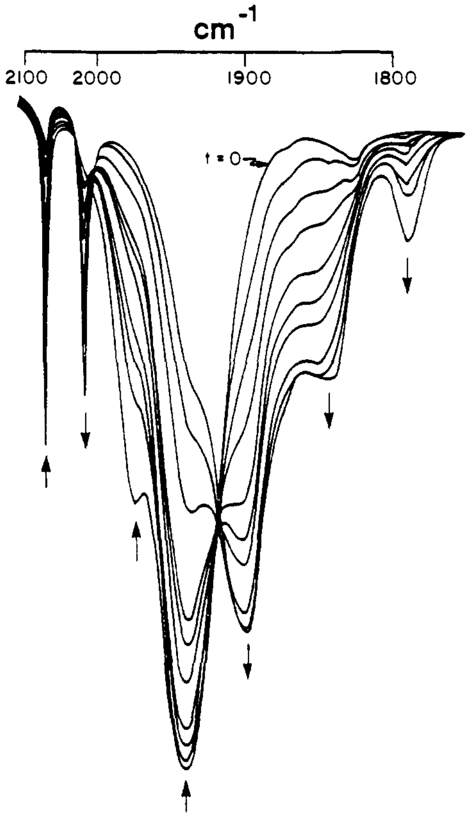


Figure 3. Infrared spectral changes during 366-nm photolysis of [W(CO)$_5${C(OMe)Ph}] in CH$_3$CN solution. The arrows indicate the direction of change with increasing irradiation time. Spectra were recorded at intervals of ~60-s irradiation.

The four-band ν_{CO} pattern observed in the IR spectrum of [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] (Figure 3) implies a cis ar-

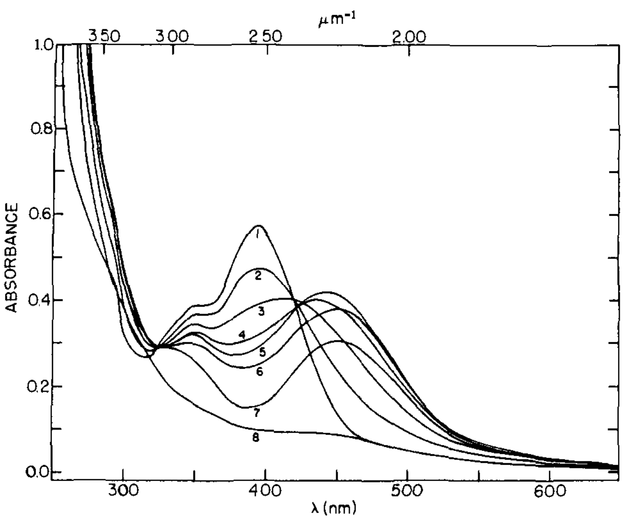


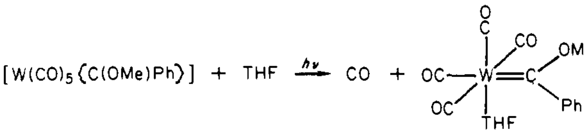
Figure 4. Electronic absorption spectral changes during 254-nm photolysis of [W(CO)$_5${C(OMe)Ph}] in CH$_3$CN solution. Spectra were recorded at the following time intervals: 1, 5 s; 2, 10 s; 3, 15 s; 4, 20 s; 5, 25 s; 6, 40 s; 7, 100 s; 8, >1 h.

rangement of the carbene and CH$_3$CN ligands. This is evidenced by data shown in Table II, which compares the IR spectra of related *cis*- and *trans*-[M(CO)$_4$L{C(OMe)Ph}] complexes.[2] *trans*-[M(CO)$_4$L$_2$] complexes of D_{4h} symmetry have only one IR-active ν_{CO} vibration (E$_u$), whereas C_{2v} *cis*-[M(CO)$_4$L$_2$] complexes have four (2A$_1$ + B$_1$ + B$_2$).[20] Although the rigorous symmetries of the *cis*- and *trans*-[M(CO)$_4$L{C(OMe)Ph}] complexes are C_s and D_{4v}, respectively, their IR spectra approximate those predicted by the higher local symmetries of C_{2v} and D_{4h}. Thus the trans complexes show one strong ν_{CO} band, whereas the cis complexes display four bands of similar intensity, as does [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}]. The CH$_3$CN adduct shows a strong solvent effect on its IR spectrum (Table II) with several of the bands shifted significantly to lower energy in CH$_3$CN solution as compared to a hexane solution of the complex. The ^{1}H NMR spectrum of [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] in benzene-d_6 solution shows two equal intensity singlets at δ 0.30 and 4.4 which may be respectivly assigned to the coordinated acetonitrile ligand and to the carbene methoxy group. Free acetonitrile in benzene-d_6 solution shows its characteristic singlet at δ 0.67, and thus coordination induces a small upfield shift in this resonance.

The 254-nm photochemistry of [W(CO)$_5${C(OMe)Ph}] is more complicated than that at 366 nm as evidence by the UV–vis spectral changes shown in Figure 4. The initial spectral changes are similar to those obtained upon 366-nm irradiation, and a new absorption band grows in at 438 nm characteristic of [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] (see Figure 2). However, this product is sensitive to 254-nm irradiation, and its absorption bands rapidly disappear upon continued photolysis. IR monitoring shows the formation of [W(CO)$_6$] and other unidentified products upon prolonged 254-nm irradiation.

The 313- and 366-nm quantum yields for photosubstitution of CH$_3$CN for CO in [W(CO)$_5${C(OMe)Ph}] are 0.011 ± 0.002 and 0.009 ± 0.001, respectively. An accurate value for the 436-nm quantum yield could not be obtained because of the very low photosensitivity of the complex at this wavelength, but an upper limit of 1×10^{-4} can be given on the basis of the sesitivity of our apparatus. Carbon monoxide at 1-atm pressure does not inhibit the rate of photosubstitution of CH$_3$CN for CO in *neat* acetonitrile, presumably because of the high CH$_3$CN concentration compared to that of dissolved CO. However, complete inhibition of the photoreaction results when hexane solutions containing a 20-fold excess of CH$_3$CN over [W(CO)$_5${C(OMe)Ph}] are irradiated under a CO atmosphere.

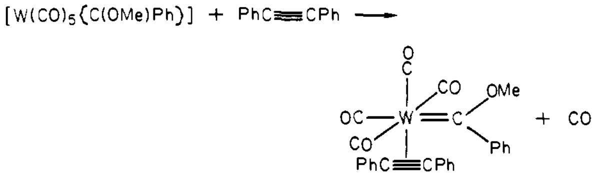
Smooth UV–visible and IR spectral changes also result upon 366-nm photolysis of [W(CO)$_5${C(OMe)Ph}] in THF solution, providing the solvent is doubly distilled from Na/benzophenone ketyl and vacuum transferred immediately prior to reaction. Irreproducible spectral changes result if the THF is not carefully purified. As the irradiation proceeds, a new UV–visible absorption band grows in at 467 nm which may be attributed to [W(CO)$_4$(THF){C(OMe)Ph}]. Two new bands appear in the IR spectrum of the irradiated solution at 2024 (m) and 1898 (m) cm^{-1} (Table II) similar in position to two of the bands of the acetonitrile adduct. It has not proven possible to drive the photoreaction to completion, and the remaining IR bands are apparently obscured by absorption of the starting complex and THF solvent absorption. The overall reaction shown in eq 6 is indicated



(6)

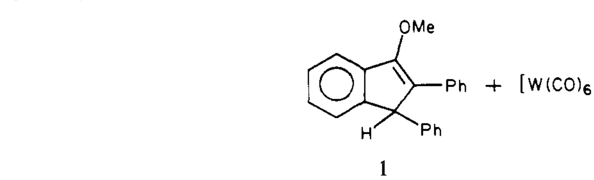
by the spectral data. Although not as extensively investigated, photolysis of [W(CO)$_5${C(OMe)Ph}] in Et$_2$O solution gives IR spectral changes similar to those observed in THF solution and indicates the formation of [W(CO)$_4$(Et$_2$O){C(OMe)Ph}].

Photolysis of [W(CO)$_5${C(OMe)Ph}] in the Presence of PhC≡CPh. Infrared and ^{1}H NMR data show that 366-nm irradiation of [W(CO)$_5${C(OMe)Ph}] in hexane solution in the presence of PhC≡CPh leads to photosubstitution of the alkyne for CO (eq 7) to give an insolable alkyne–carbene complex *as long as the temperature is maintained at −30 °C or below*. The complex is represented as a cis-disubstituted octahedral complex in eq 7 although the exact structure is unknown (see Discussion). As the irradiation proceeds, new IR bands grow in at 2030, 1940, 1915, and 1890 cm^{-1} as the bands due to the initial carbene complex smoothly decrease. Photolysis of concentrated solutions at −30 °C in preparative-scale experiments leads to the deposition of small quantities of burgundy crystals of the alkyne adduct on the sides of the irradiation vessel. These crystals can be isolated by decanting the solvent at low temperature (see Experimental Section). The alkyne adduct appears to be stable for hours in the solid state at room temperature in the absence of air, and a satisfactory C, H analysis was obtained for the complex. IR data for the isolated complex are set out in Table II and imply a tetracarbonyl formulation with a cis arrangement of the carbene and alkyne ligands. The observed four-band pattern is remarkably similar in both band positions and relative intensities to the spectrum of [W(CO)$_4$(CH$_3$CN){C(OMe)Ph}] in hexane solution and to the spectra of the various *cis*-[Cr(CO)$_4$L{C(OR)R′}] complexes studied by Fischer[2] (Table II).



(7)

The alkyne adduct rapidly decomposes in solution at temperatures above −20 °C. The principal decomposition products have been identified as [W(CO)$_6$] and 1-methoxy-2,3-diphenylindene, **1** (eq 8). Tungsten metal also appears to be formed as evidenced



(8)

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by a clouding of the solution and deposition of an insoluble

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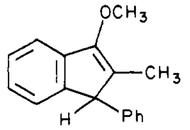
[20] (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; 3rd ed.; Wiley: New York, 1978.

green-black precipitate during decomposition. These same products also result when irradiation of $[W(CO)_5\{C(OMe)Ph\}]$ is carried out in the presence of $PhC{\equiv}CPh$ at 25 °C. Presumably, $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ forms at 25 °C, but it must rapidly decompose under these conditions. The δ 3.90 singlet due to $[W(CO)_5\{C(OMe)Ph\}]$[21] smoothly decreases in intensity upon 366 nm or Pyrex-filtered irradiation of benzene-d_6 solutions containing a 1:1 ratio of $PhC{\equiv}CPh$ and $[W(CO)_5\{C(OMe)Ph\}]$, and new singlets appear and grow in at δ 4.70 and 3.62 in a 1:3.1 intensity ratio. These correspond exactly to the resonances reported for 1-methoxy-2,3-diphenylindene, **1**.[22] Conversion of the carbene complex to the indenyl ether occurs to greater than 90% as estimated by integration of the ^1H NMR spectrum of the irradiated solution. Other resonances appear at δ 4.08 (t), 3.49 (s), 3.24 (s), 3.17 (s), and 3.11 (s), but the total intensity of these is <2% that of the resonances due to **1**. The conversion of the carbene complex to **1** can be driven to completion by prolonged photolysis (6–10 days). Chromatography of the photolyzed solution led to extensive decomposition, but a small sample of **1** was isolated in <10% yield which showed the expected parent ion at *m/e* 298 in its mass spectrum.

The −40 °C ^1H NMR spectrum of a toluene-d_8 solution of $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$, prepared from an isolated solid sample of the complex that had been stored at −50 °C for several days, showed the resonances attributed to **1**[22b] but also a singlet at δ 3.48. Upon warmup to −20 °C the latter resonance decreases and fully disappears into the base line as the resonances of **1** increase in intensity. The δ 3.48 singlet is thus attributed to the CH_3O group of the carbene ligand in the thermally unstable complex $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$. The IR spectrum of an isolated sample of $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ in CH_2Cl_2 at ~−40 °C showed bands at 2030 (m), 1930 (br s), and 1865 (s) cm^{-1}. Upon warmup to 25 °C these bands disappear and a strong band at 1978 cm^{-1} grows in due to $[W(CO)_6]$. Also present in the decomposed sample are weak bands at 2060, 2040, 2020, 1962, 1925, and 1880 cm^{-1}. However, when this decomposition is allowed to occur under a CO atmosphere, the bands of $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ are smoothly replaced by the strong 1978 cm^{-1} band of $[W(CO)_6]$ and the other bands are not observed. Significantly, the characteristic bands of $[W(CO)_5\{C(OMe)Ph\}]$ are completely absent from this spectrum. At −40 °C, the alkyne adduct is stable under a CO atmosphere and does not react to form either $[W(CO)_6]$ or $[W(CO)_5\{C(OMe)Ph\}]$. The mass spectrum of an isolated sample of $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ showed only ions derived from **1** and $[W(CO)_6]$. The thermally unstable complex apparently decomposes on the mass spectrometer probe during the measurement.

Photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ in the Presence of Other Alkynes. Qualitatively similar results to those obtained with $PhC{\equiv}CPh$ were observed when $[W(CO)_5\{C(OMe)Ph\}]$ was irradiated in the presence of phenylacetylene, methylphenylacetylene, dimethylacetylene, and 1-hexyne at low temperature (≤−30 °C). In each case irradiation of hexane solutions containing approximately equimolar concentrations of the complex and the alkyne rapidly leads to development of the burgundy-red color characteristic of $[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$ and new IR bands grow in at 2025 cm^{-1} and in the 1860–1890 cm^{-1} range (Table II) as the bands of the initial carbene complex decrease. These bands are similar to those observed for $[W(CO)_4(CH_3CN)\{C(OMe)Ph\}]$ in hexane solution and for the $PhC{\equiv}CPh$ adduct and imply a similar product. However, in no case has it proven possible to drive these reactions to completion or to isolate solid samples of the adduct complexes since each rapidly decomposes upon warmup to room temperature, as evidenced by the disappearance of the characteristic IR bands and the growth of the 1978-cm^{-1} band of $[W(CO)_6]$.

The nature of the organic product obtained upon decomposition of the initially formed alkyne–carbene complex is dramatically dependent on the nature of the alkyne. With $MeC{\equiv}CPh$, ^1H NMR and mass spectra indicate the production of the indenyl ether **2** analogous to the formation of **1** upon photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ in the presence of $PhC{\equiv}CPh$. Thus, when an equimolar mixture of $[W(CO)_5\{C(OMe)Ph\}]$ and $PhC{\equiv}CMe$ in toluene-d_8 solution is irradiated at 25 °C or when a sample irradiated at low temperature is allowed to warm to 25 °C, new ^1H NMR signals appear at δ 4.0 (s), 3.60 (s), and 1.7 (s) in a relative intensity of 1:3:3 as the δ 3.9 singlet of $[W(CO)_5\{C(OMe)Ph\}]$ decreases. These signals are logically attributed to the benzylic proton, the methoxy substituent, and the methyl group of 1-methoxy-2-methyl-3-phenylidene, **2**. In one experiment, chromatography gave a very small amount of an amber-yellow solid which showed a parent ion at *m/e* 236, consistent with the presence of **2**. The indenyl ether **2** is apparently a new compound as we can find no previous mention of it in the literature. Significantly, the ^1H NMR spectrum shows that only one regioisomer is formed, and the lack of coupling between the benzylic hydrogen and the methyl group implies the isomer shown in **2**. This photochemical reaction has not proven possible to drive to completion, and after 72 h irradiation at 25 °C, ~50% of the initial carbene complex remains. Importantly, the only other ^1H NMR resonances apparent in such a sample are those due to **2**, implying that little if any products other than **2** are formed upon photolysis.



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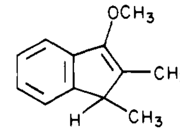

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Different results are obtained with $MeC{\equiv}CMe$. Upon irradiation of toluene-d_8 solutions containing equimolar quantities of $[W(CO)_5\{C(OMe)Ph\}]$ and $MeC{\equiv}CMe$ at 25 °C, the solution viscosity increases and an insoluble jellylike material is deposited, identified as poly-2-butyne by its IR spectrum.[15b] When the photoreaction is monitored by ^1H NMR spectroscopy, new weak signals of approximately equal intensity appear at δ 3.65 (s), 1.80 (s), and 1.17 (br d) which may be attributed to the methoxy and the two methyl substituents of 1-methoxy-2,3-dimethylindene, **3**.[23] The expected quartet of relative intensity 0.33 due to the benzylic proton of **3** was not resolved because of insufficient overall intensity. Chromatography of the photolyzed solution gave a small light yellow fraction which slowed a parent ion in its mass spectrum at *m/e* 174, consistent with that expected for **3**. It is clear from the ^1H NMR changes that **3** is a minor product of the reaction formed in less than 10% yield with most of the $MeC{\equiv}CMe$ being converted to polymer.

No evidence for products analogous to the indenyl ethers **1**–**3** was obtained upon photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ in the presence of either $PhC{\equiv}CH$ or 1-hexyne. Instead only polyacetylenes appear to be produced. For example, upon photolysis of an equimolar mixture of $[W(CO)_5\{C(OMe)Ph\}]$ and $PhC{\equiv}CH$, the δ 2.7 resonance of the acetylenic proton rapidly decreases in intensity and disappears after ~24 h of 366-nm irradiation. The only new resonance which appears is a relatively weak singlet at δ 3.4, but this also disappears upon continued photolysis. However, the δ 3.9 signal due to the initial carbene complex decreases by only ~10% from its initial intensity during this time, and continued photolysis causes no further change. The viscosity of the solution markedly increases during photolysis such that it takes about 30 s for the liquid to flow from one end to the other of the inverted ^1H NMR tube after ~51-h photolysis.

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[21] The $-OCH_3$ ^1H NMR resonance of $[W(CO)_5\{C(OMe)Ph\}]$ shows a marked solvent dependence appearing at δ 4.8 in CD_3CN solution but at δ 3.9 in benzene-d_6 and toluene-d_8 solutions at 25 °C. It is also temperature dependent, shifting to δ 3.7 at −40 °C in toluene-d_8 solution.

[22] (a) Halton, B.; Kulig, M.; Battiste, M. A.; Perreten, J.; Gibson, D. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 2327. (b) The δ 4.70 and 3.62 resonances are temperature dependent, shifting to δ 4.46 and 3.58 at −40 °C in toluene-d_8 solution.

[23] (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) *J. Organomet. Chem.* **1977**, *140*, 177. (c) *Chem. Ber.* **1980**, *113*, 3597 and references therein. (d) Dötz, K. H.; Fügen-Köster, B. *Ibid.* **1980**, *113*, 1449.

Similar results were obtained with 1-hexyne. The viscosity of the solution increases markedly during irradiation and the ^1H NMR spectrum showed a general broadening of the 1-hexyne resonances and a small decrease in intensity of the $[W(CO)_5\{C(OMe)Ph\}]$ resonance.

Thermal Reactions of $[W(CO)_5\{C(OMe)Ph\}]$ with Alkynes. While the thermal reactivity of $[Cr(CO)_5\{C(OMe)Ph\}]$ with alkynes has been thoroughly explored by Dötz and his co-workers,[23] the thermal reactivity of $[W(CO)_5\{C(OMe)Ph\}]$ with alkynes has received relatively little attention. In an important series of studies, Katz and co-workers[15] showed that when $[W(CO)_5\{C(OMe)Ph\}]$ is heated in the presence of terminal alkynes, polyacetylenes are produced. As controls for the above mentioned photolyses experiments, we briefly studied the corresponding thermal chemistry. In each case we found the thermal results to be similar to those obtained upon photolysis. For example, when approximately equimolar quantities of PhC≡CPh and $[W(CO)_5\{C(OMe)Ph\}]$ were heated to 100 °C in toluene-d_8 solution for 3 h, ^1H NMR monitoring showed complete disappearance of the initial carbene complex, with 1-methoxy-2,3-diphenylindene, **1**, accounting for 90% of the product mixture. Similarly, when $[W(CO)_5\{C(OMe)Ph\}]$ was heated with $PhC{\equiv}CCH_3$ to 100 °C for 18 h, ^1H NMR monitoring showed total reaction of the carbene complex to give 1-methoxy-2-methyl-3-phenylindene, **2**, in >90% yield. The high yields of these reactions and the relative ease of preparation of the precursor carbene complex may make them attractive synthetic routes to substituted indenyl ethers, a subject which we are presently pursuing.[24]

Discussion

Photochemistry of $[W(CO)_5\{C(OMe)Ph\}]$. The results reported herein clearly demonstrate that ultraviolet irradiation of $[W(CO)_5\{C(OMe)Ph\}]$ leads smoothly to CO loss as the only detectable photoreaction under our conditions (eq 9). Photoinduced

$$[W(CO)_5\{C(OMe)Ph\}] \xrightarrow{h\nu} CO + [W(CO)_4\{C(OMe)Ph\}] \qquad (9)$$

CO loss is evidenced by the formation of *cis*-$[W(CO)_4(CH_3CN)\{C(OMe)Ph\}]$ as the only product of photolysis in CH_3CN solution and by the inhibition of the conversion to the CH_3CN adduct when irradiation is conducted under a CO atmosphere. Also supporting the conclusion of photoinduced CO dissociation are Fischer's earlier studies[2] in which *cis*-$[W(CO)_4(PR_3)\{C(OR')R''\}]$ complexes were formed upon irradiation of the corresponding pentacarbonyl carbene precursor complexes in the presence of PR_3 ligands and also Casey's studies of photoinduced $^{13}CO/^{12}CO$ exchange in these carbene complexes and the photoreaction shown in eq 2.[3] The spectral changes shown in Figures 2 and 3 show that the photosubstitution of CH_3CN for CO is remarkably clean and that it can be driven to virtual completion under the appropriate conditions.

While the above conclusion of photoinduced CO dissociation is apparently generally applicable to $[W(CO)_5\{C(OR)R'\}]$ complexes in which the R and R′ groups may vary (see Fischer's studies[2]), this conclusion does not necessarily carry over to the corresponding nonheteroatom-stabilized carbene complexes. Although Casey and Neumann[3c] observed facile photoinduced $^{13}CO/^{12}CO$ exchange in $[W(CO)_5(CPh_2)]$, Rausch and co-workers[5] observed photoinduced decomposition not inhibited by a CO atmosphere. We briefly examined the photochemistry of this complex but were unable to draw definitive conclusions as to its primary photochemical reactions. In dilute CH_3CN solutions ($\sim 10^{-4}$) necessary for UV–vis monitoring, the complex rapidly decomposes upon standing in the dark at 25 °C as evidenced by a smooth decrease in intensity and eventual disappearance of the characteristic 485-nm W → carbene charge-transfer band over a 2-h period. This thermal reaction is slowed considerably upon cooling to 0 °C, but it is still apparent. Irradiation (366 nm) of carefully degassed and dried CH_3CN solutions of $[W(CO)_5(CPh_2)]$ at 0 °C led to an enhanced rate of loss of the visible W → carbene charge-transfer band with complete disappearance in 5 min, but not to spectral changes similar to those obtained for $[W(CO)_5\{C(OMe)Ph\}]$ (Figure 2). The loss of the charge transfer band implies destruction of the W–carbene unit during the photoreaction, as noted by Rausch and co-workers.[5] However, the thermal instability of this complex does not allow definitive conclusions to be drawn as to its photochemistry, and caution must be exercised in interpreting the complex's photosensitivity because of its thermal instability. It should be noted that thermal decomposition of $[W(CO)_5(CPh_2)]$ has been reported[25] to give the same products as those observed in the above-mentioned photochemical study.[5]

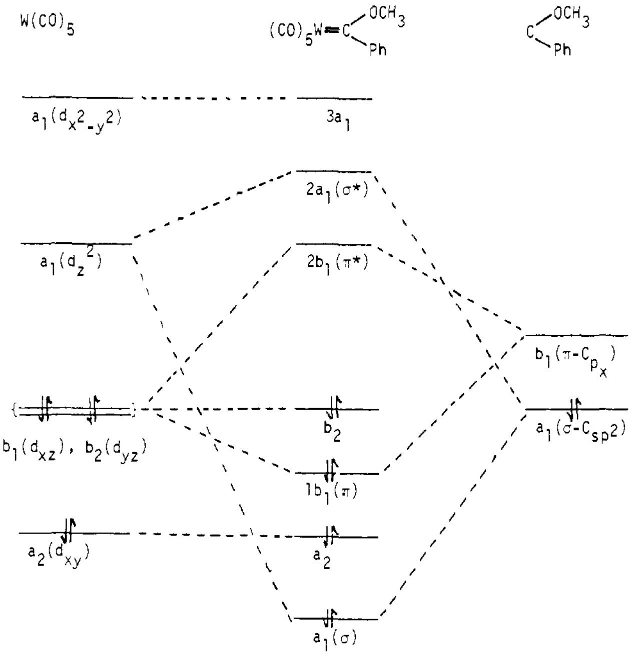

Figure 5. Simplified one-electron energy level diagram for $[W(CO)_5\{C(OMe)Ph\}]$.

An observation which must be explained is the marked wavelength dependence of the quantum yield of photosubstitution of CO in $[W(CO)_5\{C(OMe)Ph\}]$. Although the complex absorbs strongly at 436 nm, it is not appreciably photosensitive at that wavelength ($\phi \leq 0.0001$), in contrast to the 313- and 366-nm photosensitivity ($\phi = 0.01$). These results imply the population of excited states of differing reactivity at the different wavelengths of irradiation. A simplified one-electron energy level diagram for $[W(CO)_5\{C(OMe)Ph\}]$ is shown in Figure 5. In the C_{2v} point group appropriate for the local symmetry of the complex the C_2 axis is colinear with the W–carbene σ bond and the *yz* plane contains the carbene ligand. The filled carbene sp^2 orbital overlaps with the empty metal d_{z^2} orbital to give bonding $\{a_1(\sigma)\}$ and antibonding $\{2a_1(\sigma^*)\}$ combinations. A similar overlap of the empty carbene p_x orbital with a filled $d\pi$ orbital gives rise to bonding $\{b_1(\pi)\}$ and antibonding $\{2b_1(\pi^*)\}$ molecular orbitals. The particular ordering of orbitals, $2b_1(\pi^*)$ below $2a_1(\sigma^*)$, is in accord with a molecular orbital calculation on $[Cr(CO)_5\{C(OMe)Me\}]$ which implied the π^* orbital to be the lowest unoccupied orbital in the complex.[26] This orbital is localized largely on the carbene carbon atom.[26]

The electronic absorption spectrum of $[W(CO)_5\{C(OMe)Ph\}]$ shows three low-lying bands at 521 (ϵ 576 L mol^{-1} cm^{-1}), 402 (ϵ 10 560 L mol^{-1} cm^{-1}), and 352 nm (ϵ 6080 L mol^{-1} cm^{-1}) (Figure 1). These are respectively assigned to a spin-forbidden W → carbene(π^*) metal-to-ligand charge-transfer (MLCT) transition,

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(24) Targos, T. S.; Williams, G.; Geoffroy, G. L., to be submitted for publication.

(25) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

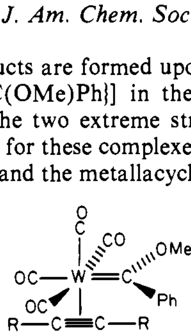
(26) Block, T. J.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441.

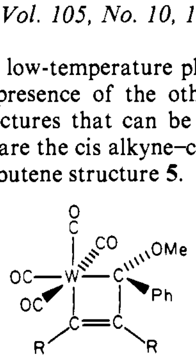
a spin-allowed W → carbene(π^*) MLCT transition, and a $^1A_1 \rightarrow {}^1B_2$ (... $b_2{}^2 \rightarrow$ ... $b_2{}^1 2a_1{}^1$) ligand field (LF) transition. Similar assignments are given for the bands of the other [W(CO)$_5${C(OR)R'}] complexes listed in Table I. The intense 402-nm band of [W(CO)$_5${C(OMe)Ph}] is simply too low in energy to be due to an LF transition. The lowest energy spin-allowed LF bands of [W(CO)$_6$] are at 334 and 314 nm[16] (Table I and Figure 1). The corresponding LF bands for a series of [W(CO)$_5$L] complexes, in which L is a nitrogen-donor ligand fall within the 400–410-nm range.[17] However, the carbene ligand should be positioned substantially higher in the spectrochemical series than these nitrogen donor ligands since it is a strong σ-donor and has π-acceptor properties, both attributes which lead to increased LF splitting. The LF bands would be expected to fall near those of [W(CO)$_6$], and such an assignment is made for the 352-nm band of [W(CO)$_5${C(OMe)Ph}]. Thus, the intense 402-nm band is attributed to a W → carbene(π^*) transition which terminates in the empty $2b_1(\pi^*)$ orbital, in accord with the MO calculations[26] on the analogous Cr complex which imply this orbital to be the lowest unoccupied orbital.[27] Similar W → L(π^*) MLCT assignments have been given for the lowest energy bands (435–469 nm) in the spectra of a series of [W(CO)$_5$(NC$_5$H$_4$X)] complexes and also for the low-lying bands of [W(CNPh)$_6$] (319–446 nm).[17b,28]

The wavelength dependence of the photosubstitution quantum yields can be readily understood in view of these spectral assignments. Numerous studies have shown that photoinduced CO loss generally occurs from LF excited states.[29] For [W(CO)$_5$L] complexes which have LF bands lowest in energy, photosubstitution of CO occurs with quantum yields greater than 0.4.[17b,29] However, it has also been shown that irradiation of complexes which have W → L CT excited states lowest in energy leads to photosubstitution of CO with quantum yields of the order of 0.1 or less.[4,17b,30] Significantly, the quantum yield drops sharply when irradiation is directly into the MLCT band. The latter behavior is exactly analogous to that observed for [W(CO)$_5${C(OMe)Ph}]. The 366- and 313-nm quantum yields are unusually low (0.01) for photoinduced CO dissociation and drop to virtually zero when irradiation is directly into the W → carbene(π^*) CT band at 436 nm. The very low 313- and 366-nm quantum yield values imply that intersystem crossing from the initially populated LF states to the low-lying MLCT state is quite efficient for [W(CO)$_5${C(OMe)Ph}], more so than for the [W(CO)$_5$L] complexes examined by Wrighton and co-workers.[17b]

Interestingly, IR evidence indicates that the photosubstitution reactions lead to cis products in all cases. This result is seemingly inconsistent with the notion that the $^1A \rightarrow {}^1B_2$ LF transition should lead to labilization along the *z* axis as a consequence of population of the d_{z^2} orbital. Similar behavior has been observed for [ReX(CO)$_5$] (X = Cl, Br, I) in which the lowest lying LF transition also involves population of a d_{z^2} orbital, but photolysis gives only cis-substituted products rather than the expected trans products.[31] It was proposed that an axial CO ligand dissociates from the [ReX(CO)$_5$] complexes in the primary photoprocess but that the resultant five-coordinate photoproduct rearranges so that the substituting ligand can enter in a cis position.[31] A similar rearrangement of the photogenerated [W(CO)$_4${C(OMe)Ph}] intermediate would account for the observed cis-substituted products reported here.

Characterization and Reactivity of Alkyne–Carbene Complexes. The new alkyne–carbene complex [W(CO)$_4$($PhC\equiv CPh$){C(OMe)Ph}] was isolated as a microcyrstalline solid from the low-temperature photolysis of [W(CO)$_5${C(OMe)Ph}] in the presence of $PhC\equiv CPh$. IR spectral data indicate that similar alkyne adducts are formed upon low-temperature photolysis of [W(CO)$_5${C(OMe)Ph}] in the presence of the other alkynes studied. The two extreme structures that can be considered appropriate for these complexes are the cis alkyne–carbene formulation **4** and the metallacyclobutene structure **5**. Structures intermediate between these two extremes may also be considered. There have been three examples of crystalline alkyne–carbene complexes whose structures have been determined by X-ray diffraction. Tebbe and Harlow[32] showed that [Cp$_2$TiCH$_2$(PhC$_2$Ph)] possesses a ligand arrangement more appropriate for the metallacyclobutene description, whereas [Cp$_2$TiCH$_2$(Me$_3$SiC$_2$SiMe$_3$)] was shown to adopt a ligand arrangement partway between the metallacyclobutene and the separated alkyne–carbene formulations.[33] The unsymmetrical alkyne complex [Cp$_2$TiCH$_2$(Me$_3$SiC$_2$Ph)] has a structure intermediate between those of the symmetrically substituted alkynes.[33] There are no examples of complexes for which the separated alkyne–carbene formulation has been established.


4


5

The available spectroscopic data does not allow a distinction to be made between structures **4** and **5** for [W(CO)$_4$($PhC\equiv CPh$){C(OMe)Ph}], and extensive efforts have not yet led to crystals suitable for an X-ray diffraction study. The four-band pattern observed in the IR spectrum of [W(CO)$_4$($PhC\equiv CPh$){C(OMe)Ph}] argues for a *cis*-[W(CO)$_4$L$_2$] formulation, but both structures **4** and **5** meet this requirement. A significant change in hybridization of the carbene carbon occurs in moving from structure **4** to **5**, and thus ^{13}C NMR spectral data should prove useful in distinguishing these structures. However, we were repeatedly frustrated in our attempts to obtain a ^{13}C NMR spectrum of [W(CO)$_4$($PhC\equiv CPh$){C(OMe)Ph}], even when ^{13}C enriched, because of its decomposition during the time required to obtain a satisfactory signal-to-noise ratio. The −40 °C ^1H NMR spectrum of a sample of the isolated alkyne adduct showed a resonance at δ 3.48 attributable to the carbene methoxy group in the adduct complex. The position of this resonance is closer to the methoxy resonance (δ 3.58[22b]) of the isolated 1-methoxy-2,3-diphenylindene, **1**, than it is to the carbene methoxy resonance in [W(CO)$_5${C(OMe)Ph}] (δ 3.7[21]). This would seem to imply that the metallacyclobutene formulation is more appropriate for the complex, as would the observation that the alkyne ligand cannot be readily displaced from the adduct complex by CO. However, a truly definitive answer to this structural question will have to await the results of an X-ray diffraction study once suitable crystals are obtained.

None of the alkyne–carbene adducts are particularly stable, and in solution they decompose to give products which depend markedly upon the nature of the alkyne. With $PhC\equiv CPh$ and $PhC\equiv CMe$, the indenyl ethers **1** and **2** form in near quantitative yield. In contrast, the terminal alkynes $PhC\equiv CH$ and *n*-Bu$C\equiv CH$ give only polymeric products. However, reaction with $MeC\equiv CMe$ leads to both poly-2-butyne and to 1-methoxy-2,3-dimethylindene, **3**. Before proceeding to discuss the probable mechanisms by which these products form, we must first mention some pertinent literature. Katz and co-workers[15] have reported that [W(CO)$_5${C(OMe)Ph}] thermally initiates the polymerization of a variety of alkynes. The polymerizations were carried out at 40–50 °C, generally without solvent, and were fairly slow. However, polymerizations were equal to or better than any previously reported examples for several of the alkynes studied. These reactions were suggested to proceed through a metallacyclobutene

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(27) Other workers[4] have also assigned to lowest energy band in [W(CO)$_5${C(OMe)Ph}] to a MLCT transition.

(28) Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Labertin, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97.

(29) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

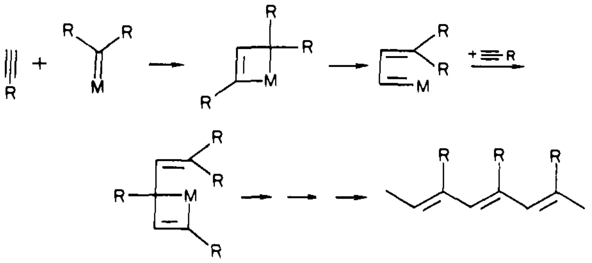
(30) Dahlgren, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 1948.

(31) Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111.

(32) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

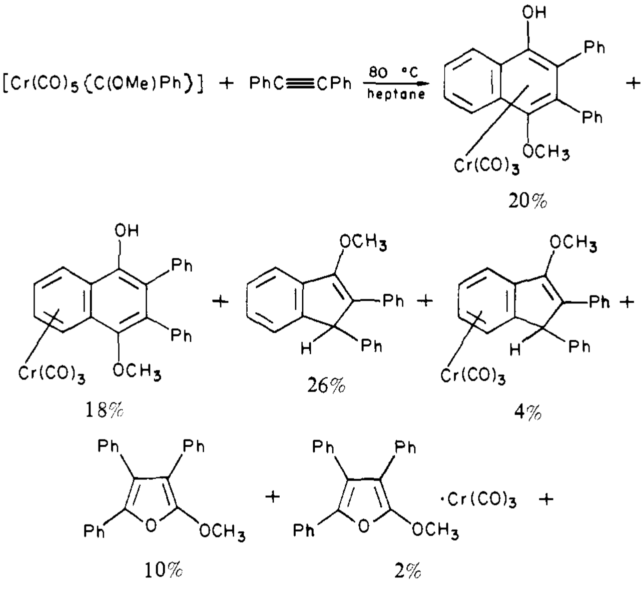
(33) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Collbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584.

intermediate of undefined composition (eq 10).[15] A later study of the effect of added PhC≡CH on the molecular weight distribution of polymers derived by [W(CO)$_5${C(OMe)Ph}]/PhC≡CH induced metathesis of cyclopentene led to the conclusion that [W(CO)$_5${C(OMe)Ph}] thermally reacts much faster with alkynes than it does with alkenes.[15b] Similar alkyne polymerization reactions have also been observed with binuclear tungsten carbene complexes.[34] Significantly, no mention was made of any indenyl ether product analogous to **1**, **2**, or **3** from any of these reported reactions with alkynes.



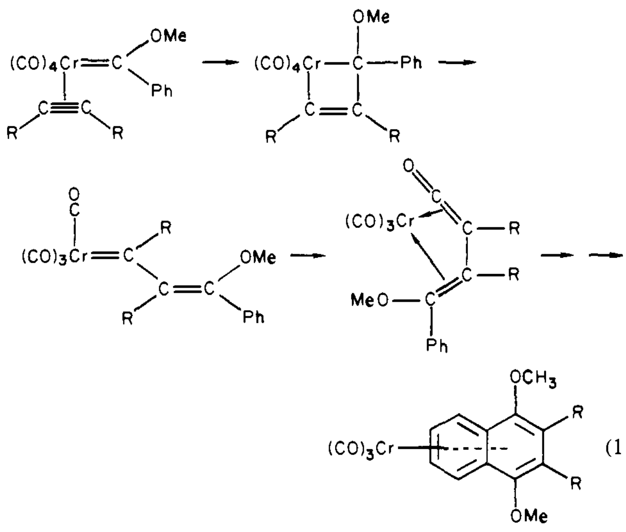
(10)

Dötz and co-workers[23] have extensively examined the thermal reactivity of a series of [Cr(CO)$_5${C(OR)R′}] complexes with a variety of alkynes. The products observed depend markedly on the nature of the alkyne, the carbene substituents, and the reaction conditions. Of particular relevance to this study is the reaction of [Cr(CO)$_5${C(OMe)Ph}] with PhC≡CPh which was reported to yield the variety of products shown in eq 11.[23b] The predominant products in most of the reactions examined by Dötz are napthol derivatives with the extra C–O linkage coming from one of the carbonyl ligands of the initial complex. It was suggested that these compounds derive by alkyne coordination to Cr, rearrangement to give a new carbene, migration of CO to yield a coordinated ketene, and finally collapse to the napthol (eq 12).[23] The corresponding reaction with the *tungsten* carbene complexes have not been systematically explored.



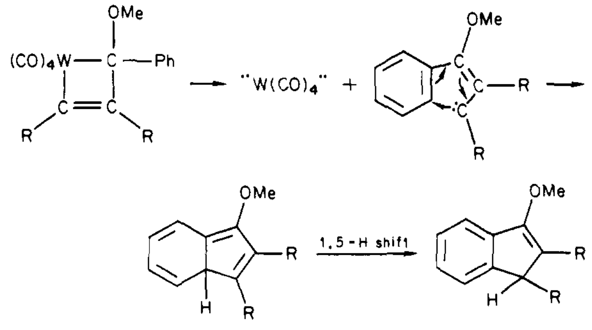
$C_{23}H_{18}O_2 \cdot Cr(CO)_3$ + · · · (11)

The alkyne–carbene complexes described herein are of obvious relevance to both the alkyne polymerization reactions of Katz and the various studies of Dötz and their co-workers since in each case an alkyne–carbene complex appears to be the first intermediate formed. Also in each case rearrangement to a metallacyclobutene intermediate is presumed to occur. Opening of the metallacyclobutene to give a new carbene in which the alkyne has inserted between the metal and the initial carbene carbon can account for both the polymerization reactions (eq 10) and the formation of napthol derivatives (eq 12).

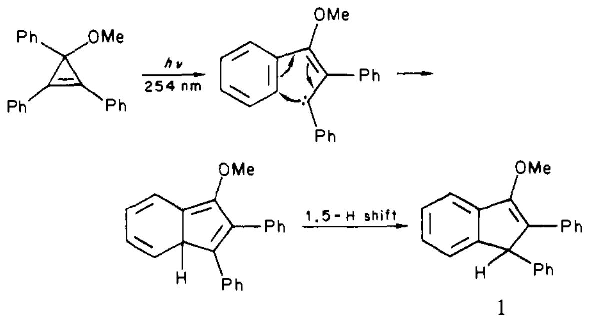


(12)

Metallacyclobutene intermediates, if not the actual structures of the alkyne–carbene adducts described herein (see above), can also account for the chemistry that we have observed (Scheme I). Production of the polyacetylenes is readily rationalized by the mechanism suggested by Katz and co-workers for the thermal polymerizations (eq 10) with the only difference being the formation of the initial alkyne–carbene complex via a photochemical route rather than a thermal one. Formation of the indenyl ether products could form via decay of the metallacyclobutenes to give free vinylcarbenes which subsequently rearrange to the observed products (eq 13). Vinyl carbenes have been suggested as intermediates in the photoinduced conversion of cyclopropenes to indenes, a reaction which is believed to proceed from singlet excited states.[35,36] Of particular relevance to this study is the report by Battiste and co-workers[22] that 254-nm photolysis of 1,2-diphenyl-3-phenyl-3-methoxycyclopropene leads smoothly to 1-methoxy-2,3-diphenylindene, **1** (eq 14). However, there is no true precedent for the formation of free carbenes via the cleavage



(13)



(14)

1

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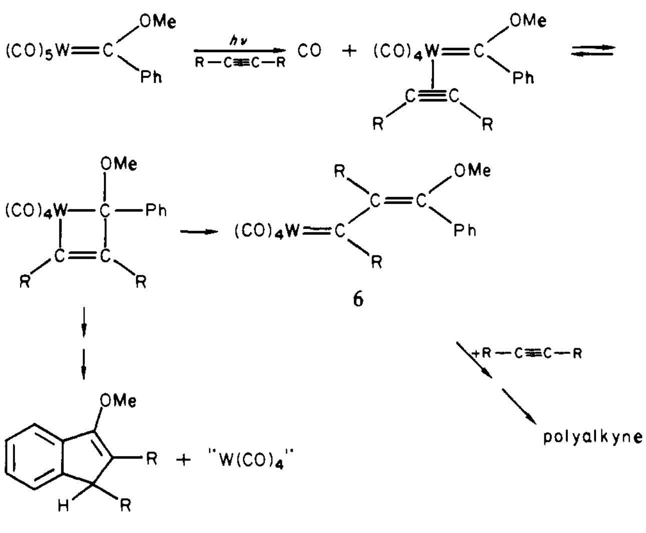
[34] Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J.-C.; Dromzee, Y.; Jeannin, Y.; Ades, D.; Fontanille, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1055.

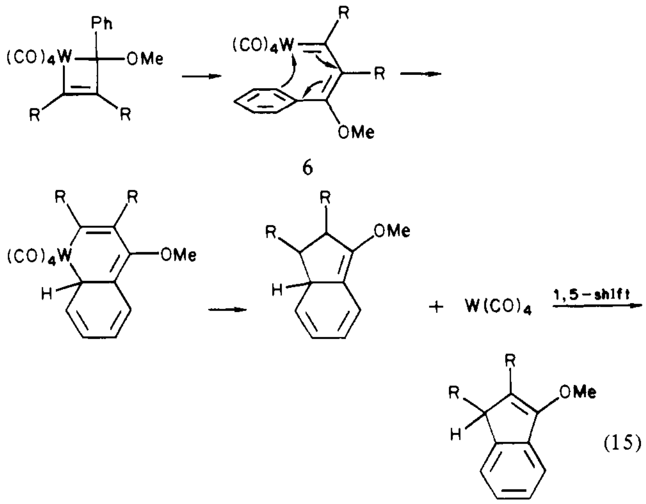
[35] Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

[36] (a) Pincock, J. A.; Morchat, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 7536. (b) Padwa, A.; Blacklock, T. J.; Loza, R.; Polngiszek, R. *J. Org. Chem.* **1980**, *45*, 2181.

Scheme I



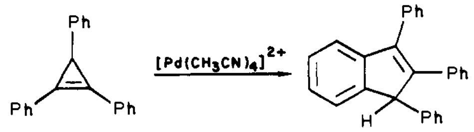
of metal–carbene double bonds or via the collapse of metallacycles and thus the intermediacy of uncomplexed vinyl carbenes seems unlikely. On the other hand, a related transformation could occur with the organic ligand still complexed to the metal and one possible sequence that has been suggested by Casey[37] is that shown in eq 15.



(15)

The presumed metallacyclobutene intermediate in Scheme I can thus apparently decay via cleavage of the initial tungsten–carbene carbon bond to give a new carbene **6** which either leads to polymer formation or to cyclization to give indene derivatives. Our limited experimental data do not allow a definitive conclusion to be drawn as to the factors which affect the partitioning of the intermediate along the two reaction paths. However, polyacetylene formation from terminal alkynes and indene formation from internal alkynes is suggestive of steric control of the mode of metallacyclobutene/carbene decay with increased steric hinderance favoring production of indenes. The observation that 2-butyne gives both an indene derivative and polymer formation is probably a reflection of the relatively small size of the methyl substituents.

It could be argued that the metallacyclobutenes formed from internal alkynes collapse to give free cyclopropene derivatives which then subsequently undergo photochemical conversion to the indenes. Two observations argue against this mechanism. First, the cyclopropene derivatives would not absorb an appreciable fraction of the 366-nm irradiation used in the photolysis study and hence their conversion to the indenes would be slow. Thus, they should be detectable by ^{1}H NMR spectroscopy, but they were not. More convincingly, the formation of the indene derivatives from the preformed alkyne–carbene adducts occurs *in the complete absence of irradiation* when solutions of these complexes are warmed to 25 °C, conditions under which the cyclopropenes are stable. Perhaps the metallacyclobutenes decay to form cyclopropenes, but metal-catalyzed ring opening rapidly converts these into indenes. Several metal complexes are known to catalyze such conversions.[38] To test this hypothesis, both $[W(CO)_6]$ and $[W(CO)_5\{C(OMe)Ph\}]$ were irradiated in the presence of 1,2,3-triphenylcyclopropene, but no conversion to 1,2,3-triphenylindene was observed by ^{1}H NMR spectroscopy. This latter reaction is known to be catalyzed by Pd^{2+} (eq 16).[38d] As a further test for



(16)

such a mechanism, $[W(CO)_5\{C(OMe)Ph\}]$ was irradiated in the presence of an equimolar quantity of diphenylacetylene and 1,2,3-triphenylcyclopropene. ^{1}H NMR monitoring showed that the cyclopropene was not affected, whereas the carbene complex and the alkyne were smoothly converted to indene derivative **1**. Thus the experimental evidence strongly argues against free cyclopropenes as reaction intermediates in route to the indenyl ether products.

Finally, one must consider why the formation of indene derivatives from $PhC{\equiv}CPh$ and $PhC{\equiv}CMe$ is nearly quantitative with $[W(CO)_5\{C(OMe)Ph\}]$, whereas Dötz and co-workers[23] have shown that $[Cr(CO)_5\{C(OMe)Ph\}]$ gives mostly napthol derivatives. This is likely a consequence of the greater strength of the tungsten–carbonyl bonds ($\Delta H_{W\text{-}CO}$ = 178 kJ/mol[39]) as compared to chromium–carbonyl bonds ($\Delta H_{Cr\text{-}CO}$ = 108 kJ/mol[39]). Thus a CO does not insert into the W–carbene bond as readily as it does into a Cr–carbene bond.

Summary

Photolysis of $[W(CO)_5\{C(OMe)Ph\}]$ has been shown to give rise to CO loss as the only detectable photoreaction. This reaction is proposed to proceed through ligand field excited states with the lowest lying W → carbene(π^*) charge transfer state being inactive with respect to CO loss. The photogenerated $[W(CO)_4\{C(OMe)Ph\}]$ intermediate readily adds CH_3CN and $PhC{\equiv}CPh$ to give isolable $[W(CO)_4L\{C(OMe)Ph\}]$ complexes. Other alkynes lead to spectroscopically detectable alkyne–carbene adducts. The alkyne derivatives are not stable at 25 °C and decay in solution to give indene derivatives and polyacetylenes. Indenes are produced in high yield from $PhC{\equiv}CPh$ and $PhC{\equiv}CMe$, whereas $n\text{-}BuC{\equiv}CH$ and $PhC{\equiv}CH$ lead to polyacetylenes. Reaction with $MeC{\equiv}CMe$ gives both products. The high-yield conversion of the internal alkynes to the indene derivatives using $[W(CO)_5\{C(OMe)Ph\}]$ may be an attractive synthetic route to these species and this aspect is being further explored.[24]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8201160) and in part by grants from the Standard Oil Co. of Ohio and Air Products and Chemicals, Inc. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978–1983) and the John Simon Guggenheim Foundation for a fellowship (1982–1983).

Registry No. 1, 65684-96-0; **2**, 85221-55-2; **3**, 85221-56-3; $[W(CO)_5\{C(OMe)Ph\}]$, 37823-96-4; *cis*-$[W(CO)_4(CH_3CN)\{C(OMe)Ph\}]$, 85221-50-7; *cis*-$[W(CO)_4(THF)\{C(OMe)Ph\}]$, 85221-51-8; *cis*-$[W(CO)_4(PhC{\equiv}CPh)\{C(OMe)Ph\}]$, 85221-52-9; *cis*-$[W(CO)_4(PhC{\equiv}CH)\{C(OMe)Ph\}]$, 85221-53-0; *cis*-$[W(CO)_4(PhC{\equiv}CMe)\{C(OMe)Ph\}]$, 85234-87-3; *cis*-$[W(CO)_4(MeC{\equiv}CMe)\{C(OMe)Ph\}]$, 85221-54-1; poly-2-butyne, 25684-85-9.

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[37] (a) Casey, C. P. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2. (b) Casey, C. P., private communication.

[38] (a) Walker, J. A.; Orchin, M. *Chem. Commun.* **1968**, 1239. (b) Monahan, A. S.; Freilich, J. D.; Fong, J.-J. *Tetrahedron Lett.* **1977**, *No. 22* 1865. (c) Fiato, R. A.; Mushak, P.; Battiste, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 869. (d) Sen, A.; Lai, L., unpublished results.

[39] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.