

formation with dibenzo-18-crown-6 and glycine hydrochloride but not glycine itself in MeOH. The only successful case involves phenylalanine transport in a photoactivated system.⁷ The present cases suggest that suitable derivatives of **1** should permit recognition of other side chains and our current research is directed at this prospect.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

(7) Sunamoto, J.; Iwamoto, K.; Mohri, Y. *J. Am. Chem. Soc.* **1982**, *104*, 5502-5504.

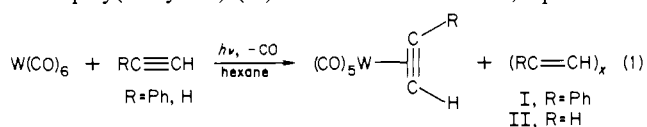
Photoassisted Polymerization of Terminal Alkynes by $W(CO)_6$ Involving Catalyst Generation by an Alkyne to Vinylidene Ligand Rearrangement

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Katz and co-workers¹ have demonstrated that $(CO)_5W\{C(OMe)Ph\}$ (**1**) catalyzes the polymerization of alkynes, and the mechanism of Scheme I which involves carbene-alkyne and metallacyclobutene intermediates has been implicated. We independently prepared the important alkyne-carbene intermediate **2** by low-temperature photolysis of **1** in the presence of alkynes and showed that it leads to alkyne polymerization upon warm-up.² Herein we demonstrate that use of a *preformed* carbene complex is not necessary since *active alkyne polymerization catalysts can be formed by photolysis of $W(CO)_6$ with terminal alkynes in hydrocarbon solutions*. A key step in the catalyst generation is rearrangement of a coordinated alkyne to a vinylidene ligand.

Irradiation of $W(CO)_6$ in the presence of alkynes has been reported to give unstable $(CO)_5W(\eta^2\text{-alkyne})$ complexes.³ We verified these earlier results with $CH_3C\equiv CCH_3$, $PhC\equiv CPh$, *t*- $BuC\equiv CH$, $PhC\equiv CH$, and $HC\equiv CH$ but also observed formation of large amounts of red poly(phenylacetylene) (I) and black *trans*-poly(acetylene) (II) in the latter two cases, eq 1.⁴ The



polymers were identified by their characteristic IR spectra and by a molecular weight measurement for $(PhC=CH)_x$, but the C, H analyses for both were persistently low, due to contamination by tungsten residues.⁵ These products were repeatedly observed

(1) (a) Katz, T. J.; Ho, T. H.; Shih, N. Y.; Ying, Y. C.; Stuart, V. I. *W. J. Am. Chem. Soc.* **1984**, *106*, 2659. (b) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (c) See also: Thoi, H. H.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2227.

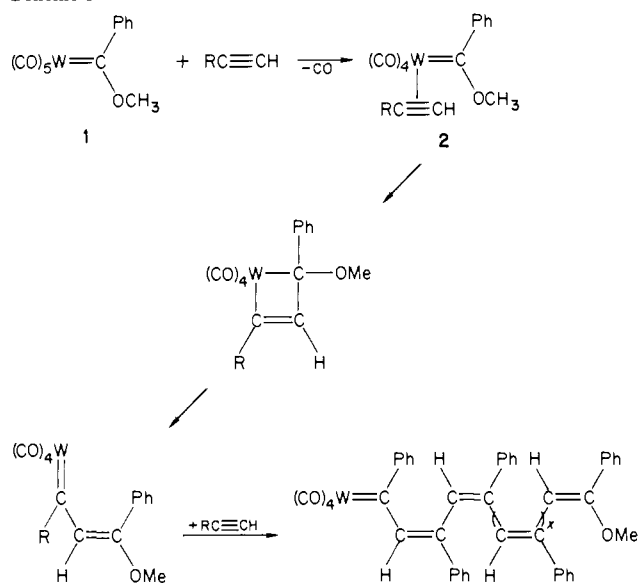
(2) Foley, H.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(3) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 1264.

(4) A typical experiment involved photolysis ($\lambda > 300$ nm) of a hexane solution (60 mL) of $W(CO)_6$ (0.135 g, 0.32 mmol) and phenylacetylene (1.0 mL, 1.05 mmol) in a Schlenk flask at 25 °C for 24 h. Similar reaction conditions were employed for $HC\equiv CH$ which was passed through a saturated $NaHSO_3$ solution to remove the acetone stabilizer.

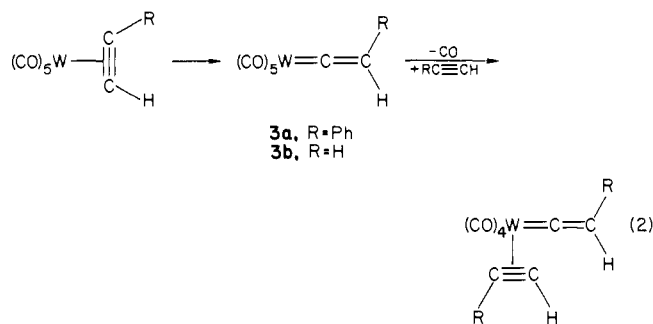
(5) $(PhC=CH)_x$: Anal. Calcd for $(C_8H_6)_x$: C, 94.12; H, 5.88. Found: C, 86.57; H, 5.81. ¹H NMR ($CDCl_3$) 7.74 ppm (br, m); mol wt (osmometry, THF) 1815, 1757 (two samples); IR (KBr) 697 s, 755 s, 1028 w, 1074 w, 1443 m, 1491 m, 3025 w, 3054 w cm^{-1} . For a discussion of the IR spectra of $(PhC=CH)_x$, see, for example: Tsonis, C. P.; Faron, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1779. Kern, R. J. *Ibid.* **1969**, *7*, 621. Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717. *trans*-($HC=CH$)_x: IR (KBr) 2965 m, 1076 m $br\ cm^{-1}$. For a discussion of the IR spectra of $(HC=CH)_x$, see: Kleist, F. D.; Byrd, N. R. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 3419. Watson, W. H.; McMordie, W. D.; Lands, L. G. *J. Polym. Sci.* **1961**, *55*, 137.

Scheme I



when either rigorously purified solvents, alkynes, and $W(CO)_6$ or as-received materials were used. With $HC\equiv CH$, irradiation was only necessary to *initiate* the polymerization since it continued 90 h after cessation of photolysis with no sign of abatement. However, polymerization of $PhC\equiv CH$ ceased when irradiation was stopped. IR monitoring of the active catalyst solutions showed only the presence of $W(CO)_6$ and $(CO)_5W(\eta^2\text{-alkyne})$, and thus the active polymerization agent must be present in trace amounts and must be extremely active.

In related work, Masuda et al.⁶ reported that polymerization occurred when $W(CO)_6$ was irradiated with alkynes in *halocarbon solvents*. This polymerization may proceed by the generation of halocarbene complexes which catalyze the polymerization by the mechanism of Scheme I or by the route suggested below for $W(CO)_6$ in hydrocarbon solutions. We suggest that irradiation of $W(CO)_6$ with terminal alkynes in *hydrocarbon solvents* leads to the formation of catalytically active vinylidene complexes by rearrangement of the initially formed η^2 -alkyne complexes, eq 2.

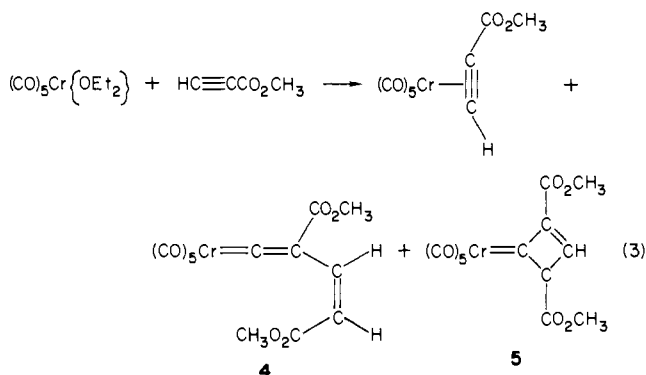


Thermal or photochemical loss of CO from **3** and coordination of alkyne then allow entry into a catalytic cycle similar to that of Scheme I. The metal-assisted rearrangement of terminal alkynes to vinylidene ligands is now quite well established,⁷ although the reaction has never been used for the present purpose. The proposed vinylidene intermediates **3a,b** have not been reported although related vinylidene complexes $(CO)_5M=C=CRR'$ (M = Cr, W) have been mentioned.⁸ In one instance a vinylidene

(6) (a) Masuda, T.; Kuwane, Y.; Yamamoto, K.; Higashimura, T. *Polym. Bull.* **1980**, *2*, 823. (b) Masuda, T.; Yamamoto, K.; Higashimura, K. *Polymer* **1982**, *23*, 1663. (c) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

(7) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789.

complex has been suggested to lead to alkyne dimerization. Berke and co-workers^{8a} observed that addition of $\text{HC}\equiv\text{CCO}_2\text{CH}_3$ to solutions of photogenerated $(\text{CO})_5\text{Cr}\{\text{OEt}_2\}$ gave the products of eq 3, with **4** and **5** proposed to arise via intermediacy of the vinylidene complex $(\text{CO})_5\text{Cr}=\text{C}=\text{C}(\text{CO}_2\text{CH}_3)\text{H}$.



To test the mechanistic suggestion of eq 2, we attempted to generate the proposed vinylidene intermediate **3a** by protonation of $[\text{PPN}][(\text{CO})_5\text{WC}\equiv\text{CPh}]$,⁹ a well-established route to vinylidene complexes.^{7a,b} This complex forms at -77°C , but it rapidly decomposes upon warm-up. In contrast, the vinylidene complex $(\text{CO})_5\text{W}=\text{C}=\text{C}(\text{Me})-t\text{-Bu}$ (**6**), which was recently prepared by Mayr et al.^{8b} by addition of $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ to $[(\text{CO})_5\text{WC}\equiv\text{C}-t\text{-Bu}]^-$, can be isolated as a dark green oil. We repeated the preparation of **6** and found by IR monitoring that no reaction occurred between **6** and excess $\text{PhC}\equiv\text{CH}$ when these reagents were stirred together at 22°C for 1 h. However, 366-nm photolysis induced an immediate reaction as evidenced by the rapid green to red color change and the deposition of red poly(phenylacetylene). Thus the vinylidene complex **6** is capable of affecting alkyne polymerization, presumably by loss of CO, coordination of alkyne, and then entry into the mechanism of Scheme I. By analogy, the vinylidene complex **3a** should also initiate polymerization. In support of this suggestion, we find that complex **6**, like **1**,² cleanly loses CO upon 366-nm irradiation in CH_3CN solution to give UV and IR spectral changes indicative of formation of $\text{cis}-(\text{CO})_4(\text{CH}_3\text{CN})\text{W}=\text{C}=\text{C}(t\text{-Bu})\text{CH}_3$.¹⁰

Further evidence for the suggested mechanism comes from experiments with $\text{CH}_3\text{C}\equiv\text{CCH}_3$. Both Katz¹ and we² showed that poly(2-butyne) results when $(\text{CO})_5\text{W}\{\text{C}(\text{OMe})\text{Ph}\}$ is heated or irradiated in the presence of 2-butyne. However, unlike $\text{PhC}\equiv\text{CH}$, 2-butyne cannot form a vinylidene complex upon interaction with photogenerated $\text{W}(\text{CO})_5$ since it does not have an acidic hydrogen. Consistent with the proposed vinylidene intermediate in our mechanism, photolysis of $\text{W}(\text{CO})_6$ in the presence of 2-butyne does not lead to polymer, but only to the η^2 -2-butyne complex. However, when a trace of $\text{PhC}\equiv\text{CH}$ (<1%) is added to the $\text{W}(\text{CO})_6$ /2-butyne mixture, photoinduced polymerization of 2-butyne occurs after an induction period of 30–40 min. The vinylidene complex **3a** presumably forms under these conditions and initiates the polymerization of 2-butyne.

The most significant aspect of this study is the demonstration that an active carbene-containing catalyst can be generated from a simple carbonyl complex and free alkyne via the alkyne to vinylidene rearrangement. It should be noted that a similar initiation process may occur in the patented thermal (100 – 150°C) polymerization of terminal alkynes by $\text{W}(\text{CO})_6$ and a related series of group 6¹³ metal carbonyls¹¹ as well as that reported to

occur upon heating (arene) $\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with terminal alkynes.¹²

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(12) Woon, P. S.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1749.

(13) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering; e.g., III \rightarrow 3 and 13.)

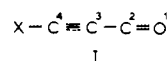
Anti-Michael Carbolithiation of Silicon and Phenyl-Substituted α,β -Unsaturated Secondary Amides

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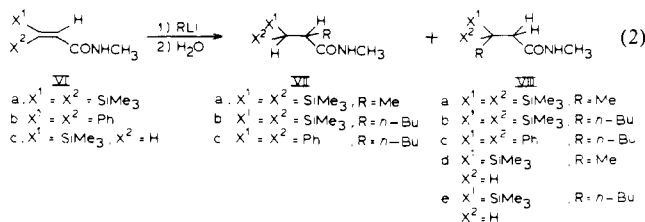
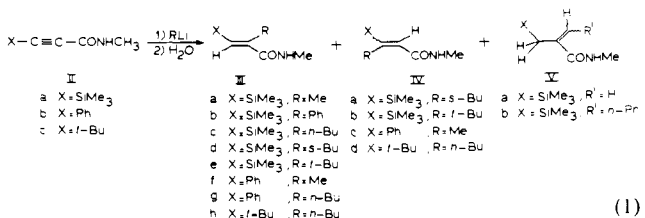
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The notion that α,β -unsaturated carbonyl systems (I) add



nucleophiles *only* at C-2 and/or C-4 pervades organic texts.¹ We have observed attack at C-3 (anti-Michael addition) when we treated the ynamides II and the enamides VIa, b with σ -organolithiums. Subsequent hydrolysis gave III (sometimes accompanied by small amounts of the double-bond isomers V) and VII, either exclusively or together with the Michael isomers IV and VIII, respectively (eq 1 and 2, Table I). The Z isomers of IIIa–h could



not be detected. Deuterolysis of the reaction mixtures led to nearly quantitative incorporation of one carbon-bonded deuterium into

(1) (a) "Y⁻ never attacks the 3 position": March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 679. (b) See also: Eicher, T. In "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Interscience: New York, London, 1966; p 672. Posner, G. H. *Org. React.* **1972**, *19*, 1. Wakefield, B. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, p 28. (c) Faith in the generality of the "rule" expressed in the citation above may have prevented the detection of C-3 attack in earlier work: Wotiz, J. H.; Matthews, J. S.; Greenfield, H. *J. Am. Chem. Soc.* **1953**, *75*, 6343 and ref 3. A low yield (52%) of 4,4-diphenyl-3-buten-2-one and the appearance of a deep red color from β -phenylcinnamic acid and methylolithium were suggested to have arisen from competing anti-Michael addition (Jorgenson, M. J. *Org. React.* **1970**, *18*, 1, 18.

(8) (a) Berke, H.; Harter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.*, **B** **1981**, *36B*, 929. (b) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517.

(9) Prepared via metathesis of $\text{PPN}[(\text{CO})_5\text{WCl}]$ with $\text{LiC}\equiv\text{CPh}$. See: Schlientz, W. J.; Ruff, J. K. *J. Chem. Soc. A* **1971**, 1139.

(10) Isosbestic points were maintained in both the IR and UV-vis spectral changes observed upon photolysis of **6** in degassed CH_3CN solution. The final IR spectrum showed bands at 2020 w, 1939 w, 1900 s, and 1840 br, cm^{-1} indicative of a cis coordination of CH_3CN .²

(11) Letto, J. R. U.S. Patent 3051.693, 1966.